ADVANCES IN INORGANIC CHEMISTRY, VOL. 41

THE COORDINATION CHEMISTRY OF TECHNETIUM

JOHN BALDAS

Australian Radiation Laboratory, Yallambie, Victoria 3085, Australia

I. Introduction
II. Technetium(−I)
III. Technetium(0)
IV. Technetium(I)
  A. Carbonyl Complexes
  B. Cyclopentadienyl and Arene Complexes
  C. Cyano and Isonitrile Complexes
  D. Dinitrogen, Phosphine, Phosphite, and Related Complexes
  E. Complexes with Nitrogen Ligands
  F. Nitrosyl and Thionitrosyl Complexes
V. Technetium(II)
  A. Organometallic Complexes
  B. Halide Complexes and Clusters
  C. Complexes with Nitrogen Ligands
  D. Phosphine, Arsine, and Related Complexes
  E. Complexes with Sulfur Ligands
  F. Nitrosyl and Thionitrosyl Complexes
VI. Technetium(III)
  A. Carbonyl Complexes
  B. Cyclopentadienyl Complexes
  C. Cyano, Isonitrile, and Thiocyanato Complexes
  D. Aqua, Halide, and Related Dimeric Complexes
  E. Carboxylato and β-Diketonato Complexes
  F. Complexes with Dioximes, Schiff Bases, and Other Nitrogen Ligands
  G. Complexes with Monodentate Phosphines and Related Ligands
  H. Complexes with Bidentate Phosphine, Arsine, and Related Ligands
  I. Complexes with Sulfur Ligands
  J. Nitrosyl and Thionitrosyl Complexes
VII. Technetium(IV)
  A. Isonitrile and Thiocyanato Complexes
  B. Halide and Related Complexes
  C. Complexes with Oxygen Ligands and Oxo-Bridged Complexes
  D. Complexes with Schiff Base and Other Nitrogen Ligands
  E. Complexes with Phosphine and Arsine Ligands
  F. Complexes with Sulfur Ligands

VIII. Technetium(V)
  A. Mononuclear $[TcO]^{3+}$ Complexes
  B. Complexes of the *trans*-$[TcO(OH)]^{2+}$ and $[TcO_2]^+$ Cores
  C. Oxo-Bridged $[Tc_2O_3]^{4+}$ and Other Binuclear Complexes
  D. $[TcS]^{3+}$ Complexes
  E. Nitrido Complexes
  F. Imido and Hydrazido Complexes
  G. Complexes Not Containing Multiply Bonded Ligands
IX. Technetium(VI)
  A. Oxo Complexes
  B. Nitrido Complexes
  C. Imido and Hydrazido Complexes
  D. Dithiolene and Related Complexes
X. Technetium(VII)
  A. Oxo and Sulfido Complexes
  B. Nitrido and Imido Complexes
  C. Complexes Not Containing Multiply Bonded Ligands
XI. Appendix: Abbreviations
References

I. Introduction

Technetium, the ekamanganese of Mendeleev and the first of the artificially produced elements, was discovered in 1937 by Perrier and Segrè in a molybdenum plate that had been bombarded with deuterons (*1, 2*). The name technetium is derived from the Greek word for artificial. Twenty-one isotopes, all radioactive, of mass number 90–110 and several metastable isomers are known (*3*). Because the half-life of the longest lived isotope, ^{98}Tc, is 4.2×10^6 years, primordial technetium has long ceased to exist on earth but minute traces occur in nature (1 ng of ^{99}Tc in 5.3 kg of pitchblende) as a result of the spontaneous fission of uranium (*4*). The long-lived ^{99}Tc [$t_{1/2} = 2.111(12) \times 10^5$ years; β^- decay energy = 293.6 keV] (*5, 6*) is produced in 6% yield from ^{235}U fission and is isolated in quantity from spent nuclear fuel (*7*). Technetium-99 is available commercially in gram quantities, usually as ammonium pertechnetate in aqueous solution. This is the only isotope used for macroscopic chemical studies and is here designated simply by the symbol Tc. The ground-state electronic configuration of the Tc atom is $[Kr]4d^5 5s^2$ with a $^6S_{5/2}(^{2s+1}S_J)$ term symbol (*8*). Technetium metal dissolves in the oxidizing acids nitric, aqua regia, and concentrated sulfuric and in bromine water. Like rhenium, technetium dissolves in neutral and alkaline solutions of hydrogen peroxide to form the pertechnetate anion. In oxygen the metal burns to form the oxide Tc_2O_7 (*7*). Apart from radioactivity considerations, the chemistry of technetium may be investigated by conventional synthetic and spectroscopic methods. Chemically, technetium resembles its third-row congener rhenium, but there are significant differences. In particular, there are the greater ease of reduction of the higher oxidation states of technetium and the greater substitution lability of the lower oxidation states compared with those of the rhenium analogs (*9*). The organometallic chemistry of technetium, however, rather closely resembles that of rhenium (*10*). Technetium complexes with the metal in oxidation states from -1 to $+7$ are known but, although there is now much research activity in the area, the chemistry of technetium remains relatively undeveloped compared with that of manganese, rhenium, and the neighboring Group 6 and 8 transition metals. The results obtained to date are nonetheless very considerable and show the chemistry of technetium to be among the most varied and interesting of the transition metals.

In the last 20 years or so the study of the coordination chemistry of technetium has assumed major practical importance due to the widespread use of the short-lived metastable isomer ^{99m}Tc in diagnostic nuclear medicine (*11–19*). Generally, a ^{99m}Tc-labeled compound (radiopharmaceutical) is injected intravenously into the patient and the *in vivo* distribution determined by the use of scintillation techniques, including single photon emission computed tomography (SPECT) (*15*). The physical properties of ^{99m}Tc are near ideal. The gamma ray energy of 140 keV is sufficiently energetic to penetrate deeply seated tissue and is easily externally collimated and detected. The absence of α or β emission and the short half-life of 6.01 hr result in a low radiation dose to the patient and activities of up to 1 GBq may be administered. Technetium-99m in the form of Na^{99m}TcO$_4$ is usually obtained from a ^{99}Mo/^{99m}Tc generator based on the decay scheme

$$^{99}\mathrm{MoO_4}^{2-} \xrightarrow[t_{1/2}=66\ \mathrm{hr}]{\beta^-} {}^{99m}\mathrm{TcO_4}^- \xrightarrow[t_{1/2}=6\ \mathrm{hr}]{\gamma} {}^{99}\mathrm{TcO_4}^-.$$

Fission-produced $^{99}\mathrm{MoO_4}^{2-}$ loaded onto an alumina column decays to $^{99m}\mathrm{TcO_4}^-$, which is conveniently eluted from the column by physiological saline (0.15 *M* NaCl) while the parent $^{99}\mathrm{MoO_4}^{2-}$ is strongly retained (*20, 21*). The generator eluate contains $^{99m}\mathrm{TcO_4}^-$ and a variable quantity of $^{99}\mathrm{TcO_4}^-$ (depending mainly on the time interval since the previous elution) with a total Tc concentration in the range of 10^{-8} to 10^{-6} *M* (*22, 23*). This mixture of $^{99m}\mathrm{TcO_4}^-/^{99}\mathrm{TcO_4}^-$ is referred to as "no carrier added" and is denoted simply as $^{99m}\mathrm{TcO_4}^-$. Radiopharmaceuticals are usually prepared by the reduction of $^{99m}\mathrm{TcO_4}^-$ in the presence of a ligand to give a ^{99m}Tc complex with the desired physiological behavior. A commonly used reducing agent is stannous tin. The ^{99m}Tc radiopharmaceutical is formed in high yield and radiochemical purity in aqueous solution at near-neutral pH and should be stable in the chemically aggressive *in vivo* environment at a Tc concentration of the order of $10^{-10} M$, which results from dilution by the blood volume (*24, 25*). In a number of cases chromatographic comparisons have shown the structure of ^{99m}Tc radiopharmaceutical to be the same as the ^{99}Tc complex prepared at the macroscopic level but in others the structure and oxidation state are uncertain (*19*). ^{99m}Tc radiopharmaceuticals are now available for skeletal, myocardial, renal, hepatobiliary, thyroid, and lung imaging and for a variety of physiological function studies (*15*). Specific examples are described together with the ^{99}Tc analogs. The impact of technetium in medical diagnosis may be judged by the 1990 estimate that six to seven million administrations of ^{99m}Tc radiopharmaceuticals are performed annually in the United States (*17*). As a result the study of technetium chemistry has to a degree been driven by the need to understand the chemistry of ^{99m}Tc radiopharmaceuticals and to develop new or improved organ-specific agents. Some of this chemistry is now being transferred to rhenium, whose high-energy β^- emitting ^{186}Re and ^{188}Re radioisotopes show promise for the development of therapeutic radiopharmaceuticals (*9*).

The aim of this chapter is to provide a fairly comprehensive overview of the status of technetium coordination chemistry up to the latter part of 1993. The term "coordination" is taken to include organometallic compounds. Binary halides are briefly described for the sake of completeness. The material is grouped into oxidation states, with the nitrosyl and thionitrosyl groups being treated as NO^+ and NS^+, the hydrido ligand as H^-, and "noninnocent" ligands such as dithiolenes in the dianionic form. The literature of technetium chemistry consists of two now out-of-date books (*26, 27*) and a more recent Russian text (*28*) together with a comprehensive survey of the literature in two volumes of Gmelin published in 1982 and 1983 (*29*). Much information is to be found in three conference volumes (*30–32*) and there are numerous reviews of technetium chemistry (*11–13, 15, 33–36*). Specific areas to have been reviewed are crystal structures (*37, 38*), EPR spectroscopy (*39–41*), cluster compounds (*42*), and analytical chemistry (*43*) and a useful correlation chart of ^{99}Tc NMR chemical shifts and oxidation states of technetium is available (*44*). Single-crystal X-ray diffraction has been particularly useful. The considerable fraction of technetium complexes to have been characterized by this method may be due to some extent to the difficulty in working with radioactive material but is no doubt largely due to the recent development of the chemistry and the greater availability of crystallographic structure determination facilities. There is a vast literature developed in the search for potential ^{99m}Tc radiopharmaceuticals. In many cases the complexes are poorly, if at all, characterized, although the charge is usually determined by electrophoresis. Such complexes will, in general, be considered here only if there are points of specific chemical interest. "No carrier added" preparations will always be denoted as ^{99m}Tc.

II. Technetium(−I)

This is the rarest oxidation state for technetium. The IR spectrum of a solution prepared by the addition of Na amalgam to $[Tc_2(CO)_{10}]$ in THF showed two $\nu(CO)$ bands at 1911 and 1865 cm^{-1}, which were assigned to the carbonyl anion $[Tc(CO)_5]^-$ by comparison with the spectra of $[M(CO)_5]^-$ (M = Mn, Re). Solutions of $Na[Tc(CO)_5]$ in THF undergo the expected reactions, including the formation of volatile $[HTc(CO)_5]$ on treatment with H_3PO_4 (*45*). The $[Tc(CO)_5]^-$ anion has been used as a nucleophile for the preparation of mixed-metal decacarbonyls (*46*) by reactions such as

$$[Tc(CO)_5]^- + [Re(CO)_5Br] \longrightarrow [TcRe(CO)_{10}] + Br^-.$$

Photolysis of a mixture of $[Tc_2(CO)_{10}]$ and $[Fe(CO)_5]$ in THF is reported to give $NEt_4[TcFe_2(CO)_{12}]$, where $Tc(CO)_4^-$ replaces $Fe(CO)_4$ the triangular structure of $[Fe_3(CO)_{12}]$ (*47*).

III. Technetium(0)

Best known, and of great synthetic utility, is the colorless diamagnetic dimer $[Tc_2(CO)_{10}]$ (m.p., 159–160°C) (*48, 49*), which may be prepared in up to 96% yield by the reaction of NH_4TcO_4 with CO (90 atm initial pressure) in toluene at 200°C with a reaction time of 4 hr (*50*). The $[M_2(CO)_{10}]$ (M = Mn, Tc, Re) carbonyls are isomorphous (*51*). The structure of $[Tc_2(CO)_{10}]$ (Fig. 1) shows the Tc atoms octahedrally coordinated with a Tc–Tc single bond distance of 3.036(6) Å and the equatorial carbonyl groups staggered (approximate D_{4d} symmetry) (*51*). The equatorial carbonyl groups on each Tc are bent away from the axial carbonyl toward the other half of the dimer. The greater π-acceptor character of the axial CO ligands is reflected in C–O bond distances

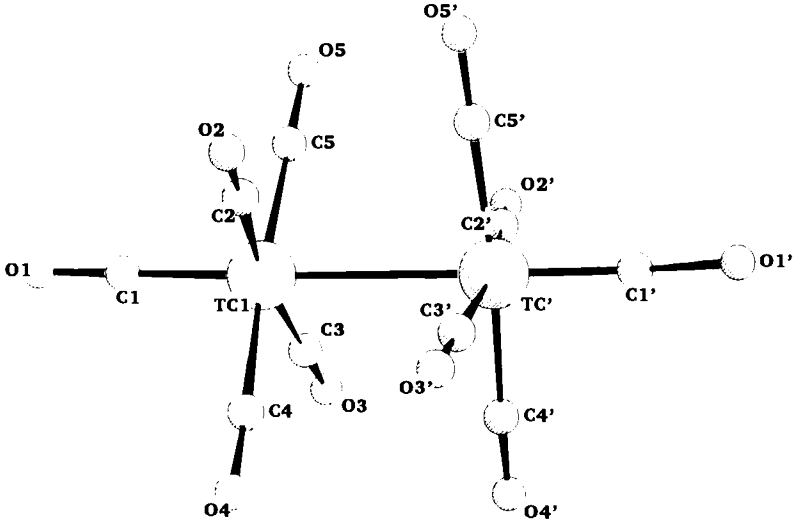


FIG. 1. The structure of $[Tc_2(CO)_{10}]$ (*51*).

0.09 Å longer and Tc–C bond distances 0.10 Å shorter than those of the equatorial ligands. The vibrational spectra of $[M_2(CO)_{10}]$ (M = Mn, Tc, Re) have been extensively investigated and compared (*52*). For $[Tc_2(CO)_{10}]$ the equatorial and axial CO stretching force constants of 16.642 and 16.316 mdyn $Å^{-1}$, respectively, again demonstrate the greater π-acceptor character of the axial CO ligands. The ^{99}Tc NMR spectrum of $[Tc_2(CO)_{10}]$ consists of single sharp signal ($\Delta\nu_{1/2}$ = 1.4 Hz) at −2477 ppm relative to TcO_4^- (*53*). The $[^{99m}Tc(CO)_5]^{\cdot}$ radical is produced in the β^- decay of $[^{99}Mo(CO)_6]$ and reacts with carrier $[Mn(CO)_5I]$ to form $[^{99m}Tc(CO)_5I]$ (*54*). The heteronuclear carbonyls $[MnTc(CO)_{10}]$ and $[TcRe(CO)_{10}]$ have been prepared by the reaction of a carbonylate anion with a carbonyl halide and characterized by IR and mass spectrometry. The IR spectra of the six possible $[M_2(CO)_{10}]$ (M = Mn, Tc, Re) compounds are closely similar, with the three ν(CO) peaks expected in local C_{4v} symmetry (*46*), a point that emphasizes the general similarity of the structures of Group 7 carbonyls. A mixed cobalt carbonyl $[(CO)_4CoTc(CO)_5]$ has also been reported (*55*) and the CO stretching force and interaction constants have been determined (*56*). A polymeric $[Tc(CO)_4]_n$, thought to be a trimer, has been claimed but remains inadequately characterized (*57*).

Substitution of the CO ligands in $[Tc_2(CO)_{10}]$ by the strong π-acceptor PF_3 is achieved either thermally or photolytically. In one study up to eight CO ligands were replaced to give at least 24 $[Tc_2(CO)_{10-n}(PF_3)_n]$

isomers, which were assigned on the basis of mass spectra, gas chromatographic retention times, and comparison with the rhenium analogs (*58*). The monosubstituted *ax*-[$Tc_2(CO)_9(PF_3)$] has been studied by ^{99}Tc and ^{19}F NMR (*59*). Reaction of Tc vapor with PF_3 at 77 K gives the volatile [$Tc_2(PF_3)_{10}$] (*60*). On the basis of IR evidence, the formation of [$Tc_2(CO)_9(PPh_3)$] and [$Tc_2(CO)_8(PPh_3)_2$] has been proposed in the reaction of [$Tc_2(CO)_{10}$] with PPh_3 in decalin at 100–150°C (*61*). Photolysis of [$Tc_2(CO)_{10}$] in the presence of butadiene at −20°C gives [$Tc_2(CO)_8(\mu\text{-}C_4H_6)$], which is isomorphous with the Mn and Re analogs. The *trans*-butadiene ligand bridges the Tc atoms, which are separated by 3.117(1) Å. The $Tc–C_{butadiene}$ bond distances (av., 2.389 Å) are markedly longer than Tc–CO (av., 1.945 Å) (*62*). A dinitrogen complex originally reported as [$Tc(N_2)(dppe)_2$] (*63*) has been shown to be the hydride [$HTc^I(N_2)(dppe)_2$] (*64*).

IV. Technetium(I)

A notable feature of this oxidation state is that a considerable number of Tc and ^{99m}Tc complexes can be prepared in high yields in aqueous media (*36*). As a consequence the coordination chemistry of Tc(I) has been intensively investigated in the search for ^{99m}Tc cationic myocardial imaging agents. Tc(I) complexes have the low-spin d^6 configuration and are diamagnetic. The 18-electron rule is generally applicable and nicely explains the stability and the prevalence of six-coordinate complexes.

A. CARBONYL COMPLEXES

Complexes containing cyclopentadienyl and related ligands are considered in Section B.

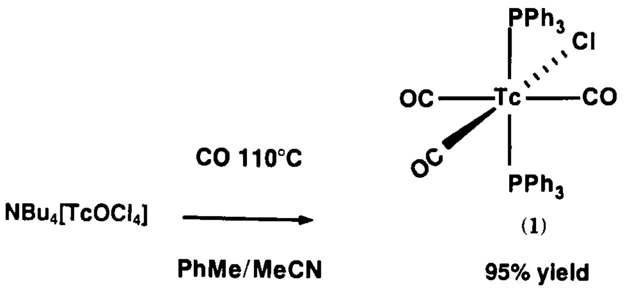
1. Mononuclear Complexes

Complexes containing from one to six carbonyl groups are known and all obey the 18-electron rule. The colorless salt [$Tc(CO)_6$]$AlCl_4$ is formed by the reaction of [$Tc(CO)_5Cl$] with $AlCl_3$ under 300 atm CO pressure and is soluble in THF, acetone, and methanol and stable in aqueous solution (*65*). The carbonyl halides [$Tc(CO)_5X$] (X = Cl, Br, I) may be prepared by the reaction of the halogen with [$Tc_2(CO)_{10}$]. Reaction with chlorine and bromine occurs readily at room temperature but reaction with iodine is extremely slow. The iodide has been prepared by the high-pressure carbonylation of [$Tc(CO)_4I$]$_2$ (*45*). An alternative preparation of the carbonyl halides is by the reaction of $K_2[TcX_6]$ with CO under pressure at 230–250°C in the presence of Cu powder (*65*). The IR spectra of $[Tc(CO)_5X]$ (X = Cl, Br, I) show the three ν(CO) bands ($2A_1 + E$) expected in C_{4v} symmetry in the region 2153–1991 cm^{-1} and a weak ^{13}CO isotope peak of the intense E mode (*45*). The ease of halide substitution in $[Tc(CO)_5X]$ (usually with the loss of one or more CO groups) makes these compounds key starting materials in technetium carbonyl chemistry (*65*). Simple substitution of X^- occurs in the reaction of CF_3COOAg with $[Tc(CO)_5Cl]$ to give $[Tc(CO)_5(OOCCF_3)]$. The asymmetry introduced by the CF_3COO^- ligand results in the B_1 mode becoming IR active and four ν(CO) bands are observed (*66*). Oxidation of $[Tc_2(CO)_{10}]$ with $NOPF_6$ in MeCN gives $[Tc(CO)_5(CH_3CN)]PF_6$ in quantitative yield. This complex is a useful synthetic precursor for the preparation of cationic carbonyl complexes with a variety of ligands (*67*). The volatile, colorless hydride $[HTc(CO)_5]$ is produced in only low yield by the reaction of $[Tc(CO)_5]^-$ with H_3PO_4 (*45*).

Complexes based on the $[Tc(CO)_4]$ core are $[Tc(CO)_4(S_2CNR_2)]$ (R = Me, Et), the cationic $[Tc(CO)_4(PPh_3)_2]AlCl_4$ (*65*), and $[Tc(CO)_4(acac)]$ (*68*). The dithiocarbamato complexes are formed by the reaction of $Na(S_2CNR_2)$ with $[Tc(CO)_5Cl]$ in acetone or THF. Grinding of $[Tc(CO)_5Cl]$ with K(β-diketonate) under a layer of CCl_4 yields the unstable tetracarbonyl β-diketonates (*68*).

A considerable number of complexes containing the $[Tc(CO)_3]$ core have been prepared and a number of crystal structures have been reported. Cationic complexes are of the type $[Tc(CO)_3L_3]X$, where L_3 represents three neutral monodentate ligands, a monodentate and bidentate neutral ligand, or a neutral tridentate ligand. Reaction of $[Tc(CO)_5Br]$ with $AgPF_6$ in MeCN gives a near quantitative yield of $[Tc(CO)_3(MeCN)_3]PF_6$ and $[Tc(CO)_3(MeCN)(PPh_3)_2]PF_6$ and $[Tc(CO)_3(MeCN)(dppe)]PF_6$ may be prepared by ligand exchange (*69*). Of particular interest in relation to potential ^{99m}Tc radiopharmaceuticals is the air-stable, water-soluble $[Tc(CO)_3(L_3)]PF_6$ (L_3 = tan; 1,4,7-trimethyltan; 1,4,7-trithiacyclononane) (*67*). Only one monoanionic ligand seems to be supported to give neutral complexes of the type $[TcX(CO)_3L_2]$, where some examples are X = Cl, Br, I, O_2CR; L = PR_3, AsR_3, SbR_3, $P(OR)_3$, py, MeCN, CNR, Et_2NH; or L_2 = bpy, phen, dppe, en (*65, 66, 68, 70–72*); $[Tc(CO)_3\{HB(pz)_3\}]$ (*73*). A novel preparative method with CO at atmospheric pressure yields 1 (*74*).

Fac and *mer* isomers may be distinguished by the IR spectrum; two ν(CO) bands ($A_1 + E$ in local C_{3v} symmetry for the CO groups) are expected for a *fac* isomer and three ($2A_1 + B_1$ in local C_{2v} symmetry), for a *mer* isomer (*67, 72*). The ^{99}Tc NMR spectra of neutral complexes



(1)

show chemical shifts of −940 to −1820 ppm and those of cationic complexes, −2070 to −3520 ppm against TcO_4^- (*70, 75*). The crystal structure of 1 shows almost undistorted octahedral geometry with a P–Tc–P angle of 174.59(2)° (*74*), whereas that of *fac*-$[TcBr(CO)_3(en)]$ is distorted with the Tc–C and C–O bond distances the same for all three CO groups (*76*). A "piano stool" structure with C_{3v} symmetry is found for $[Tc(CO)_3L]$ [L = $HB(pz)_3$, $HB(3,5\text{-}Me_2pz)_3$], which is isostructural with the Mn and Re analogs (*73*). An unusual complex is $[TcBr(CO)_3(Ph\text{-}\beta\text{-}glup)]$, prepared by the reaction of $[Tc(CO)_5Br]$ with a neutral chiral phosphinoglucose derivative (*77*).

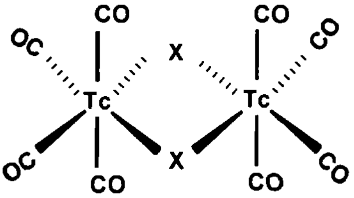
Complexes containing the $[Tc(CO)_2]$ core may be prepared by substitution or carbonylation reactions. The thiolato complexes $[Tc(CO)_2(PPh_3)_2L]$ [L = S_2CNEt_2, S_2COEt, $S_2P(OMe)_2$] are formed on heating *trans*-$[Tc(CO)_3Cl(PPh_3)_2]$ with the ligand in acetone or THF (*78*). The *cis*- and *trans*-isomers of $[Tc(CO)_2\{P(OEt)_2Ph\}_4]ClO_4$ are formed by the reaction of $[TcCl_2\{P(OEt)_2Ph\}_4]ClO_4$ with CO (1 atm) at 50°C (*79*). The *cis*-isomer is a distorted octahedron with the two Tc–CO bond distances both 1.90(2) Å. *mer*-$[TcX_3(PMe_2Ph)_3]$ (X = Cl, Br) reacts with CO (1 atm) in refluxing $MeO(CH_2)_2OMe$ containing added phosphine to give only *cis*-$[TcX(CO)_2(PMe_2Ph)_3]$ (*72*). A variety of $[Tc(CO)_2(PPh_3)_2L]$ complexes, where L is a carboxylato, mixed amido, or thiazolato ligand (*80*), and $[Tc(CO)_2L\{P(OR)_3\}_2]PF_6$ (L = bpy, 4,4-Me_2bpy) (*67*) have been prepared. Crystal structures of the Schiff base complex $[Tc(CO)_2(PPh_3)_2\{(C_3H_2NS)N{=}CHC_6H_4O\text{-}o\}]$ (*81*) and the pseudoallyl complexes $[Tc(CO)_2(PMe_2Ph)_2(p\text{-}MeC_6H_4N\overset{..}{-}N\overset{..}{-}NC_6H_4Me\text{-}p)]$, $[Tc(CO)_2(PMe_2Ph)_2(PhN\overset{..}{-}C(Me)\overset{..}{-}NPh)]$ (*82*), and $[Tc(CO)_2(PPh_3)_2\{SC(NHPh)S\}]$ (*83*) show distorted octahedral geometry with the two CO ligands mutually *cis* and the PPh_3 ligands *trans*. Structurally characterized complexes with a tridentate ligand are *cis*-$[Tc(CO)_2(PPh_3)(tan)]Cl$ and *cis*-$[Tc(CO)_2(PPh_3)\{HB(pz)_3\}]$ (*74*). Electrochemical oxidation of $[Tc(CO)_2Cl(PMe_2Ph)_3]$ results in the formation of $[Tc^{III}(CO)Cl(MeCN)_2$

$(PMe_2Ph)_3](ClO_4)_2$ (*84*), an example of the oxidation of one 18-electron species to another.

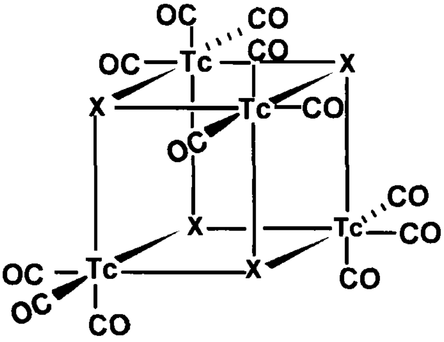
Reaction of $[HTc(N_2)(dppe)_2]$ with CO in benzene or with methanol in the presence of pyridine gives $[HTc(CO)(dppe)_2]$. In the latter reaction methanol serves as the source of CO. On reflux in MeCN, $[HTc(CO)(dppe)_2]$ is converted to $[Tc(CO)(MeCN)(dppe)_2]PF_6$ (*85*).

2. *Dimeric and Polynuclear Complexes*

The dimers $[Tc(CO)_4X]_2$ (X = Cl, Br, I) are formed by the reaction of the halogen with $[Tc_2(CO)_{10}]$ (*45*). The ease of thermal decarbonylation of $[Tc(CO)_5X]$ in an inert solvent or during vacuum sublimation increases in the order I < Br < Cl and decarbonylation proceeds in the sequence $[Tc(CO)_5X] \rightarrow [Tc(CO)_4X]_2 \rightarrow [Tc(CO)_3X]_4$ (*86*). Decarbonylation occurs more easily than that for the Mn or Re analogs. The presence of four ν(CO) bands and the TcCO bending region in the IR spectra is consistent with the D_{2h} halide-bridged structure (**2**) for the dimers (*87*) and has been confirmed crystallographically by the isostructural nature of $[M(CO)_4Br]_2$ (M = Tc, Re) (*88*).



(**2**)



(**3**)

Structure **3** (X = Br), consisting of a cube with μ_3-Br bridges, was assigned to the tetrameric $[Tc(CO)_3Br]_4$ on the basis of X-ray diffraction data (*88*). This is confirmed by the single-crystal structure determination of **3** (X = Cl), which shows that the tetramer has crystallographic T_d symmetry with bond distances Tc–C, 1.903(3) Å; C–O, 1.128(4) Å; and Tc–Cl, 2.559(1) Å. The Tc···Tc distance of 3.840(1) Å shows the absence of a direct Tc–Tc interaction (*76*). The reaction of $[Tc(CO)_3Cl]_4$ with chlorine is reported to give the trimer $[(OC)_3Tc^I(\mu\text{-}Cl)_3Tc^{IV}(\mu\text{-}Cl)_3Tc^I(CO)_3]$ (*89*). The reaction of thiols, sulfides, diarsines, and Hacac with $[Tc(CO)_5X]$ gives the dimers $[Tc(CO)_4(SPh)]_2$ (*65*), $[Tc(CO)_3Cl(EPh_2)]_2$ (E = P, S, Se, As) (*90, 91*), $[Tc(CO)_3BrL]_2$ (L = THF, MeCN; for which the IR spectra are consistent with a centrosymmetric structure) (*71*), and $[Tc(CO)_3(acac)]_2$ (*92*). Extensive mass spectral data have been reported (*93*).

Partial carbonylation of $NaTcO_4$ in methanol gives the unprecedented cubane-type structure $Na[Tc_3(CO)_9(OMe)_4]$ (**4**) (Fig. 2), with each Tc atom obeying the 18-electron rule. The Na^+ cation in **4** forms one corner of the cube with Na–OMe distances of ca. 2.38 Å and Na···OC interactions (ca. 2.51 Å) with adjoining cubes completing the coordination octahedron. In solution, **4** exists as the cubane cluster and not the Na^+ salt. The $[Tc_3(CO)_9(OMe)_4]^-$ group may thus be likened to an anionic crown ether with a high affinity for Na^+ (*94*). The reaction of $KTcO_4$ with HCOOH gives $[Tc(CO)_3OH]_n$, which is most likely the cubic tetramer (**3**) (X = OH) (*95*). The cubic structure of **3** has been established crystallographically for $[M(CO)_3(\mu_3\text{-}OH)]_4$ (M = Mn, Re) (*96*).

Reaction of $[Tc_2(CO)_{10}]$ with *meso*-tetraphenylporphine (H_2tpp) or mesoporphyrin IX dimethyl ester (H_2mp) gives the unusual dimers $[L\{Tc(CO)_3\}_2]$ (L = mp, tpp) (*97, 98*). These dimers are also formed by the thermal disproportionation of $[(HL)Tc(CO)_3]$. The crystal structure of $[tpp\{Tc(CO)_3\}_2]$ shows the two $Tc(CO)_3$ moieties arranged in a tripod

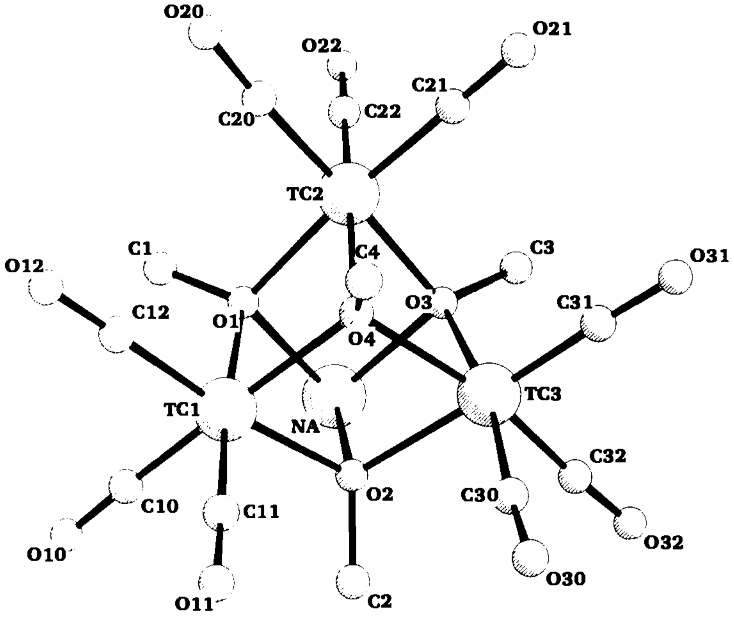
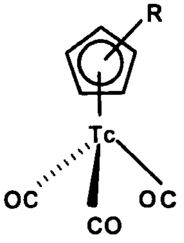


FIG. 2. The structure of $Na[Tc_3(CO)_9(OMe)_4]$ (**4**) (*94*).

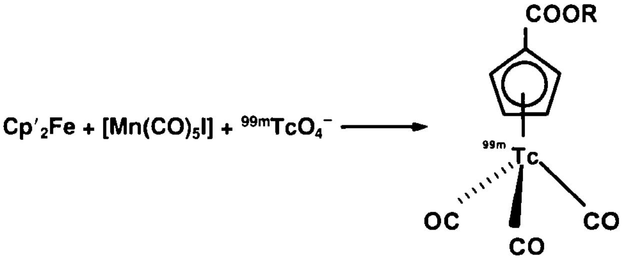
configuration, with one on each side of the porphine ring and each out-of-plane Tc atom coordinated to three N atoms. The Tc···Tc distance of 3.101 Å is somewhat long to constitute bonding, but is short enough to indicate some metal–metal interaction (*97*). The dark-red air-stable heteronuclear [mp{$(OC)_3TcRe(CO)_3$}] is formed on heating [Hmp{$Re(CO)_3$}] with [$Tc_2(CO)_{10}$] in decalin (*98*).

B. Cyclopentadienyl and Arene Complexes

η^5-Cyclopentadienyl complexes of the type [$Cp'Tc(CO)_3$] may be prepared by the reaction of $TcCl_4/CO/Cu$ or [$Tc(CO)_5X$] with NaCp′ or LiCp′ (*99, 100*). Crystal structures of [$LTc(CO)_3$] (L = C_5Me_5, C_5Me_4Et, indenyl) (*101*) and [{$Me_3N(CH_2)_3C_5Me_4$}$Tc(CO)_3$]I (*100*) show the piano stool arrangement (**5**). [$CpTc(CO)_3$] undergoes acylation on reaction with PhCOCl to give the PhCOCp derivative (*102*).



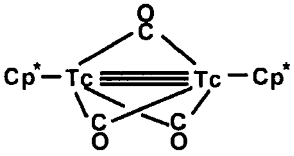
(**5**)



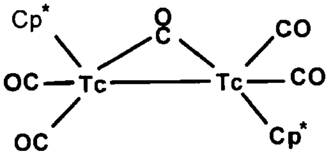
(**6**)

The ^{99m}Tc complexes (**6**) (R = *N*-methylpiperidine, quinuclidine) may be prepared in 30–90% radiochemical yield by the route shown on heating for 1 hr in THF at 150°C. These esters show high brain uptake in animals (*103*).

Irradiation of [$(C_5Me_5)Tc(CO)_3$] in cyclohexane produces the η^5-C_5Me_5 carbonyl-bridged dimers **7** and **8**. The structure of **7** was established crystallographically and that of **8** was confirmed by spectroscopic comparison with the structurally characterized Re analog (*104*).



(**7**)



(**8**)

The short Tc–Tc bond distance of 2.413(3) Å in **7** corresponds to a triple bond and for **8** a Tc–Tc single bond has been proposed. These bond orders are those needed to satisfy the 18-electron rule. As expected, the ν(CO) IR absorptions in **7** occur at 1821–1771 cm^{-1}, whereas for **8**, which contains terminal and bridging CO groups, the range is 2012–1738 cm^{-1}. The $[Tc(arene)_2]PF_6$ (arene = benzene, substituted benzene, aromatic hydrocarbon) complexes are formed by reaction of the arene with $TcCl_4/AlCl_3/Al$ (*105, 106*). The cations are stable to the air and to acids and bases. A large number of $[^{99m}Tc(arene)_2]^+$ complexes have been prepared and the structure has been demonstrated by HPLC comparisons with the ^{99}Tc complexes. The lipophilic ^{99m}Tc complexes of benzene substituted with four to six carbon atoms show promising myocardial uptake (*107*).

C. CYANO AND ISONITRILE COMPLEXES

Olive-green $K_5[Tc(CN)_6]$ has been prepared by the reduction of TcO_4^- with K/CN^- and shown to be isostructural with $K_5[M(CN)_6]$ (M = Mn, Re) (*108*). The low CN force constant of 14.57 mdyn $Å^{-1}$ indicates that cyanide is acting as a relatively strong π-acceptor (*109*). Following the discovery that the $[^{99m}Tc(CN^tBu)_6]^+$ cation is concentrated in the human myocardium, this class of complexes has been intensively investigated in the search for improved imaging agents (*19, 110*). The air- and water-stable $[Tc(CNR)_6]X$ salts may be prepared by the reaction of $[Tc^{III}(tu)_6]Cl_3$ with RNC but a more convenient method is the reduction of TcO_4^- by $Na_2S_2O_4$ in aqueous ethanol in the presence of the ligand (*111, 112*). The energy of the ν(CN) IR absorption is 50–80 cm^{-1} lower than that in the free ligand, consistent with extensive π-donation from Tc(I). Reversible one-electron oxidation occurs at 0.82–0.88 V vs SCE for alkyl derivatives, with the phenyl derivative more difficult to oxidize at 1.18 V vs SCE (*112*). The ^{99}Tc NMR spectra show a single signal at about −1900 ppm relative to TcO_4^-, with small but significant chemical shift differences due to the substituents (*44, 113*). The crystal structure of $[Tc(CN^tBu)_6]PF_6$ establishes that the geometry is octahedral with Tc–C bond distances of 2.029(5) Å and that the complex is isomorphous with the Re analog (*114*). Systematic variation of the R group has led to the development of $[^{99m}Tc(CNR)_6]^+$, where CNR is (2-methoxy-2-methylpropyl)isonitrile, as a radiopharmaceutical for myocardial imaging (*19*). *In vivo,* the methoxy groups are sequentially metabolized to hydroxy groups to give seven products of increasing hydrophilicity and the resulting desired faster blood and lung clearance in comparison with $[^{99m}Tc(CN^tBu)_6]^+$ (*115*). At high pH $[Tc(CNCMe_2COOMe)_6]Cl$ undergoes random base-catalyzed ester hydrolysis of the coordinated ligands. The nine possible carboxylic acid products have been isolated and identified by HPLC, FABMS, IR, and ^{99}Tc NMR (*116*). Mixed-ligand complexes of the type $[Tc(CNR)_n(CNR')_{6-n}]^+$ (n = 0–6) and $[Tc(CN^tBu)_n(PPh_3)_{6-n}]PF_6$ (n = 4, 5) have been prepared by synthesis with a mixture of ligands (*117, 118*), and *trans*-$[Tc(dppe)_2(CN^tBu)_2]PF_6$ (*119*) and $[HTc(CNR)(dppe)_2]$ (*85*) have been prepared by substitution of $[HTc(N_2)(dppe)_2]$. Photolysis of $[Tc(CNR)_6]PF_6$ in the presence of bpy, phen, or mixed ligand synthesis from TcO_4^- gives a series of complexes of the type $[Tc(CNR)_4L]PF_6$. The crystal structure of $[Tc(CN^tBu)_4(bpy)]PF_6$ shows that one of the isonitrile ligands is considerably bent, with a C≡N-C angle of 148°, suggesting a "pseudo" internal oxidation of Tc(I) to Tc(III) (*120*). Oxidative addition of chlorine or bromine to $[Tc(CN^tBu)_6]PF_6$ produces the seven-coordinate $[Tc^{III}(CN^tBu)_6X](PF_6)_2$ in 75% yield (*121*).

D. DINITROGEN, PHOSPHINE, PHOSPHITE, AND RELATED COMPLEXES

Crystallography and ^1H NMR have confirmed the formula $[HTc(N_2)(dppe)_2]$ for the product of the reduction of $[TcCl_4(PPh_3)_2]$ by Na amalgam under nitrogen in the presence of dppe. The Tc atom is octahedrally coordinated with the hydrido ligand *trans* to dinitrogen. The Tc–N and N–N distances are 2.05(1) and 0.98(1) Å, respectively, and the Tc–N–N angle is 178(1)° (*64*). The ease of substitution of dinitrogen and hydride makes this compound a versatile starting material for the preparation of Tc(I) mixed-ligand complexes (*85*). On UV irradiation $[Tc(CO)_3\{HB(3,5\text{-}Me_2pz)_3\}]$ reacts with nitrogen to give the air-stable dinitrogen-bridged dimer $[\{(HB(3,5\text{-}Me_2pz)_3)Tc(CO)_2\}_2(\mu\text{-}N_2)]$. The N–N bond distance of dinitrogen is 1.160(3) Å and the Tc–N–N angle is close to linear at 174°. In the electronic spectrum a band at 21,552 cm^{-1} (ε = 3175) has been assigned to a $Tc \rightarrow N_2(\pi^*)$ MLCT transition (*122*).

Excess ligand serves as the reductant in the preparation of $[Tc(dmpe)_3]CF_3SO_3$ from TcO_4^- and dmpe. EXAFS analysis of the fluoride salt has established octahedral geometry with a Tc–P bond distance of 2.40 Å (*123*). The $[TcL_3]^+$ (L = dmpe, depe) complexes undergo reversible electrochemical oxidation to $[Tc^{II}L_3]^{2+}$, a reaction that may be chemically produced by H_2O_2 (*124*). The Tc(II)/Tc(I) couple for depe as ligand is 164 mV more negative than that for dmpe, indicating that $[Tc(depe)_3]^+$ is considerably more easily oxidized than $[Tc(dmpe)_3]^+$. Thus, both oxidation states are air-stable for dmpe as ligand, whereas

$[Tc(depe)_3]^{2+}$ is air-stable but $[Tc(depe)_3]^+$ must be prepared under air-free conditions. Pulse radiolysis studies show that the oxidation of $[Tc(dmpe)_3]^+$ to $[Tc(dmpe)_3]^{2+}$ by the strong oxidant Cl_2^- proceeds at, or near, the diffusion-controlled limit ($k = 1 \times 10^9\ M^{-1}\ sec^{-1}$) by an outer-sphere mechanism (*125*). The self-exchange rate of the $[Tc(dmpe)_3]^{+/2+}$ couple has been calculated by application of the Marcus theory to be $2 \times 10^6\ M^{-1}\ sec^{-1}$ (*126, 127*). The diamagnetic mixed phosphine–phosphite complex $[Tc(dppe)(tmp)_4]PF_6$ has been prepared by substitution of $[HTc(N_2)(dppe)_2]$ and characterized by FABMS and ^1H and ^{99}Tc NMR (*128*). A number of homoleptic phosphite, phosphonite, and phosphinite cationic complexes of the type $[TcL_6]X$ [L = tmp, $PR(OMe)_2$, $PEt_2(OMe)$] have been prepared, either from TcO_4^- or by reductive substitution of $[Tc^{III}(tu)_6]Cl_3$, and characterized by ^{99}Tc and ^{31}P NMR, FABMS, or X-ray photoelectron spectroscopy (*129–132*). The $[^{99m}Tc(dmpe)_3]^+$ and $[^{99m}Tc(tmp)_6]^+$ cations proved disappointing as potential myocardial imaging agents in humans due to slow blood clearance, although the clearance in dogs was fast. This species difference is due to the strong binding of the cations to a plasma component present in human but not in dog blood (*24*).

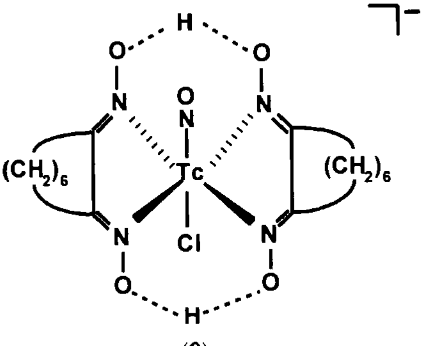
E. COMPLEXES WITH NITROGEN LIGANDS

Electrochemical reduction of a mixture of TcO_4^- and phen allowed the isolation of the purple crystalline $[Tc(phen)_3]PF_6$. Conductivity measurements in MeCN confirmed a 1:1 electrolyte and cerimetric titration confirmed the +1 oxidation state (*133*).

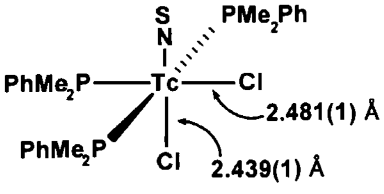
F. NITROSYL AND THIONITROSYL COMPLEXES

By the reduction of $(NH_4)_2[TcCl_6]$ with $NH_2OH{\cdot}HCl$ and addition of ammonia Eakins *et al.* obtained pink crystals, which they formulated as a hydroxylamine complex (*134*), but which were later shown to be the diamagnetic nitrosyl complex *trans*-$[Tc(NO)(NH_3)_4(OH_2)]Cl_2$ (*135*). The ammine ligands are remarkably stable to substitution in acid solution and the nitrosyl group is stable to nucleophilic attack. The crystal structure reveals bond distances of 2.168(4) Å for $Tc{-}OH_2$ and 2.164(5) Å (av.) for $Tc{-}NH_3$ (*136*). The short Tc–NO distance of 1.716(4) Å and the relatively long N–O distance of 1.203(6) Å together with the low $\nu(NO)$ IR absorption at 1680 cm^{-1} and the surprisingly acidic water ($pK_a = 7.3$) indicate very strong back-donation from Tc to NO (*135*). The NO group has been estimated to carry a half-negative charge, which assigns an oxidation state of +2.5 to Tc rather than the +1 based on the NO^+ formalism (*136*). Oxidation gives the green *trans*-

$[Tc^{II}(NO)(NH_3)_4(OH_2)]Cl_3$ with $\nu(NO)$ at 1830 cm^{-1} and a highly acidic *trans* water ($pK_a = 2.0$) (*135*). The novel hydride $[Tc(NO)(PPh_3)_3(H)_2]$ is formed by borohydride reduction of a mixture of $[Tc^{II}(NO)(PPh_3)_2Cl_3]$ and PPh_3 (*137*). The TcH IR absorptions occur at 1733 and 1185 cm^{-1}, and $\nu(NO)$ at 1636 cm^{-1} is shifted to 1659 cm^{-1} in the dideuterio complex, indicating a strong coupling of the nitrosyl and hydrido ligands. Reaction of $[Tc(CN^tBu)_6]NO_3$ with $NOPF_6$ or $HNO_3/HOAc$ gives a high yield of $[Tc(NO)(CN^tBu)_5](PF_6)_2$. The high value of 1865 cm^{-1} for $\nu(NO)$ is consistent with NO^+ coordination (*138*). Similarly, $[(C_5Me_5)Tc(CO)_3]$ undergoes substitution of CO by the isoelectronic NO^+ to produce a good yield of $[(C_5Me_5)Tc(NO)(CO)_2]PF_6$, for which $\nu(NO)$ occurs at the lower value of 1745 cm^{-1} as a result of the increased back-bonding induced by the anionic Cp′ ligand (*100*). $NBu_4[Tc^{II}(NO)Br_4]$ is reduced by CN^tBu to the neutral *trans*-$[Tc^{I}(NO)Br_2(CN^tBu)_3]$ [$\nu(NO)$ at 1755 cm^{-1}], for which the stereochemistry has been crystallographically established (*138*). Electrochemical or hydrazine reduction of the deep-purple $(NBu_4)_2[Tc^{II}(NO)(NCS)_5]$ results in rust-colored crystals of $(NBu_4)_3[Tc(NO)(NCS)_5]$ (*139*). The crystal structure of $[Tc(NO)Cl(dppe)_2]Cl \cdot H_2O$ has been briefly described (*140*). Reaction of $AsPh_4[Tc^{V}OCl_4]$ with an excess of cyclooctane-1,2-dioxime ($codoH_2$) yields brown crystals, shown by crystallography to be $AsPh_4[Tc(NO)Cl(codoH)_2] \cdot HCl$ (**9**) (*141*). The nitrosyl group appears to be derived from NH_2OH formed by partial hydrolysis of the dioxime. The intense $\nu(NO)$ IR absorption occurs at 1701 cm^{-1}.



(**9**)



(**10**)

Although nitrosyl complexes have been long known, the first thionitrosyl complex was reported only in 1974 (*142*). The Tc≡N group shows a marked tendency to abstract sulfur to form Tc(NS) complexes in the +1, +2, and +3 oxidation states. The $Tc^{I}(NS)$ complex (**10**) is prepared by the reaction of $[Tc^{V}NCl_2(PMe_2Ph)_3]$ with 1 eq. of S_2Cl_2 (*143*) and *mer*-$[Tc(NS)Cl_2(pic)_3]$ by a remarkable reaction in which $[Tc^{VI}NCl_4]^-$ abstracts sulfur from the $S_2O_4^{2-}$ anion (*144*). The ν(NS) IR absorptions occur at 1177 [shifted to 1147 cm^{-1} on ^{15}N labeling (*145*)] and 1173 cm^{-1} for **10** and the picoline complex, respectively. The nearly linear Tc–N–S angles of 177° and 176° are consistent with coordination by NS^+. Structure **10** shows a small but distinct shortening of the Tc–Cl bond *trans* to NS relative to the *cis* bond, whereas for *mer*-$[Tc(NS)Cl_2(pic)_3]$ the reverse is observed with NSTc–Cl_{cis}, 2.430(2) Å, and *trans*, 2.443(1) Å (*143, 144*).

V. Technetium(II)

Technetium(II) complexes are paramagnetic with the d^5 low-spin configuration. A characteristic feature is the considerable number of mixed-valence halide clusters containing Tc in oxidation states of +1.5 to +3. This area has been reviewed (*42*). For convenience, all complexes, except those of $[Tc_2]^{6+}$, are treated together here. EPR spectroscopy is particularly useful in both the detection of species in this oxidation state and the study of exchange reactions in solution. The nuclear spin of ^{99}Tc ($I = \frac{9}{2}$) results in spectra of 10 lines with superimposed hyperfine splitting. The d^5 low-spin system is treated as a d^1 system in the hole formalism (*40*).

A. ORGANOMETALLIC COMPLEXES

Although carbonyl and cyclopentadienyl complexes are well known for Tc(I) and Tc(III), none appear to have been reported for Tc(II). This may be ascribed to the tendency to follow the 18-electron rule, which, due to the odd number of electrons, would require dimer formation for compliance. Similarly, no Tc(II) cyano or isonitrile complexes appear to have been isolated.

B. HALIDE COMPLEXES AND CLUSTERS

1. *Mononuclear and Binuclear Complexes*

The only monomeric complex is the tetrahedral $[TcBr_4]^{2-}$, identified crystallographically in the product (**11**) of the remarkable reaction

$$NBu_4[Tc^{VI}NBr_4] \xrightarrow[EtOH]{bpy} [Tc^{V}NBr(bpy)_2]_2[Tc^{II}Br_4]. \qquad (11)$$

The mechanism of formation of **11** is unknown. The Br–Tc–Br bond angles in $[TcBr_4]^{2-}$ are approximately tetrahedral, in the range 106.1–112.1°, and the Tc–Br bond distances of 2.388–2.417 Å are very short (*146*).

From the reduction of $KTcO_4$/HCl by hydrogen (30 atm at 140°C), crystals of the d^5–d^5 cluster $K_2[Tc^{II}_2Cl_6]\cdot 2H_2O$ were separated (*147, 148*). Structural analysis shows a polymer of $Tc_2Cl_8^{4-}$ units with strongly distorted D_{4d} symmetry, linked by bridging Cl in infinite zigzag chains, with the very short Tc–Tc bond distance of 2.044(1) Å. On the basis of the short Tc–Tc distance a "quintuple" bond was suggested (*148*). The crystal structure has been reexamined at 15 and −53°C and Tc–Tc bond distances of 2.047(1) and 2.042(2) Å found (*149*). These very short distances are not anomalous for a triple bond with the $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration because, even though the δ bond order is 0, the low oxidation state of the $[Tc_2]^{4+}$ core strongly enhances the σ and π bonding (*149*). The bromo complex $K_2[Tc_2Br_6]\cdot 2H_2O$ has also been prepared (*147*). Both complexes are diamagnetic (*150*).

The turquoise-blue salts $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$ and $Y[Tc_2Cl_8]\cdot 9H_2O$ of the mixed-valence d^4–d^5 $[Tc_2Cl_8]^{3-}$ anion, with an average oxidation state of +2.5, were first prepared in 1963 by the reduction of $[TcCl_6]^{2-}$ with Zn/HCl (*134*). Improved synthetic methods have been developed and a variety of $[Tc_2Cl_8]^{3-}$ salts, with inorganic or organic cations, is now known (*42, 151*). Crystal structures are available for $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$ (*152*) and the K^+ (*153, 154*), Y^{3+} (*155*), and pyH^+ (*156*) salts. Also, the metal cation may be partially replaced by H_3O^+, as in the structurally characterized $K'_6K''_{3-x}(H_3O)_x[Tc_2Cl_8]_3\cdot nH_2O$ (*157*). The $[Tc_2Cl_8]^{3-}$ anion possesses virtual D_{4h} symmetry with the square-pyramidal end groups in the eclipsed conformation (Fig. 3). The short Tc–Tc distances of 2.117(2) for the K^+ (*154*) and 2.1185(5) Å for the pyH^+ salt (*157*) and the observed paramagnetism [$\mu_{eff} = 1.78(3)$ BM for the NH_4^+ and Y^{3+} salts (*158*)] are consistent with a strong metal–metal bond order of 3.5 and a $\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration (*159*), a conclusion supported by the EPR spectra (*158*) and self-consistent field Xα scattered-wave calculations (*160*). In fact, $[Tc_2Cl_8]^{3-}$ is the first species in which a bond order of 3.5 was recognized (*159*). In the electronic spectrum of $K_3[Tc_2Cl_8]$, the main component of the 15,700-cm^{-1} (638-nm) band has been assigned to the $\delta^* \rightarrow \pi^*$ transition, and the band originating at 5900 cm^{-1} in the near IR, to the $\delta \rightarrow \delta^*$ transition (*161*). The $[Tc_2Cl_8]^{2-}/[Tc_2Cl_8]^{3-}$ couple is electrochemically quasireversible in HCl/EtOH (*158*). In HCl solution $[Tc_2Cl_8]^{3-}$ undergoes hydrolysis, disproportionation, and oxidation by oxygen, with rupture of the Tc–Tc bond (*162*). At 280°C, anhydrous $(NH_4)_3[Tc_2Cl_8]$ starts to disproportion-

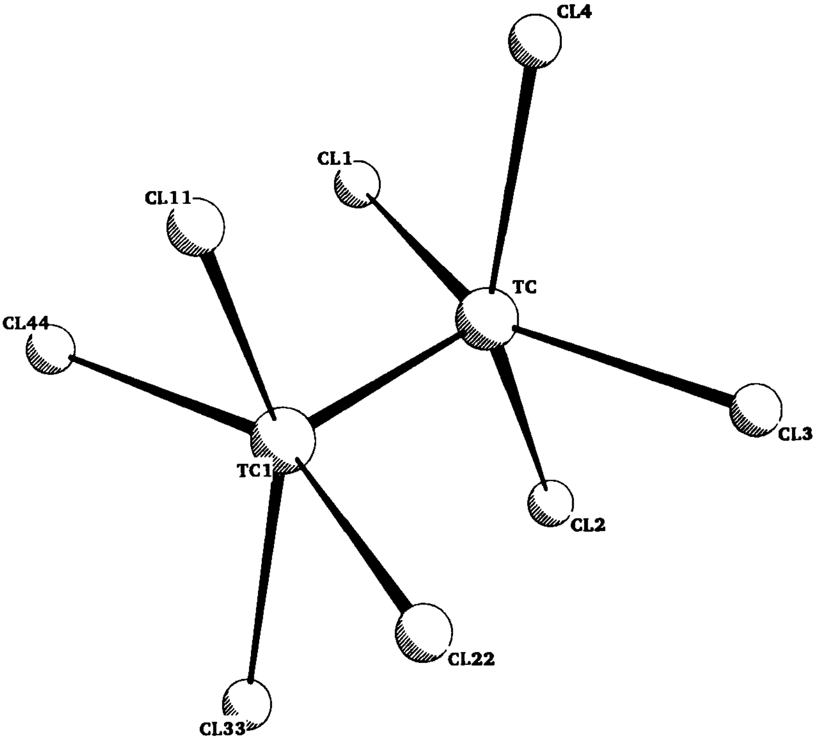


FIG. 3. The structure of the $[Tc_2Cl_8]^{3-}$ anion in $K_3[Tc_2Cl_8]\cdot nH_2O$ (*154*).

ate to $(NH_4)_2[TcCl_6]$ and Tc metal (*163*). The $[Tc_2Br_8]^{3-}$ anion is rather less stable than the chloro analog but the gold-colored $(NBu_4)_3[Tc_2Cl_8]$ may be obtained in 70% yield by the reduction of $(NBu_4)_2[Tc_2Cl_8]$ with BH_4^- in CH_2Cl_2. The $Cs_3[Tc_2Cl_8]$ salt at 6 K shows a well-resolved vibronic structure of the $\delta \rightarrow \delta^*$ transition, with electronic origin at about 5970 cm^{-1} (*164*).

Reaction of $K_3[Tc_2X_8]\cdot 2H_2O$ (X = Cl, Br) with glacial acetic acid results in substitution to yield green crystals of $[Tc_2(OAc)_4X]$ (*42, 165*), and reaction of $(NH_4)_3[Tc_2Cl_8]$ with molten 2-hydroxypyridine (Hhp) gives the dark-green $[Tc_2(hp)_4Cl]$ (*166*). Crystal structures of these three complexes reveal the familiar "lantern" arrangement, with the bidentate ligands bridging the two Tc atoms of each cluster and axial halide bridging the clusters. Infinite linear chains occur in $[Tc_2(hp)_4Cl]$ [Tc–Tc, 2.095(1) Å; Tc–Cl, 2.679(1) Å] and $[Tc_2(OAc)_4Br]$ [Tc–Tc, 2.112(1) Å; Tc–Br, 2.843(1) Å] (*167a*) complexes and zigzag chains with a Tc–Cl–Tc angle of 120° for $[Tc_2(OAc)_4Cl]$ [Tc–Tc, 2.117(1) Å] (*167b*).

Also isolated from the acetic acid reaction is $K[Tc_2(OAc)_4Cl_2]$, the structure of which shows a distinctly longer Tc–Tc bond distance of 2.1260(5) Å, with two axial chlorides at 2.589(1) Å (*167c*). The effective magnetic moment for the three acetate dimers is 1.78 ± 0.05 BM and the EPR spectra are consistent with the unpaired electron equally shared by the two Tc centers in the δ^* (b_{1u}) antibonding molecular orbital (*168, 169*).

2. *Polynuclear Clusters*

The development of this area has been entirely due to the work of Russian chemists (*42*). Reduction of $HTcO_4$ in concentrated HX (X = Cl, Br, I) by hydrogen under pressure yields a mixture of products with average oxidation states of +1.5–2.0 for Tc and with varying H_2O and H_3O^+ contents (*42, 170, 171*). Crystal structure determinations have identified three basic structural arrangements of the Tc atoms (*157, 172, 173*), the trigonal prismatic $\{[Tc_6X_6(\mu\text{-}X)_6]X_2\}^{n-}$ (X = Cl, Br; n = 2,3), $(NMe_4)_2[Tc_6Cl_6(\mu\text{-}Cl)_6]$ (*172, 174, 175*), the octahedral $[Tc_6Br_6(\mu_3\text{-}$

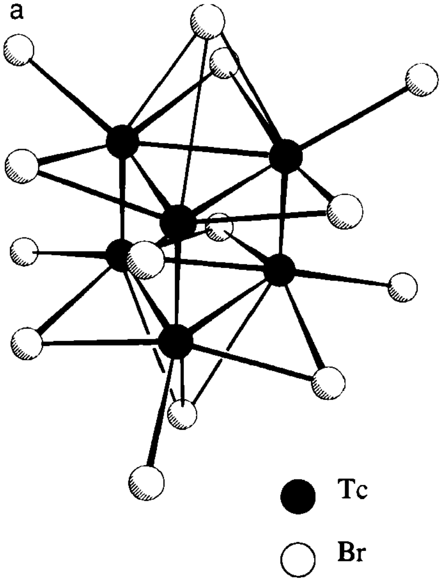
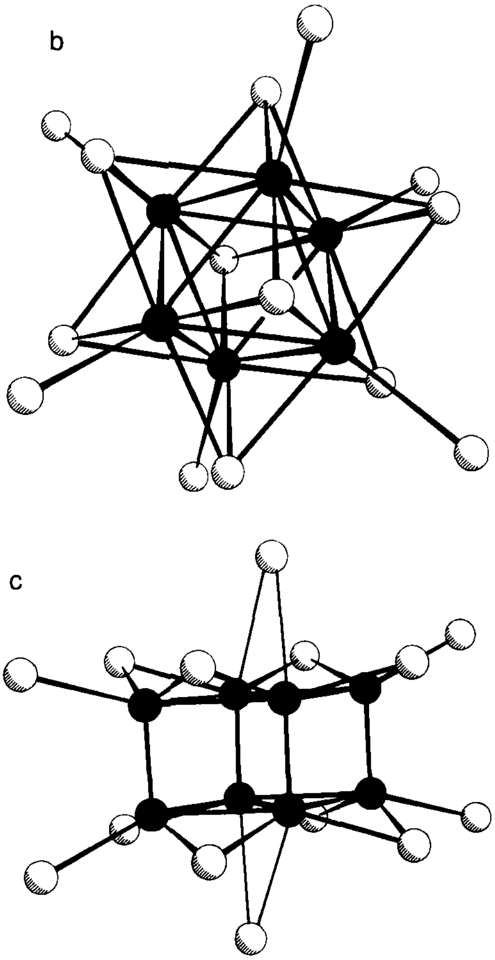


FIG. 4. The structures of technetium bromo clusters. (a) Fragment of the structure of the trigonal prismatic clusters $(NEt_4)_2[Tc_6Br_6(\mu\text{-}Br)_6]Br_2$ and $(NMe_4)_3[Tc_6Br_6(\mu\text{-}Br)_6]Br_2$ (*175*). (b) Fragment of the structure of the octahedral clusters $[H_3O(H_2O)_3]_2[Tc_6Br_6(\mu_3\text{-}Br)_5]$ and $(NBu_4)_2[Tc_6Br_6(\mu_3\text{-}Br)_5]$. Eight equivalent μ_3-Br atoms are shown but the positions are not fully occupied (*172*). (c) Fragment of the structure of the tetragonal prismatic clusters $[Tc_8Br_4(\mu\text{-}Br)_8]Br\cdot 2H_2O$, $[H(H_2O)_2][Tc_8Br_4(\mu\text{-}Br)_8]Br$, and $[H(H_2O)_2]_2[Tc_8Br_4(\mu\text{-}Br)_8]Br_2$ (*172*).

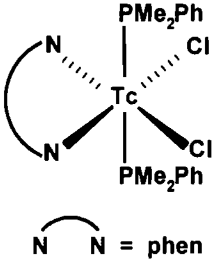


Br)$_5$]$^{2-}$ (*172, 176*), and the tetragonal prismatic {[$Tc_8X_4(\mu\text{-}X)_8$]X_n}$^{x-}$ (X = Br, I; $n = 1, x = 1, 0$; $n = 2, x = 2$; D_{2h} symmetry) (*172, 177–178*). Structural examples are shown in Fig. 4 (*172, 175*). The main structural features of the novel trigonal and tetragonal prismatic clusters are the presence of dimeric Tc–Tc units with strong, localized multiple bonds of the order of 3.0–4.0 and Tc–Tc bond distances in the range 2.16–2.19 Å, forming the vertical edges and a system of formally single Tc–Tc bonds (2.51–2.70 Å) delocalized along the metal skeleton. In the octahedral $(NBu_4)_2[Tc_6Br_6(\mu_3\text{-}Br)_5]$ cluster, the Tc–Tc bond distances are

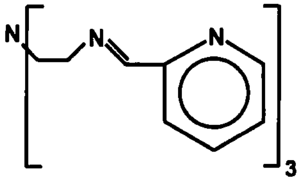
2.578(1)–2.609(1) Å (*172*). The trigonal prismatic cluster chlorides readily undergo substitution by bromide in HBr at ~140°C, with the preservation of the Tc framework. The reaction goes to completion and no mixed-ligand clusters can be isolated. In acetone, $[H(H_2O)_2]_2[Tc_8Br_4(\mu\text{-}Br)_8]Br_2$ undergoes partial substitution with HI at room temperature. Addition of NBu_4^+ gives brown crystals shown by an X-ray structure determination to be the mixed-ligand tetragonal prismatic cluster $(NBu_4)_2[Tc_8(Br_{0.5}I_{0.5})_4(\mu\text{-}Br_{0.5}\mu\text{-}I_{0.5})_8]I_2$ (*179*). X-ray photoelectron spectra (*180*),magnetic properties, and EPR studies of the Tc clusters have been reported and the mechanism of Tc–Tc bond formation has been discussed (*181*). A molecular orbital analysis of the trigonal prismatic $[Tc_6Cl_{12}]^{2-}$ shows electron-rich $\sigma^2\pi^4\delta^2\delta^{*2}$ triple bonding in each dimer unit, single bonding in the triangles, and two electrons in a net antibonding a_2'' orbital (π^* with respect to the dimers) so that the number of framework bonding electrons is 30. This is very different from the magic numbers of 16, 24, or 14 known for octahedra and 18 for trigonal prisms (*182*). Recently, crystal structures of six ternary chalcogenides of the type $M_4[Tc_6X_n]$ (n = 12 or 13; X = S or Se; M = K, Rb, or Cs) have revealed the presence of octahedral Tc clusters with Tc–Tc bond distances of 2.60–2.65 Å (*183*).

C. COMPLEXES WITH NITROGEN LIGANDS

The reaction of $[Tc^{III}Cl_3(CH_3CN)(PPh_3)_2]$ with bpy, phen, and terpy yields the blue-black Tc(II) complexes $[TcL_3]^{2+}$ (L = bpy, phen) and $[Tc(terpy)_2]^{2+}$, which may be isolated as the BPh_4^- or PF_6^- salts. The crystal structure of $[Tc(bpy)_3](PF_6)_2$ shows exact D_3 symmetry for the cation with all Tc–N bonds distances 2.077(10) Å. The cyclic voltammogram of $[Tc(bpy)_3](BPh_4)_2$ indicates three diffusion-controlled reversible one-electron reduction processes at $E_{1/2}$ −0.34, −1.36, and −1.70 V vs SCE, corresponding to successive reduction of $Tc^{II} \rightarrow Tc^{I} \rightarrow Tc^{0} \rightarrow Tc^{-I}$ (*184, 185*). An EPR study of $[Tc(bpy)_3](PF_6)_2$ has shown that the unpaired electron occupies the d_{xy} orbital and that extensive metal–ligand covalent interactions reduce the spin–orbit coupling to about 49% (*186*). The effective magnetic moment of $[Tc(phen)_3]^{2+}$ is 1.89 BM, in good agreement with the spin-only value for a Tc(II) octahedral d^5 configuration(*133*). A variety of mixed-ligand complexes, including $[TcCl_2(PMe_2Ph)_2L]$ (L = bpy, phen) and $[TcCl(PMe_2Ph)_2(terpy)]PF_6$, has been prepared and electrochemically investigated. Crystal structures have established the coordination arrangement for the distorted octahedral (**12**) and *trans*(*P*)-$[TcBr(PMe_2Ph)_2(terpy)]SO_3CF_3$ (*187*).



(12)



(13)

Crystallography, FABMS, and EPR spectroscopy have shown that the deep-purple major product isolated from the reaction of $[Tc^{III}Cl_3(PPh_3)_2(MeCN)]$ with tris(2-aminoethyl)amine and 2-pyridinecarboxaldehyde in methanol is $[Tc^{II}(tren\text{-}py_3)](PF_6)_2$ [tren-py_3 (**13**)] (*188*). The mean Tc–imine and Tc–pyridine nitrogen bond distances are 2.071 and 2.109 Å, respectively, and the Tc···tertiary amine nitrogen distance is 2.933(7) Å. The coordination geometry has been described as pseudo-seven coordinate capped octahedral. It is arguable whether the long $Tc \cdots N_{tert}$ distance constitutes coordination, but a Tc···N interaction is indicated because the lone pair on this nitrogen is directed toward the Tc atom.

D. PHOSPHINE, ARSINE, AND RELATED COMPLEXES

In view of the large number of mixed halide–phosphine complexes of the binuclear $[Re_2]^{4+}$ and $[Re_2]^{5+}$ cores (*189*), it is perhaps surprising that no such complex has been reported for technetium, but this may simply reflect the lack of work in this area. Mononuclear phosphine and arsine complexes are, however, common. The first Tc(II) complex to be reported was *trans*-$[Tc(diars)_2I_2]$ in 1959 (*190*), followed by the chloro and bromo analogs in the next year (*191*). These complexes together with *trans*-$[Tc(dppe)_2X_2]$ (X = Cl, Br) were prepared by SO_2 or BH_4^- reduction of the $[Tc^{III}L_2X_2]X$ salts and characterized by electronic spectroscopy, magnetic measurements (μ_{eff} = 2.05, 2.28 BM), and by being shown to be isostructural with the Re analogs (*192*). These conclusions have been confirmed by a crystal structure determination of *trans*-$[Tc(dppe)_2Cl_2]$ (*193*). The rather long Tc–Cl bonds (av., 2.424 Å) undergo a dramatic shortening of 0.105(2) Å on oxidation to *trans*-$[Tc^{III}(dppe)_2Cl_2]^+$, behavior consistent with a ligand that binds primarily by σ-donation. In contrast, the Tc–P bond lengthens by 0.072(2) Å on oxidation from Tc(II) to Tc(III) due to π-back-bonding from Tc to P being less favored in the higher oxidation state. In nonaqueous media *trans*-[$Tc^{II}(dppe)_2X_2$] is readily oxidized by a variety of one-equivalent oxidants. The rate of reduction of [$(en)_2Co\{S(CH_2C_6H_4Me)CH_2CH_2NH_2\}]^{3+}$ by [$Tc(dppe)_2Cl_2$] in MeCN at 25°C is rapid [$k_2 = 3.0(7) \times 10^4$ M^{-1} sec^{-1}] (*193*). Spectroelectrochemical studies of the structurally characterized *trans*-[$Tc(dppe)_2(NCS)_2$] show that the π-acceptor ability of *N*-bonded thiocyanate results in a marked stabilization of the lower oxidation state (*194*). The cationic complexes [$TcL_3](PF_6)_2$ (L = dmpe, depe) are prepared by H_2O_2 oxidation of [$Tc^IL_3]PF_6$. The reduction of TcO_4^- by excess dmpe gives a mixture of products in the +5, +3, and +1 oxidation states, but neither *trans*-[$Tc^{II}(dmpe)_2Cl_2$] nor [$Tc^{II}(dmpe)_3]^{2+}$ appears to be a predominant component (*124*). Reaction of *trans*-[$Tc^VO_2(dmpe)_2]^+$ with halide may be used to prepare *trans*-[$Tc(dmpe)_2X_2$] (*123*). A series of cationic dithiocarbamato complexes [$Tc(S_2CNR_2)(depe)_2]PF_6$ has recently been similarly prepared, and the crystal structure of [$Tc(S_2CNMe_2)(depe)_2]PF_6$, determined (*195*). The dithiocarbamate is bidentate and the coordination geometry is octahedral. The $E^{\circ\prime}$ values of 0.298 to 0.312 and −0.517 to −0.544 V vs Ag/AgCl for the Tc(III)/Tc(II) and Tc(II)/Tc(I) couples, respectively, show that dithiocarbamato ligands effectively stabilize the Tc(II) oxidation state. A crystal structure determination has shown that the room temperature reduction of the tetramethylthiourea complex [$Tc^VO(tmtu)_4](PF_6)_3$ by dppe in dmf solution is accompanied by a novel rearrangement to give the dithiocarbamato complex [$Tc^{II}(dppe)_2(S_2CNMe_2)]PF_6$ (*196*). The mechanism of the rearrangement is uncertain, but the overall reaction is probably described by

$$2(Me_2N)_2CS + H_2O \longrightarrow Me_2NCS_2H + (Me_2N)_2CO + Me_2NH.$$

An interesting mixed-ligand complex is [$Tc(dppe)_2(ox)$], prepared by the reduction of TcO_4^- by dppe in hot ethanol in the presence of oxalic acid. The average Tc–O bond distances of 2.13(1) and 2.12(1) Å in two independent molecules are somewhat longer than those found in other oxalato complexes (*197*). Reaction of $(NH_4)_2[Tc^{IV}Cl_6]$ with diethyl phenylphosphonite in the presence of BH_4^- yields the yellow octahedral *trans*-[$Tc^{II}\{PhP(OEt)_2\}_4Cl_2$], with Tc–P and Tc–Cl bond distances both 2.41(1) Å. The low measured magnetic moment of 1.4 BM has been ascribed to partial decomposition (*198*).

E. COMPLEXES WITH SULFUR LIGANDS

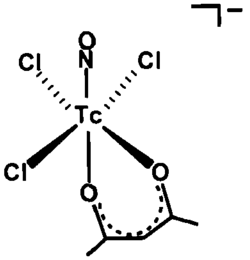
The reaction of *trans*-[$Tc^VO(OH)(dmpe)_2]^{2+}$ with excess 4-chlorobenzenethiol yields a mixture of the air-stable black *cis*- and red *trans*-

[Tc(SC_6H_4Cl-*p*)$_2$(dmpe)$_2$], which may be separated by fractional crystallization. Crystal structures have been determined for both complexes and show Tc–S–C angles of 114.0(3)° and 123.8(2)° for the *cis*- and *trans*-isomers, respectively. In CH_2Cl_2, the *trans*-isomer converts to the more stable *cis*-isomer with a half-life of about 74 min at room temperature (*199*). Similarly, *trans*-[$Tc^{V}O(OH)(diars)_2](PF_6)_2$ may be converted to [$Tc^{II}(SR)_2(diars)_2$] (*trans,* R = Me, Bz; *cis* and *trans,* R = Ph), which can then be oxidized to the Tc(III) complexes. The reversible Tc(III)/Tc(II) couple is in the range −0.32 to −0.47 vs Ag/AgCl. The crystal structure of *trans*-[$Tc(SPh)_2(diars)_2$] shows a Tc–S–C angle of 119.5(3)° (*200*). Reduction of NBu_4TcO_4 by $SnCl_2$ in the presence of 1,4,7-trithiacyclononane yields the dark-brown homoleptic complex [$TcL_2](BF_4)_2\cdot MeCN$, with Tc coordinated by the two thioether ligands in a *fac* tridentate "sandwich" fashion. The three independent Tc–S bond distances are in the narrow range 2.372(3)–2.381(3) Å. Electrochemical oxidation yields the yellow Tc(III) complex and reduction yields the air-stable cherry-red Tc(I) complex (*201*).

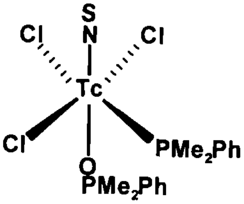
F. NITROSYL AND THIONITROSYL COMPLEXES

The first Tc(II) nitrosyl complex to be identified was the green *trans*-[$Tc(NO)(NH_3)_4(OH_2)]Cl_3$, prepared by Ce(IV) oxidation of the pink *trans*-[$Tc^{I}(NO)(NH_3)_4(OH_2)]Cl_2$ (*135*). From the reaction of $TcO_2\cdot nH_2O$ with NO gas in 4 *M* HBr, red crystals of $NBu_4[Tc(NO)Br_4]$ may be isolated (*139*). The $NBu_4[Tc(NO)X_4]$ (X = Cl, I) complexes are prepared by halide substitution (*34, 202*) and the ink-blue $(NBu_4)_2$[Tc(NO)(NCS)$_5$] is prepared by substitution with NCS^- (*139*), whereas $(AsPh_4)_2[Tc(NO)(NCS)_5]$ may be prepared by the reduction of TcO_4^- by $NH_2OH\cdot HCl$ in the presence of NCS^- (*203*). The preparation of $(NBu_4)_2[Tc(NO)Cl_5]$ has also been reported (*202*). The structure of (NBu_4)*trans*-[$Tc(NO)Cl_4(MeOH)$] shows a near-linear Tc–N–O angle of 175.5(10)° and Tc–N and N–O bond distances of 1.689(11) and 1.171(15) Å, respectively. The Tc–O(H)Me distance is fairly short at 2.128(7) Å (*204*), a reflection of the π-acceptor nature of the NO^+ ligand. For the halide complexes ν(NO) is observed in the IR spectrum at ~1800 cm^{-1}. Reaction of $[Tc(NO)Cl_4]^-$ with bpy or phen yields [$Tc(NO)Cl_3L$] (*205*). Black-green crystals of [$Tc(NO)Cl_3(PMe_2Ph)_2$] (*206*) and dark-green [$Tc(NO)Cl_3(PPh_3)_2$] [ν(NO) at 1805 cm^{-1}] (*207*) are formed by the reaction of NO with [$TcCl_3(PMe_2Ph)_3$] and [$TcCl_3(PPh_3)_2(MeCN)$], respectively. Red ($AsPh_4$)*mer*-[$Tc(NO)Cl_3(acac)$] (14) is formed when acacH is added to a solution of $[Tc(NO)Cl_4X]^{n-}$ (X = Cl, H_2O), prepared by the addition of $NH_2OH\cdot HCl$ to $[TcCl_6]^{2-}$.

The Tc–N–O angle is substantially bent at 158.6(33)° and the Tc–O_{acac} bond distances *cis* and *trans* to the NO^+ ligand are not significantly different at 2.06(1) and 2.08(1) Å (*208, 209*). $[^{99m}Tc(NO)Cl_4]^-$ for potential radiopharmaceutical applications is formed in high yield by the addition of $NH_2OH{\cdot}HCl$ to a previously heated $^{99m}TcO_4^-/HCl$ solution and may be extracted by CH_2Cl_2 after the addition of NBu_4Cl (*210*).



(14)



(15)

The $AsPh_4[Tc(NS)X_4]$ (X = Cl, Br) salts are prepared by the reaction of $(AsPh_4)_2[TcX_6]$ with $(NSCl)_3$ and $AsPh_4[Tc(NS)(NCS)_4]$ is prepared by ligand exchange. In the case of $[TcBr_6]^{2-}$, mixed-ligand complexes $[Tc(NS)Cl_nBr_{4-n}]^-$ (n = 1–3) are formed and the addition of HBr is required to effect full substitution and to give red-brown crystals of $AsPh_4[Tc(NS)Br_4]$. The ν(NS) IR absorptions occur at 1232–1214 cm^{-1}, and for the thiocyanate complex the NCS deformation mode at 501 cm^{-1} indicates that these ligands are *N*-bonded. In solution, $[Tc^{II}(NS)X_4]^-$ readily loses sulfur to form the nitrido complex $[Tc^{VI}NX_4]^-$ (*211*). Treatment of $[Tc^VNCl_2(PMe_2Ph)_3]$ with an excess of S_2Cl_2 in CH_2Cl_2 under argon has been shown by FABMS and crystallography to yield not $[Tc^{II}(NS)Cl_3(PMe_2Ph)_2]$ but the phosphine oxide complex (**15**) (*212*), and presumably this also applies to the bromo complex prepared by ligand exchange in HBr (*213*). The source of oxygen for the oxidation of the phosphine in **15** is not clear. The ν(NS) IR band at 1240 cm^{-1} has been confirmed by an isotope shift to 1206 cm^{-1} on ^{15}N labeling (*145*). On reaction with excess PMe_2Ph, **15** undergoes sulfur abstraction to yield the starting material $[Tc^VNCl_2(PMe_2Ph)_3]$. The linear Tc–N–S [179.9(1)°] angle and the Tc–N and N–S bond distances of 1.746(5) and 1.521(5) Å, respectively, in **15** are consistent with NS^+ coordination (*212*). EPR spectroscopy has confirmed that the product of the reaction of $[Tc^VNL_2]$ [L = *N*-(*N*″-morpholinylthiocarbonyl)benzamidinate(1-)] with S_2Cl_2 is $[Tc^{II}(NS)Cl_2L]$ (*214*).

The EPR spectra of low-spin $4d^5$ Tc(II) nitrosyl and thionitrosyl complexes have been examined in detail and the results, reviewed (*39–41*).

Complexes with the most π-bonding between Tc and the equatorial ligands show the largest $g_{\parallel}$ and smallest $A_{\parallel}$, as seen by $g_{\parallel} = 1.985$, and $A_{\parallel} = 260 \times 10^{-4}\ \mathrm{cm}^{-1}$ for $[\mathrm{Tc(NO)Cl_5}]^{2-}$ and $g_{\parallel} = 2.262$, and $A_{\parallel} = 155 \times 10^{-4}\ \mathrm{cm}^{-1}$ for $[\mathrm{Tc(NO)I_4}]^{-}$ (*202, 215*). In the case of $[\mathrm{Tc(NO)(NH_3)_4(OH_2)}]^{3+}$, for which there is no π-bonding in the equatorial plane, $g_{\parallel} = 1.861$ and $A_{\parallel} = 297 \times 10^{-4}\ \mathrm{cm}^{-1}$ (*216*). EPR spectroscopy is particularly useful for the study of ligand exchange such as that between $[\mathrm{Tc(NO)Br_4}]^{-}$ and $[\mathrm{Tc(NO)Cl_5}]^{2-}$ or $[\mathrm{Tc(NO)I_4}]^{-}$ (*217*). The g values and $^{99}\mathrm{Tc}$ hyperfine coupling constants are proportional to the spin–orbit coupling constants of the donor atoms and the composition of the mixed-halide coordination sphere may be unambiguously assigned (*40*).

VI. Technetium(III)

The coordination chemistry of this oxidation state is rather more extensive and varied than that of Tc(II). With appropriate ligands Tc(III) is water- and air-stable, and cationic complexes with bidentate phosphine and arsine ligands have been extensively studied in the search for myocardial imaging agents. A marked difference between Tc and Re is the absence, at present, of any Tc analog of the extensive chemistry based on the trinuclear $[\mathrm{Re_3}]^{9+}$ core (*189*). A notable feature is that nearly all the seven-coordinate Tc complexes are found in this oxidation state. This is understandable in terms of the d^4 electronic configuration of Tc(III), which requires seven singly bonded ligands to achieve an 18-electron count.

A. CARBONYL COMPLEXES

Yellow plates of the seven-coordinate $[\mathrm{TcCl_3(CO)(PMe_2Ph)_3}]\cdot\mathrm{EtOH}$ are formed by passing CO at atmospheric pressure through a refluxing solution of *mer*-$[\mathrm{TcCl_3(PMe_2Ph)_3}]$ in ethanol. The structure possesses approximate C_{3v} symmetry and may be described as a distorted capped octahedron with the CO ligand inserted along the C_3 axis on the phosphine face [Tc–C–O angle, 178(2)°] (*218*). The pentagonal-bipyramidal complex (**16**) (Fig. 5) was unexpectedly prepared by the reduction of $\mathrm{TcO_4}^{-}$ with formamidinesulfinic acid $[\mathrm{NH_2(NH)CSO_2H}]$ in the presence of $\mathrm{Na(S_2CNEt_2)}$. The CO stretch occurs as an intense band at 1895 cm^{-1} in the IR spectrum. The mechanism of the formation of the coordinated CO is unclear; a scheme that involves initial loss of $\mathrm{SO_2}$ from the coordinated sulfinic acid has been proposed. The CO ligand occupies an apical position with a near linear Tc–C–O angle of 177.8(10)° and

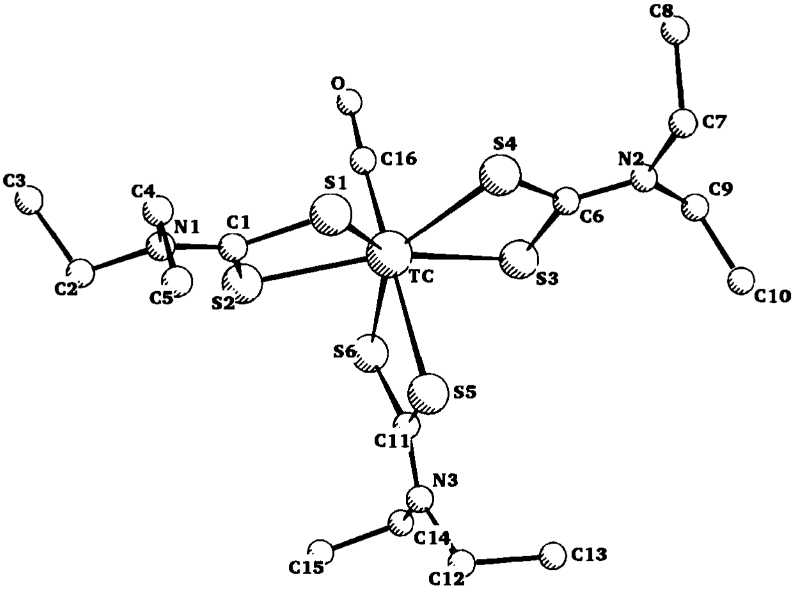


FIG. 5. The structure of [$Tc(S_2CNEt_2)_3(CO)$] (**16**) (*219*).

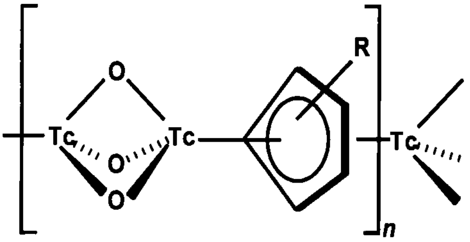
Tc–C and C–O bond distances of 1.861(12) and 1.15(1) Å, respectively. A comparison with the isostructural [$Re(S_2CNEt_2)_3(CO)$] indicates that Tc(III) is a poorer π-donor than is Re(III) (*219*). Alkyl dithiocarbamate derivatives of **16** have been prepared by the above method [ν(CO) at 1907–1895 cm^{-1}] and the CO ligand shown to be inert to substitution by EPh_3 (E = P, As) (*220*). The CO ligand is, however, readily substituted by the isoelectronic NO^+ to give seven-coordinate [$Tc(NO)(S_2CNR_2)_3$]$^+$ cations (*221*). A variety of [$^{99m}Tc(S_2CNR_2)_3(CO)$] complexes has been prepared by reduction of TcO_4^- with $S_2O_4^{2-}$ in the presence of CO and found to behave as hepatobiliary agents when injected into mice (*222*). A six-coordinate carbonyl complex is *trans-mer*-[$TcCl_3(PPh_3)_2(CO)$], prepared by the bubbling of CO through a solution of *mer*-[$TcCl_3(PPh_3)_2(MeCN)$]. The long Tc–CO bond of 1.985(9) Å, the short C–O bond of 1.12(1) Å, and the high IR ν(CO) absorption at 2054 cm^{-1} indicate the absence of significant π-back-bonding in this complex (*207*). The bubbling of CO through a solution of [$Tc(SAr)_3(MeCN)_2$] (SAr = tmbt) yields orange crystals of [$Tc(SAr)_3(CO)_2$]. One CO ligand may be displaced to give [$Tc(SAr)_3(CO)(MeCN)$] and [$Tc(SAr)_3(CO)(py)$]. Crystal structures show trigonal-bipyramidal coordination for both monocarbonyl complexes, with the three S atoms of the sterically hindered thiolates occupying the equatorial plane and the CO and MeCN or pyridine ligands in the axial positions (*223*).

B. Cyclopentadienyl Complexes

The product of the BH_4^- reduction of $TcCl_4$/NaCp in THF is the hydrido complex [$HTcCp_2$], analogous to [$HReCp_2$] and most likely with the same bent structure. The basic nature of [$HTcCp_2$] is shown by the equilibrium

$$[HTcCp_2] \underset{NaOH}{\overset{HCl}{\rightleftharpoons}} [H_2TcCp_2]Cl.$$

On addition of PF_6^- the rather insoluble [H_2TcCp_2]PF_6 salt precipitates (*224*). The $TcCl_4$/KCp reaction in THF yields the diamagnetic air-stable [$TcCp_2Cl$], which on reaction with KCp gives the red diamagnetic [$Tc(\eta^5\text{-}Cp)_2(\eta^1\text{-}Cp)$], in which one ring is σ-bonded (*225*). The structures are shown in Fig. 6. The oxidation of [$(\eta^5\text{-}C_5Me_5)Re^{I}(CO)_3$] by H_2O_2 yields the trioxo compound [$(\eta^5\text{-}C_5Me_5)Re^{VII}O_3$], but with [$(\eta^5\text{-}C_5Me_5)Tc^{I}(CO)_3$] the product has been assigned the polymeric structure (**17**), with Tc in the +3.5 oxidation state (*226*).



(**17**)

The planes of the C_5Me_5 rings and the bridging oxygens are exactly parallel but the most striking feature is the exceptionally short Tc–Tc bond distance of 1.867(4) Å. The Tc–Tc bonding has been described as $\sigma^2(\pi\delta)^4\delta^*$, with a net bond of approximate order 2.5 (*227*). IR absorptions at 909 and 880 cm^{-1} have been assigned to ν_{sym}(TcO) and ν_{asym} (TcO), respectively (*226*). The crystal structure determination of **17** has, however, been questioned and it has been suggested that the product obtained may in fact be [$(\eta^5\text{-}C_5Me_5)Tc^{VII}O_3$] (*228*). Treatment of [$Tc^{I}(C_5Me_5)(CO)_3$] with Br_2/CF_3COOH gives [$Tc(C_5Me_5)(CO)_2Br_2$] as a mixture of *cis*- and *trans*-isomers (*100*).

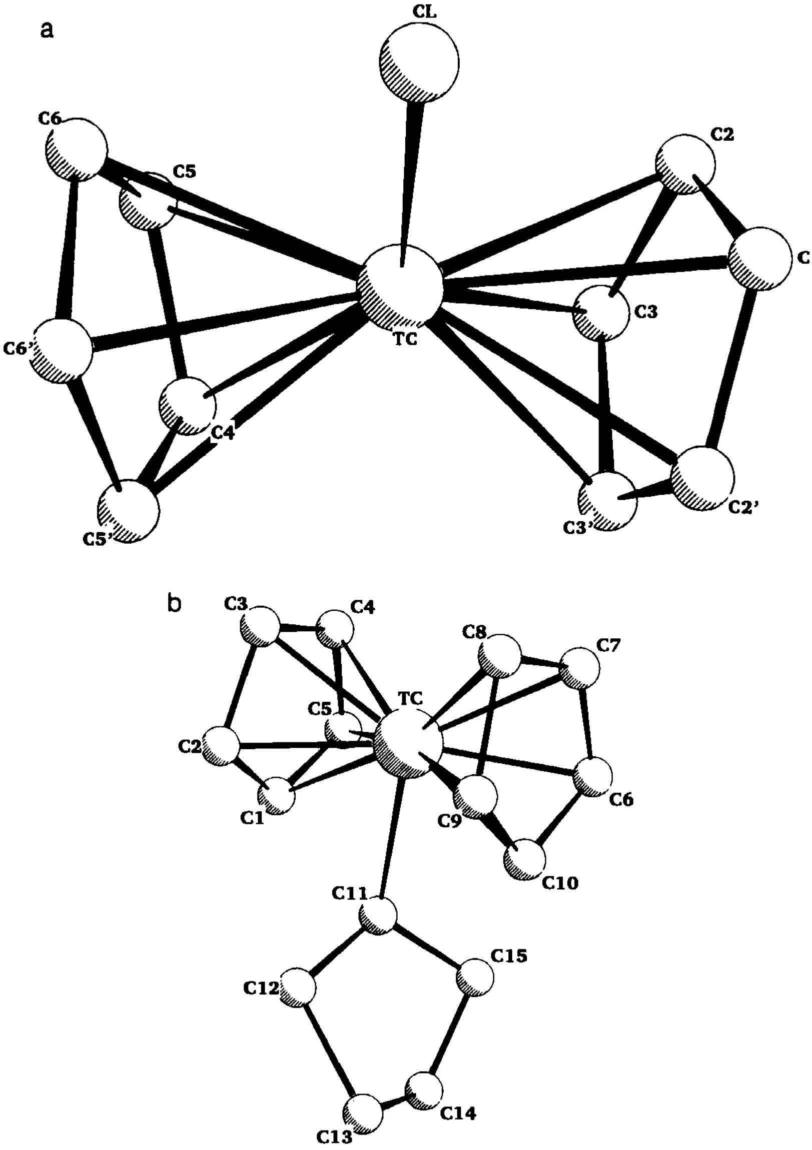


FIG. 6. The structures of (a) [TcCp$_2$Cl] and (b) [Tc(η^5-Cp)$_2$(η^1-Cp)] (*225*).

C. CYANO, ISONITRILE, AND THIOCYANATO COMPLEXES

The only Tc(III) cyano complex is the seven-coordinate yellow-orange $K_4[Tc(CN)_7]\cdot 2H_2O$ prepared by the reaction of $(NH_4)_2[Tc^{IV}I_6]$ with KCN in methanol under nitrogen. Raman and IR spectra indicate a pentagonal-bipyramidal structure (D_{5h} symmetry) both in the solid state and in solution. In aqueous solution $K_4[Tc(CN)_7]\cdot 2H_2O$ is oxidized by air to $[Tc^{V}O(CN)_5]^{2-}$ (*229*). Seven-coordinate isonitrile complexes of the type $[Tc(CNR)_6X](PF_6)_2$ (X = Cl, Br) are formed by the oxidative addition of chlorine or bromine to the six-coordinate $[Tc^{I}(CNR)_6]^+$ (*121*). The reaction of $(NH_4)_2[TcX_6]$ (X = Cl, Br) with NH_4NCS produces a mixture of the intensely purple $[Tc^{IV}(NCS)_6]^{2-}$ (λ_{max} = 500 nm; ε = 76,200) and the air-sensitive, yellow $[Tc^{III}(NCS)_6]^{3-}$ (λ_{max} = 400 nm) anions (*230*). The redox couple $[Tc(NCS)_6]^{2-} + e \rightleftarrows [Tc(NCS)_6]^{3-}$ is electrochemically reversible ($E_{1/2}$ = 0.18 V vs SCE) and the reduction of $[Tc^{IV}(NCS)_6]^{2-}$ is readily produced chemically by hydrazine. The crystal structure of $(NBu_4)_3[Tc(NCS)_6]$ shows near-perfect octahedral geomery and establishes that thiocyanate is *N*-bonded with an average Tc–N–C angle of 173(2)°.

D. AQUA, HALIDE, AND RELATED DIMERIC COMPLEXES

No mononuclear Tc(III) halide is known. Thin-layer spectroelectrochemical techniques show that the $[Tc^{IV}X_6]^{2-}$ (X = Cl, Br) complexes undergo a reversible one-electron reduction in HX/NaX aqueous media with the loss of 2.7 ± 0.1 chloro ligands and 5.9 ± 0.5 bromo ligands, respectively. These results indicate a low affinity of Tc(III) for halide and the possibility of preparing $[Tc(OH_2)_6]^{3+}$ in a weakly coordinating aqueous medium (*231*). The stability of the mixed-valence $[Tc^{II/III}{}_2Cl_8]^{3-}$ and the apparent inability to prepare $[Tc^{III}{}_2Cl_8]^{2-}$ were a puzzle for a number of years in view of the stability of $[Re_2Cl_8]^{2-}$ and the only fleeting existence of $[Re_2Cl_8]^{3-}$ (*159*). However, in 1980 the bright-green $(NBu_4)_2[Tc_2Cl_8]$ was prepared by the reduction of $[TcCl_6]^{2-}$ with Zn/HCl and converted to the carmine-red $(NBu_4)_2[Tc_2Br_8]$ by ligand exchange with HBr (*232*). A recent synthesis of $(NBu_4)_2[Tc_2Cl_8]$ by reduction of $NBu_4[TcOCl_4]$ with $NBu_4(BH_4)$, followed by carefully controlled air oxidation of the initially formed brown product in CH_2Cl_2 in the presence of HCl gas, gives yields of up to a 85% (*164*). The crystal structure of $(NBu_4)_2[Tc_2Cl_8]$ shows that the quadruple Tc–Tc $\sigma^2\pi^4\delta^2$ bond is, at 2.147(4) Å, about 0.04 Å longer than the $\sigma^2\pi^4\delta^2\delta^*$ bond in $[Tc_2Cl_8]^{3-}$ (bond order, 3.5) (*233*). This unexpected result is due to the greater influence of the change in the oxidation state of Tc than of the weak δ bonding on the Tc–Tc bond distance (*149*).

A number of complexes of the $[Tc_2]^{6+}$ core have been prepared, either by oxidative substitution of $[Tc_2Cl_8]^{3-}$ (*234, 235*), by substitution of $[Tc_2Cl_8]^{2-}$ (*236, 237*), or by the reduction of TcO_4^- by hydrogen in the presence of ligands (*238*). The crystal structure of the red [Tc₂-

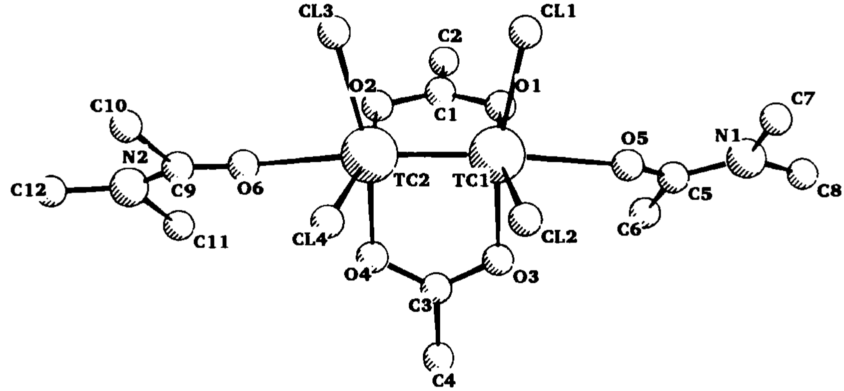


FIG. 7. The structure of *cis*-$[Tc_2(OAc)_2Cl_4(dmaa)_2]$ (*237*).

$(OOCCMe_3)_4Cl_2]$ reveals a lantern structure, with the four pivalato ligands bridging the two Tc atoms in the eclipsed configuration (D_{4h} symmetry), a Tc–Tc bond distance of 2.192(2) Å, and axial chlorides with Tc–Cl bond distances of 2.408(4) Å (*234*). Similar structures are found in $[Tc_2(OAc)_4(TcO_4)_2]$ [Tc–Tc, 2.149(1) Å] (*239*) and $K_2[Tc_2(SO_4)_4(OH_2)_2]$ [Tc–Tc, 2.155(1) Å] (*235, 157*). Reaction of $[Tc_2Cl_8]^{2-}$ with Ac_2O/HBF_4 yields *cis*-$[Tc_2(OAc)_2Cl_4(OH_2)_2]$, in which the weakly bound axial water ligands are easily replaced by donor bases to give the green adducts *cis*-$[Tc_2(OAc)_2Cl_4L_2]$ (L = dmf, dmso, $OPPh_3$, py). The structure of the dimethylacetamide (dmaa) adduct [Tc–Tc, 2.1835(7) Å; Tc–O_{dmaa}, av., 2.320 Å] is shown in Fig. 7 (*237*). Orange-red $[Tc_2(OAc)_4Br_2]$ is prepared by reaction of $[Tc_2Br_8]^{2-}$ with $HOAc/Ac_2O$ (*236*). A characteristic feature in the electronic spectra is the $\delta \rightarrow \delta^*$ transition at 600–700 nm (*232, 237*). Normal coordinate analyses of $[Tc_2(OAc)_4X_2]$ give Tc–Tc force constants of 4.08 and 3.99 mdyn $Å^{-1}$ for the chloro and bromo complexes, respectively (*236*). The Tc–Tc IR and Raman stretching frequencies of *cis*-$[Tc_2(OAc)_2Cl_4L_2]$ are lowered with increasing donor strength of the axial ligand L (*240*). Magnetic studies of $[Tc_2]^{6+}$ complexes show only temperature-independent paramagnetism (*150*).

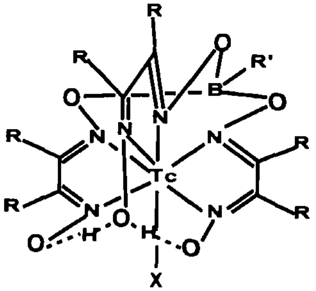
E. CARBOXYLATO AND β-DIKETONATO COMPLEXES

Technetium(III) complexes with aminocarboxylato ligands have been reported but none are well characterized (*241*). ^{99m}Tc–iminodiacetate complexes formed with 2,6-alkylphenyl $[ArNHCOCH_2N(CH_2COO)_2]^{2-}$ ligands are used to image the hepatobiliary system. Studies with ^{99}Tc show evidence for $[Tc^{III}L_2]^-$ in the radiopharmaceutical preparations, but $[Tc^{V}OL_2]^-$ is also possible (*19*). A variety of Tc(III) acac complexes and substituted analogs has been prepared by substitution/reduction of $[Tc^{IV}X_4(PR_3)_2]$ and $[Tc^{IV}X_6]^{2-}$ or by $S_2O_4^{2-}$ reduction of TcO_4^- in the presence of the ligand. These include $[Tc(acac)_3]$ (*242*); the dipivaloyl, trifluoro, and hexafluoro analogs (*243*); and $[TcX(acac)_2(PPh_3)]$ and $[TcX_2(acac)(PPh_3)_2]$ (X = Cl, Br) (*242*). The $S_2O_4^{2-}$ reduction method is suitable for the preparation of the neutral lipophilic ^{99m}Tc *tris* complexes, but these show little brain uptake (*244*). The cationic $[Tc(acac)_2(MeCN)_2]ClO_4$ is formed by the reaction of $[Tc(acac)_3]$ with MeCN in the presence of $HClO_4$ (*245*). The crystal structure of $[Tc(acac)_3]$ shows closely octahedral coordination, with an average *cis* O–Tc–O angle of 90.2° and Tc–O distances in the range 2.013(6)–2.030(6) Å (*246*). The structures of two crystalline forms of *trans*-$[TcCl(acac)_2(PPh_3)]$, which show differences in the IR spectra, have been reported (*247, 248*). The kinetics of ligand exchange of $[Tc(acac)_3]$ have been studied by the use of ^{14}C-Hacac, and the I_a mechanism has been assigned to the rate determining formation of an intermediate containing one monodentate acac and Hacac ligand (*249*). The base hydrolysis of $[Tc(acac)_3]$ is kinetically more complex than that of $[Ru(acac)_3]$ (*250*). A variety of six-coordinate *tris* complexes of monothio-β-diketonates has been prepared by substitution of $[Tc(tu)_6]Cl_3$ in refluxing methanol and characterized by IR, electronic, and mass spectrometry; ^{1}H NMR; and, for the phenyl derivative $[Tc\{SC(Ph)CHC(Ph)O\}_3]$, a crystal structure determination (251, 252).

F. COMPLEXES WITH DIOXIMES, SCHIFF BASES, AND OTHER NITROGEN LIGANDS

An alternative approach to cationic myocardial imaging agents has been the development of neutral seven-coordinate Tc(III) complexes based on 1,2-dioxime ligands (dioximeH$_2$) with one end capped by a boronic acid derivative (*19, 253*). These complexes are generally referred to as BATOs (*b*oronic acid *a*dducts of *t*echnetium di*o*ximes) and have the general structure [TcX(dioximeH)$_2$(dioxime)BR′] (X = Cl, Br; R′ = alkyl) shown in **18**.

At the uncapped end the three dioxime oxygen atoms are intramolecularly bonded to two bridging protons. BATO complexes are prepared by template synthesis from TcO_4^- and Sn^{2+} or from $NBu_4[TcOCl_4]$, $M_2[TcX_6]$ (X = Cl, Br) in the presence of the dioxime, HX, and the alkylboronic acid (*254*). The formation of BATOs from TcO_4^- and Sn^{2+} proceeds via several intermediates, including an Sn-monocapped [Tc^{III}(dioximeH)$_3$(μ-OH)SnCl$_3$], which undergoes acid decomposition to give



(18)

the uncapped $[Tc^{III}X(dioximeH)_2(dioximeH_2)]$ complex. The uncapped *tris* complex is then monocapped by the boronic acid (*255*). Interestingly, although bis(boron-capped) clathrochelates $[M(dioxime)_3(BR)_2]$ have been known for a number of years for M = Co, Fe, and Ru, the BATOs are the first monocapped examples. Crystal structures have been reported for $[TcBr(cdoH)_2(cdo)BR]$ (R = Me, Bu) and $[TcBr(dmgH)_2(dmg)BR]$ (R = Me, Bu) (*254*); the structure of the *n*-butyl dimethylglyoxime complex is shown in Fig. 8. The six nitrogen atoms form a distorted trigonal prism monocapped by Br, which causes the two flanking dioximes to be spread away by about 20° toward the third dioxime ligand, thus probably precluding the addition of a second boron cap (*254*). The $cdoH_2$ derivative $[^{99m}TcCl(cdoH)_2(cdo)BMe]$ is a radiopharmaceutical for differentiating normal from ischemic and infarcted myocardium (*19*). The axial chloride is labile to substitution and under physiological conditions is replaced by a hydroxy group with pK_a between 7 and 7.4, which indicates that there may be an equilibrium *in vivo* between the neutral hydroxy and cationic aqua forms (*24, 256, 257*). The lability of the axial chloride is consistent with X-ray photoelectron spectra of ^{99}Tc BATOs, which show that the binding energy is between that for covalent and that for ionic bonds (*258*). The mechanism of chloride–hydroxide exchange has been shown to be S_N1-CB, proceeding via a transient neutral six-coordinate complex (*256*). Electrochemically, chloro and bromo BATOs undergo an irreversible two-electron reduction that appears to be biologically inaccessible (*259*). The *S*- and *N*-bonded isomers $[TcL(cdoH)_2(cdo)BMe]$ (L = NCS, SCN) have been prepared. In solution, the *S*-isomer converts to the *N*-isomer when exposed to light (*257*). Cationic BATOs have also been prepared (*260*). The reaction

$$TcO_4^- + 3\,dioximeH_2 + 2\,SnCl_2 \longrightarrow [Tc^{III}(dioximeH)_3(\mu\text{-}OH)Sn^{IV}Cl_3] \tag{19}$$

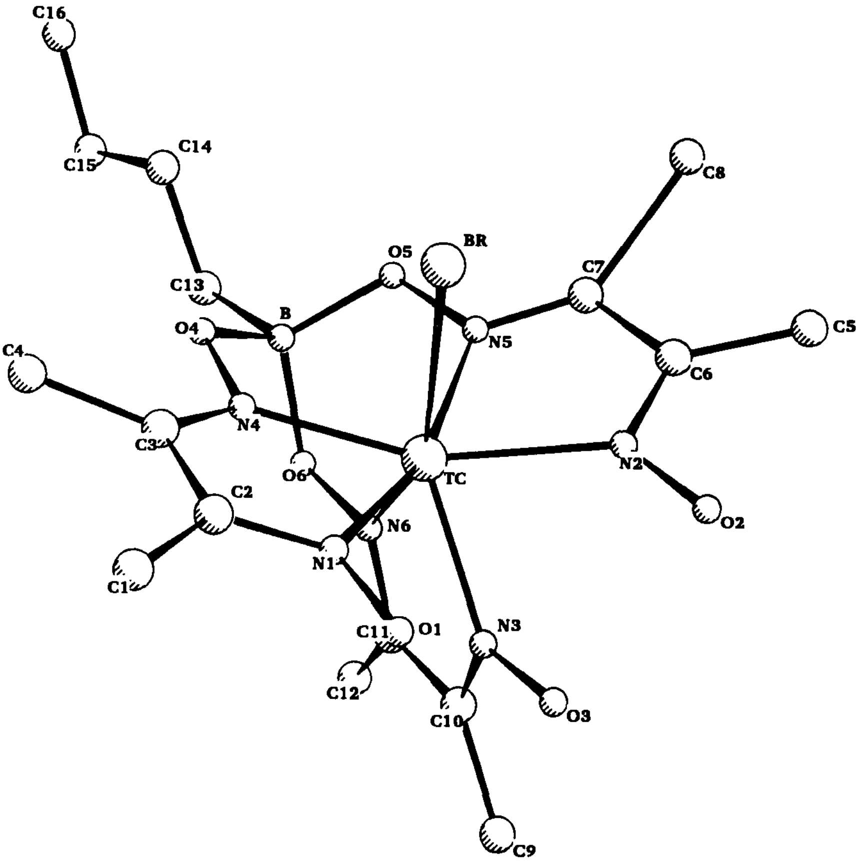
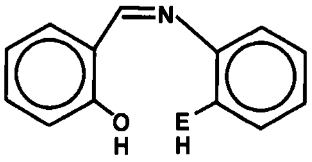


FIG. 8. The structure of [TcBr(dmgH)$_2$(dmg)BBu] (*254*).

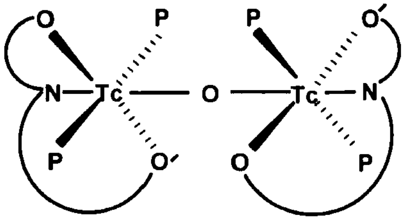
proceeds to completion. The oxygen bridge between Sn^{IV} and Tc^{III} is most likely in the hydroxyl form. Acid decomposition of **19** yields [TcCl (dioximeH)$_2$(dioximeH$_2$)], which may be reconverted to **19** in 97% yield on reaction with SnCl$_4$ (*255*). When the crystal structure of [Tc(dmgH)$_3$(μ-OH)SnCl$_3$]·3H$_2$O was reported in 1976 the oxidation state of Tc was thought to be +5 (*261*), but a +3 oxidation state is indicated by FABMS and the chemical behavior of **19** (*255*). The Sn^{IV} center is six coordinate, with the three chloro ligands in a *fac* arrangement, and, in addition to the hydroxy bridge, two oxime oxygens complete the octahedral coordination sphere (*261*). It may be noted that a +3 oxidation for Tc is also consistent with an 18-electron seven-coordinate species. In the structurally characterized [Tc^{III}Cl(dmgH)$_2$(dmgH$_2$)], the four protons are shared by the three oxygens on each trigonal face and in the ^1H NMR spectrum appear as a broad singlet at 15.3 ppm (*255*). Crystallography has established that a by-product of the reaction of $dmgH_2/[TcCl_3(MeCN)(PPh_3)_2]/EtB(OH)_2$ is [TcCl(dmg)(dmgH)(butane-2,3-dioneimineoxime)BEt], where one of the uncapped C=NOH groups has been converted to C=NH and there is only one intramolecularly bound proton (*262*). A variety of seven-coordinate Re analogs of BATOs, uncapped $[Re^{III}Cl(cdoH)_2(cdoH_2)]$, and monocapped $[Re^{III}Cl(cdo)(cdoH)_2BR]$ has been prepared. Yields from ReO_4^- are low but $[ReCl_3(MeCN)(PPh_3)_2]$ is a suitable starting material. As with Tc, the biscapped Re complexes could not be prepared. Reaction of $Mn(OAc)_3/cdoH_2/(OH)_2BPh/MeOH$, however, gives a high yield of the biscapped six-coordinate $[Mn^{II}(cdo)(cdoH)_2\{B(OMe)Ph\}_2]$, in which each cap is covalently bonded to two oxime oxygen atoms (*263*).

A series of cationic $[Tc(L)(PR_3)_2]PF_6$ (PR_3 = PEt_3, PEt_2Ph, $PEtPh_2$, PPh_3) complexes of tetradentate $(acac)_2en$ ligands and aromatic derivatives has been prepared by substitution/reduction of $[TcOCl_4]^-$ (*264*). The $E^{\circ\prime}$ for the reversible Tc(III)/Tc(II) couple is sensitive to the nature of the substituents on the Schiff base and the phosphine but is in the range −1.11 to −0.69 V vs Ag/AgCl (*265*). These cations are thus essentially biologically nonreducible and the ^{99m}Tc complexes are of interest as potential myocardial imaging agents. All complexes exhibit characteristic MLCT bands in the visible region, the energy of which correlates linearly with the potential of the Tc(IV)/Tc(III) and Tc(III)/Tc(II) couples (*264*). The crystal structure of *trans*-$[Tc\{(acac)_2en\}(PPh_3)_2]PF_6$ shows approximate octahedral coordination with the tetradentate Schiff base in the equatorial plane (*264*). The thio derivative $[Tc\{(sacac)_2en\}(PPh_3)_2]PF_6$ has also been prepared from $NBu_4[TcOCl_4]$ (*266*). A rather mixed coordination sphere is present in $[Tc(quin)(PR_3)L]$ (L = **20**; E = O, S; PR_3 = PMe_2Ph, PEt_2Ph, PPh_3). The crystal structure of $[Tc(quin)(PEt_2Ph)L]$ (L = **20**; E = O) shows approximate octahedral



(E = O, $OphsalH_2$)
(E = S, $SphsalH_2$)

(**20**)



P = PMe_2Ph

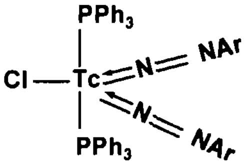
(**21**)

geometry with the tridentate ligand L spanning three *mer* positions and the phosphine *trans* to the quinoline nitrogen (*267*).

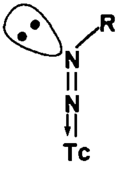
Crystallography has shown that the product of the reaction of a Schiff-base dithiocarbazate ester derivative (H_2L) with $[TcOCl_4]^-/PPh_3$ is the octahedral *cis*(*Cl*)-*trans*(*P*)-$[TcCl_2(HL)(PPh_3)_2]$, where HL functions as a bidentate *S*,*N*-ligand (*268*). For $[TcClL_2(PMe_2Ph)]$ (L = *N*-phenylsalicylidineiminate), the two bidentate chelate ligands are mutually orthogonal and the chloro and phosphine ligands, *cis* to each other (*269*). Novel complexes are $[\{TcL(PR_3)_2\}_2(\mu\text{-}O)]$ (L = **20**; E = O, S; PR_3 = PMe_2Ph, PPh_3), which represent the only examples of Tc(III) oxo-bridged dimers. In $[\{Tc(Ophsal)(PMe_2Ph)_2\}_2(\mu\text{-}O)]$ (**21**) the Tc–O–Tc angle is near-linear at 176.1(14)° and the $Tc\text{–}O_{bridge}$ distances are 1.81(2) and 1.87(2) Å (*270*).

The complexes *mer*-$[TcCl_3L_3]$ (L = py, pic) and *mer*-$[TcCl_3(pic)(PMe_2Ph)_2]$ are prepared from $NBu_4[TcOCl_4]$ dissolved in neat pyridine or picoline by the use of a phosphine as the oxygen acceptor. Linear correlations of reduction potentials in dmf with electrochemical ligand activity parameters are observed for the Tc(IV)/Tc(III), Tc(III)/Tc(II), and Tc(II)/Tc(I) couples. Crystal structures for *mer*-$[TcCl_3(pic)_3]$ and *mer*-$[TcCl_3(pic)(PMe_2Ph)_2]$ confirm the expected octahedral geometry (*271*). A variety of Tc(III) complexes containing polypyridyl ligands has been prepared by substitution of $[TcCl_3(PR_2R')_3]$ or $[Tc(tu)_6]Cl_3$ or substitution/reduction of $[TcCl_4(PPh_3)_2]$ (*272, 273*), and the electrochemical behavior has been studied (*274*). Crystal structures have been reported for $[TcCl_3(PPh_3)(bpy)]$ (*272*), *cis*(*Cl*),*trans*(*P*)-$[TcCl_2(PMe_2Ph)_2L]BPh_4$ (L = bpy, phen), and *cis*(*Cl*),*trans*(*P*)-$[TcCl_2(PEtPh_2)_2(bpy)]CF_3SO_3$ (*273*). The preparations of $[TcCl_2L\{HB(pz)_3\}]$ (L = PPh_3, $OPPh_3$, py), containing the tridentate $HB(pz)_3^-$ ligand, have been reported (*275*). Reaction of $[Tc(tu)_6]^{3+}$ with phen is thought to give $[Tc(phen)_3](PF_6)_3$ (*276*).

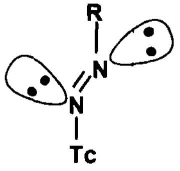
The organohydrazine chemistry of Tc parallels that of Re (*189*). The air-stable bis(diazenido) $[TcCl(N_2Ar)_2(PPh_3)_2]$ complexes are formed by the reaction of $[Tc^VOCl_4]^-$ or $[TcCl_4(PPh_3)_2]$ with excess $ArNHNH_2$ in alcoholic solution or directly from TcO_4^- (*277, 278, 140*). The use of *p*-$NO_2C_6H_4NHNH_2$ gives the lime-green monodiazenido complex $[TcCl_2(NNC_6H_4NO_2\text{-}p)(PPh_3)_2]$ in high yield (*140*). Organodiazenido ligands most commonly bond in the singly bent, three-electron-donor mode with the doubly bent, one-electron-donor mode much less common. Crystal structures of $[TcCl(NNC_6H_4X\text{-}p)_2(PPh_3)_2]$ (X = Cl, Br) (**22**) show trigonal–bipyramidal geometry with Tc–N–N angles of 166.2(6)° and 170.7(7)° for X = Br and the same essentially linear arrangement for X = Cl (*277, 140*).



(22)



singly bent
3-electron donor

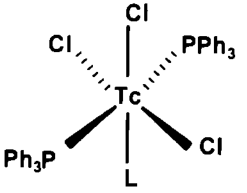


doubly bent
1-electron donor

The bond distances indicate extensive delocalization and multiple bonding in the –NNAr moieties together with significant Tc back-bonding. The diazenido ligands are thus singly bent, three-electron donors and $[TcCl(NNAr)_2(PPh_3)_2]$ complexes have a formal valence electron count of 18 (*140*). The cationic monodiazenido $[TcCl(NNAr)(dppe)_2]^+$ complexes may be prepared by substitution of $[TcCl(NNAr)_2(PPh_3)_2]$ or directly from TcO_4^- and isolated as the PF_6^- or BPh_4^- salts. The crystal structure of *trans*-$[TcCl(NNPh)(dppe)_2]PF_6 \cdot H_2O$ shows slightly distorted octahedral geometry, a Tc–N–NPh angle of 163(2)°,and Tc–N and N–NAr bond distances of 1.917(19) and 1.25(4) Å, respectively (*140*). Substitution of $[TcCl(NNC_6H_4Cl)_2(PPh_3)_2]$ with $Na(S_2CNMe_2)$ in methanol yields the dark-orange $[Tc(NNC_6H_4Cl)(S_2CNMe_2)_2(PPh_3)]$. The crystal structure shows distorted octahedral geometry, with the PPh_3 and diazenido ligands in *cis* positions and Tc–N–NAr and N–N–Ar angles of 178.6(4)° and 122.5(5)°, respectively. The Tc–N and N–NAr bond distances are 1.763(3) and 1.236(4) Å, respectively. The *trans* influence of the diazenido ligand is apparent because the *trans* Tc–S bond distance is longer [2.537(1) Å] than the other three Tc–S distances [2.412(2)–2.477(2) Å] (*279*).

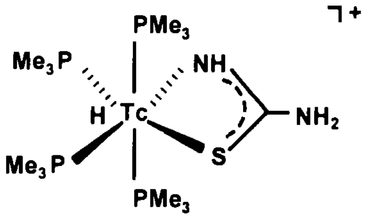
G. Complexes with Monodentate Phosphines and Related Ligands

The products of the reduction of TcO_4^- by phosphine/HX (X = Cl, Br) depend on the nature of the phosphine and the reaction conditions. With PPh_3 only *trans*-$[Tc^{IV}X_4(PPh_3)_2]$ is formed, whereas the more strongly reducing PR_2Ph (R = Me, Et) gives the Tc(IV) complex at a TcO_4^- : phoshine ratio of 1 : 5 and *mer*-$[Tc^{III}X_3(PR_2Ph)_3]$ at a ratio of 1 : 15 or higher (*280*). Alternatively, the Tc(III) complexes may be prepared by the reduction of *trans*-$[TcX_4(PR_2Ph)_2]$ with excess PR_2Ph (*281*) or by the reaction of $(NH_4)_2[TcCl_6]$ with PR_2Ph (*282*). The magnetic moment of 2.8 BM for the Tc(III) complexes is consistent with a $t_{2g}{}^4$ configuration in an octahedral environment (*280*). In MeCN solution, *mer*-$[TcCl_3(PMe_2Ph)_3]$ may be electrochemically oxidized to $[Tc^{IV}Cl_4(PMe_2Ph)_2]$ or $[Tc^{IV}Cl_3(PMe_2Ph)_3]ClO_4$ or reduced to Tc(II) and Tc(I) phosphine complexes (*283*). Reduction of $NBu_4[Tc^{V}OCl_4]$ with PMe_3 yields *mer*-$[TcCl_3(PMe_3)_3]$ (*284*) and with PPh_3/MeCN, $[TcCl_3(PPh_3)_2(MeCN)]$ (*207*), whereas reduction of $TcO_4{}^-$ by PPh_3/HCl/dmf yields **23** (L = dmf) (*285*). The MeCN complex (**23**) is a useful synthetic intermediate. On reaction with CO or NO only the MeCN ligand is substituted (*207*) but bpy and phen result in complete substitution, producing $[Tc^{II}L_3]^{2+}$ salts (*185*). The crystal structures of *mer*-$[TcCl_3(PMe_3)_3]\cdot(PhNCO)_3$ and *mer*-$[TcCl_3(PMe_2Ph)_3]$ show a marked *trans* influence of the phosphine ligands with the Tc–Cl bond distances *trans* to P about 0.08–0.13 Å longer than those *trans* to Cl (*284, 282*). Crystal structures have also been reported for **23**$\cdot 2PPh_3$ (L = dmf) (*285*) and *trans-mer*-$[TcCl_3(MeCN)\{P(m\text{-}MeC_6H_4)_3\}_2]$ (*185*). The reaction of $[Tc(S\text{-}tu)_6](PF_6)_3$ with PMe_3 in methanol gives the hydrido complex $[Tc(H)\{\eta^2\text{-}N,\text{-}S\text{-}NHC(NH_2)S\}(PMe_3)_4]PF_6$ (**24**), in which the thiourea ligand has undergone deprotonation and binds in the unusual η^2-*N*,-*S* mode. Structure **24** was established by crystallography, multinuclear NMR, and IR spectroscopy [ν(TcH) at 1898 cm^{-1}] (*284*).



(L = MeCN, dmf)

(**23**)



(**24**)

A number of Tc(III) phosphonite complexes of the type $[TcX_2\{P(OEt)_2Ph\}_4]ClO_4$ (X = Cl, Br, I) have been prepared from $(NH_4)_2[TcX_6]$. The magnetic moments are in the range 2.3–2.6 BM (*79*).

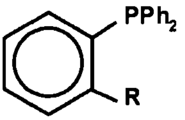
H. COMPLEXES WITH BIDENTATE PHOSPHINE, ARSINE, AND RELATED LIGANDS

The Tc(III) complexes *trans*-$[Tc(diars)_2X_2]X$ (X = Cl, Br, I) were first reported in 1959 (*190*) and the chemistry of the dppe analogs was described in detail later (*192*). These and related complexes have been intensely investigated after it was shown by Deutsch *et al.* that the +1 cation *trans*-$[^{99m}Tc(dmpe)_2Cl_2]^+$ accumulates in the heart (*286*). Complexes of the type *trans*-$[TcL_2X_2]Y$ (L = diars, depe, dmpe, dppe; X = Cl, Br, I; Y = PF_6, CF_3SO_3, BPh_4, BF_4) are prepared by the reduction of TcO_4^-, $[TcOX_4]^-$, or $[TcX_6]^{2-}$ with excess phosphine or arsine (*287*). Electrochemical and spectroelectrochemical studies have shown that the $E^{\circ\prime}$ value of the reversible Tc(III)/Tc(II) couple depends on the nature of X and of the bidentate ligand, with reduction being easier with the heavier halogen and also easier for dppe than for diars complexes (*287, 288*). These effects result from the stabilization of the Tc(II) d^5 center over the Tc(III) d^4 center by an increased ligand field. Typical $E^{\circ\prime}$ values are in the biologically accessible range of 100 to −250 mV vs Ag/AgCl. Under common laboratory conditions Tc(III) is the stable state for the chloro and bromo complexes but when X = NCS, $E^{\circ\prime}$ is 390 mV and $[Tc^{II}(dppe)_2(NCS)_2]$ is the stable state (*287*). Comparison of *trans*-$[M^{III/II}L_2X_2]^{+/0}$ (M = Tc, Re) couples has shown that the Tc complex is always easier to reduce than the Re analog, with $(E^{\circ\prime}_{Tc} - E^{\circ\prime}_{Re})$ 219 ± 15 mV (*289*). Thus, the significantly different biological behavior of $[^{99m}Tc(dmpe)_2Cl_2]^+$ and $[^{186}Re(dmpe)_2Cl_2]^+$ appears to be due to the *in vivo* reduction of the ^{99m}Tc but not the ^{186}Re complex (*290*). Interestingly, pulse radiolysis studies have shown that in aqueous anionic surfactant media the $[Tc(dmpe)_2Cl_2]^+$ cation effectively partitions into the anionic micelles and is there relatively protected from the highly reactive negatively charged strong reductant e_{aq}^- and the strong oxidant Cl_2^- (*291*). The chloro ligands in *trans*-$[Tc(dppe)_2Cl_2]^+$ are rather unreactive to exchange (*287*). Reaction of *trans*-$[Tc(dppe)_2Cl_2]$ with $LiAlH_4$ yields yellow crystals of $[Tc^{III}(H)_2(dppe)_2Cl]$ [ν(TcH) at 1851 and 1775 cm^{-1}] (*292*).

The electronic spectra of *trans*-$[TcL_2X_2]^+$ (X = Cl, Br; L = diphosphine, diars) exhibit well-defined intense bands in the visible region (~20,000–23,000 cm^{-1}) that are 2500 ± 370 cm^{-1} lower in energy than in the corresponding Tc(II) complex (*287*). These bands have been assigned to X → Tc LMCT transitions, and for Tc(III) Cl/Br pairs the difference is about 1600 cm^{-1}. All complexes are paramagnetic; the magnetic moment of *trans*-$[Tc(dppe)_2Br_2]Br$ is 2.47 BM (*192, 287*). FABMS has proven useful in the study of these Tc(III) cationic complexes (*293, 294*). Crystal structures for *trans*-$[Tc(diars)_2Cl_2]Y$ (Y = Cl, ClO_4) (*295, 296*), *trans*-$[Tc(dppe)_2Br_2]BF_4$ (*287*), *trans*-$[Tc(dmpe)_2Cl_2]CF_3SO_3$ (*123*), and *trans*-$[Tc(dppe)_2Cl_2]NO_3{\cdot}HNO_3$ (*193*) reveal the expected distorted octahedral geometry.

The search for nonreducible Tc(III) cations has led to the preparation of a variety of thiolato complexes of the type $[Tc(SR)_2L_2]^+$ (L = depe, dmpe, dppe, diars) (*297, 298, 200*). The geometry is generally *trans*, but for dmpe complexes with R being an aryl group the *cis*-isomer is formed (*299*). These complexes exhibit a reversible Tc(III)/Tc(II) couple for which $E^{\circ\prime}$ spans a range of values from ~−200 to −600 mV vs Ag/AgCl and are thus generally more difficult to reduce than the halide complexes (*300*). Again, the Re complexes are more difficult to reduce than the Tc analogs (*301*). A general method of synthesis is by the reaction of the thiolate with *trans*-$[Tc^{V}O(OH)L_2](PF_6)_2$ (*297*). FABMS (*298, 302*) and spectroelectrochemical studies have been reported (*303*). Crystal structures are available for *trans*-$[Tc(SMe)_2L_2]Y$ (L = depe, Y = PF_6; L = dmpe, Y = CF_3SO_3) (*297*), *trans*-$[Tc(SMe)_2(diars)_2]PF_6$ (*200*), and *cis*-$[Tc(SPh)_2(dmpe)_2]PF_6$ (*299*). In the *cis* complex a *trans* influence is evident with the averaged Tc–P distance *trans* to P, 2.42(1) Å, and that *trans* to S, 2.49(3) Å. A crystal structure of the product of the reaction of *trans*-$[TcO(OH)(dmpe)_2](PF_6)_2$ with $Na(S_2CNEt_2)$ has shown this to be *trans*-$[Tc^{III}(scp)_2(dmpe)_2](PF_6)_3$, where scp represents the zwitterionic ligand $^{-}SCH_2P^{+}Me_2(CH_2)_2P(S)Me_2$. This unusual ligand appears to be formed by nucleophilic attack of a dmpe phosphorus center on the CS_2 elimination product of the dithiocarbamate, followed by a molecular rearrangement (*300*). Dithiolene ligands are well known to stabilize trigonal prismatic geometry, and the structure of the 3,4-toluenedithiolato complex $[Tc(tdt)(dmpe)_2]PF_6$ (Fig. 9) shows a mean twist angle of 33(3)°, which is about midway between the 60° of ideal octahedral geometry and the 0° of the ideal trigonal prism. Electrochemical and spectroelectrochemical studies show reversible Tc(III)/Tc(II) and Tc(II)/Tc(I) couples at −0.600 and −1.217 V, respectively, and a quasireversible Tc(IV)/Tc(III) couple at 0.680 V vs Ag/AgCl (*304*). A related cationic complex is $[Tc(o\text{-}SC_6H_4O)(dmpe)_2]BPh_4$, prepared by the reaction of 2-mercaptophenol with $[Tc(dmpe)_2Cl_2]Cl$ in ethanol. The geometry of the cation is described as distorted octahedral with a dihedral angle of 18.1(3)° between the TcOS plane and the "*trans*" TcPP plane containing one P atom from each ligand (*305*). An interesting series of Tc(III) complexes based on the mixed bidentate ligands **25** and **26** has been prepared by the reduction of TcO_4^- by the ligand and complex formation (*306–309*).

Crystal structures have been reported for the octahedral phenolate $[Tc(dppo)_3]$ (*307*), thiolate $[Tc(dppbt)_3]$ (*307, 308*), and propionate $[Tc(dppp)_3]\cdot 2dmso$ (*306*). In each case the three P atoms occupy *mer* positions. For the amine ligand (**25**) (R = NH_2) an acid–base equilibrium is established and either the triply deprotonated $[Tc(dppba)_3]$ or salts of the doubly deprotonated $[Tc(dppba)_2(dppbaH)]^+$ may be isolated depending on the pH. The crystal structure of $[Tc(dppba)_2(dppbaH)]$-



R = NH_2 (dppbaH)
R = SH (dppbtH)
R = OH (dppoH)
R = COOH
(25)

$Ph_2P(CH_2)_nCOOH$
n = 1
n = 2 (dpppH)
(26)

$E(CH_2CH_2PPh_2)_3$
E = N, P
(27)

ClO_4 again shows a *mer* arrangement for the phosphorus atoms. The proton is thought not to be delocalized over the three nitrogen atoms but to reside on the single nitrogen which corresponds to the longest of the 1.948(5)-, 1.979(5)-, and 2.048(5)-Å Tc–N bond distances (*309*).

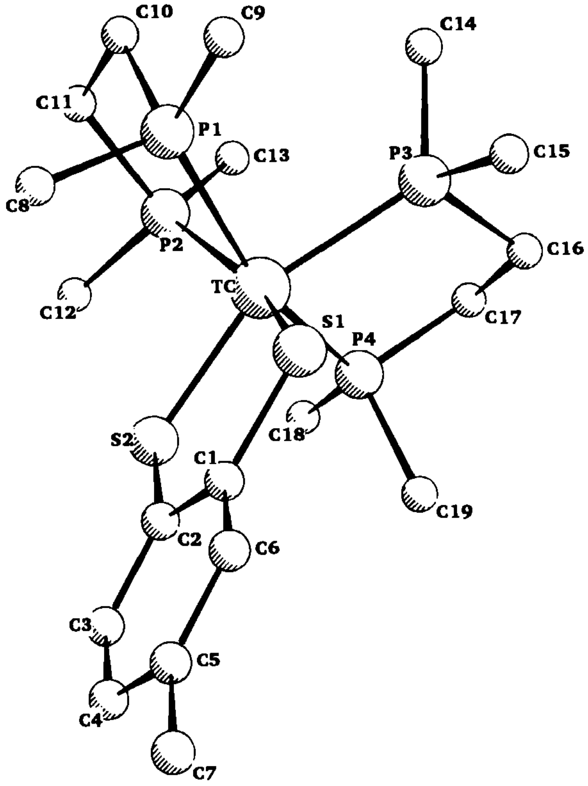


FIG. 9. The structure of the cation in $[Tc(tdt)(dmpe)_2]PF_6$ (*304*).

The corresponding Tc–N–C bond angles of 128.3(4)°, 126.6(4)°, and 129.1(4)°, however, seem to offer little distinction between neutral and anionic nitrogen. Cationic complexes of the type $[TcCl_2L]^+$ have been prepared by the reaction of $[TcCl_4(PPh_3)_2]$ with the tetradentate ligands (**27**) (*310*).

I. COMPLEXES WITH SULFUR LIGANDS

Only complexes in which sulfur ligands form the major part of the coordination sphere are discussed here; other sulfur complexes are described under various headings. Most important is the homoleptic orange-red thiourea complex $[Tc(tu)_6]Cl_3$, which precipitates in high yield from a concentrated HCl/ethanol solution containing TcO_4^- and thiourea (*111*). The thiourea ligands are readily replaced, making this, and related complexes, valuable synthetic precursors for the preparation of Tc(III) and other low-valent technetium complexes. Thus, for example, reaction of $[Tc(tu)_6](PF_6)_3$ with CN^tBu results in reduction, giving a 62% yield of $[Tc^I(CN^tBu)_6]PF_6$ (*111*). Crystal structures for $[Tc(tu)_6]Cl_3{\cdot}4H_2O$ (*111*) and $[TcL_6](PF_6)_3$ (L = *N*-methylthiourea, *N,N'*-dimethylthiourea) (*311*) establish approximate octahedral geometry with *S*-bonded thiourea ligands. Another complexes with an all-sulfur coordination sphere is the cationic $[TcL(SR)_2]PF_6$, where L represents a linear tetradentate thioether. The crystal structure of $[TcL(SPh)_2]PF_6$ (L = 5,8,11,14-tetrathiaoctadecane) shows the two benzenethiolato ligands to occupy *cis* positions with the thioether wrapped around the remaining four coordination sites to give strongly distorted octahedral geometry (*312*).

Complexes of the type $[TcL'L_3]$, where L represents a dithiocarbamato or xanthato ligand, have been prepared by various routes. Crystal structures for $[Tc(PMe_2Ph)(S_2CNEt_2)_3]$ (*313*), $[Tc(PMe_2Ph)(S_2COEt)_3]$ (*314*), and $[Tc(PPh_3)(S_2COC_4H_9)_3]$ (*315*) show pentagonal–bipyramidal geometry, similar to that of $[Tc(S_2CNEt_2)_3(CO)]$ in Fig. 5, with the monodentate ligand in an apical position. Reaction of $NH_4\{S_2P(OMe)_2\}$ (Me_2dtp) with *mer*-$[TcCl_3(PMe_2Ph)_3]$ yields orange-red crystals, shown by crystallography to be the octahedral *trans*(*Cl*)-*cis*(*P*)-$[TcCl_2(PMe_2Ph)_2(Me_2dtp)]$ (*314*), whereas reaction with $Na_2(mnt)$ yields $PPh_4[Tc(PMe_2Ph)_2(mnt)_2]$ (*316*). The preparation of neutral $[TcL_3]$ complexes with bidentate *N, N*-substituted benzoylthiourea ligands has been reported (*317*). The reaction of the sterically hindered anions tmbt and 2,4,6-triisopropylbenzenethiolate (SAr) with $[Tc^{IV}Cl_6]^{2-}$/L/Zn dust (L = MeCN, py, PEt_3) in the absence of air yields the diamagnetic $[Tc(SAr)_3L_2]$ (*318, 319*). The crystal structure of the tetramethylbenzenethiolato complex, $[Tc(tmbt)_3(MeCN)_2]$, reveals trigonal–bipyramidal geometry, with the two MeCN ligands in the axial positions and the three S atoms in the equatorial plane, with the bulky aryl groups arranged two above and one below this plane. The orientation of the aryl rings observed in the crystal structure is shown by the ^1H NMR spectra to persist in solution. The $[Tc(tmbt)_3L_2]$ (L = MeCN, py) complexes can be oxidized to Tc(V) oxo compounds by oxygen atom transfer from dmso and other oxygen donors, and $[Tc^VO(tmbt)_3(py)]$ may be reduced to $[Tc(tmbt)_3(PEt_3)_2]$ by PEt_3. In the oxidation of the MeCN complex, an intermediate Tc(III) complex was isolated and shown by FABMS and crystallography to be $[Tc(tmbt)_3(MeCN)(dmso)]$. A catalytic amount of $[Tc^VO(tmbt)_3(py)]$ results in the oxidation of PPh_3 to $OPPh_3$ by dmso via an oxidative and reductive oxo-transfer cycle, with the catalyst still fully active after 500 turnovers (*319*). Reduction of TcO_4^- by $S_2O_4^{2-}$ in the presence of CN^iPr and the tetradentate "umbrella" ligand $P(o\text{-}C_6H_4SH)_3$ (H_3L) yields the trigonal–bipyramidal 14-electron complex $[TcL(CN^iPr)]$, with the isonitrile in an axial position [Tc–CNR, 2.06(8) Å]. In the presence of a large excess of the isonitrile, a sixth ligand is bound, giving the octahedral 16-electron *cis*-$[TcL(CN^iPr)_2]$ [PTc–CNR, 2.058(8) Å; STc–CNR, 2.081(7) Å] (*320*).

J. NITROSYL AND THIONITROSYL COMPLEXES

Reaction of $NBu_4[Tc^{II}(NO)Cl_4]$ with tmbtH yields orange crystals of the neutral $[Tc^{III}(NO)Cl(tmbt)_3]$. The nitrosyl and chloro ligands occupy the axial positions in the trigonal–bipyramidal structure. The Tc–N and N–O bond distances are 1.767(6) and 1.150(7) Å, respectively, and the Tc–N–O angle is 176.8(6)°. The ν(NO) IR absorption occurs at 1798 cm^{-1} (*321*). A variety of seven-coordinate dithiocarbamato complexes $[Tc(NO)(S_2CNR_2)_3]Y$ ($Y = BF_4, PF_6, ClO_4$) is prepared by substitution of $[Tc(S_2CNR_2)_3(CO)]$ with $NOBF_4$. These complexes show ν(NO) at 1795–1771 cm^{-1} (*221*). The seven-coordinate $[Tc(NS)X_2(S_2CNEt_2)_2]$ (X = Cl, Br) is prepared by sulfur abstraction from S_2Cl_2 or $SOCl_2$ (X = Cl) and $SOBr_2$ (X = Br) by $[TcN(S_2CNEt_2)_2]$. Absorptions at 1248 cm^{-1} (X = Cl) and 1250 cm^{-1} (X = Br) in the IR spectra have been assigned to ν(NS). Crystal structures for both complexes show pentagonal–bipyramidal coordination geometry with the NS ligand, one halide in the axial positions, and Tc–N–S angles of 177(2)° and 174(2)° for the two independent molecules of the chloro complex and 177.2(7)° for the bromo complex. In $[Tc(NS)Br_2(S_2CNEt_2)_2]$ the SNTc–Br_{trans} bond distance of 2.595(1) Å is lengthened by a small but significant amount over that of Tc–Br_{cis} [2.564(1) Å] (*322, 323*).

VII. Technetium(IV)

This oxidation state is intermediate between the low oxidation states stabilized by π-acceptor ligands and the high oxidation states stabilized by π-donor ligands. Thus, carbonyl complexes are unknown and, although bridging oxo groups are not uncommon, terminal oxo groups are at present unknown. The most useful starting material for the preparation of Tc(IV) complexes is $[TcX_6]^{2-}$ (X = Cl, Br), but TcO_4^- or $[Tc^VOX_4]^-$ may also be used.

A. ISONITRILE AND THIOCYANATO COMPLEXES

Complexes of the type $[TcX_4L_2]$ (X = Cl, Br) are formed by the reaction of MeCN or CNR with TcX_4. The IR spectra indicate that the yellow chloro and red bromo crystalline products are the *cis*-isomers (*324*). The deep red-violet color (λ_{max} = 500 nm) produced when TcO_4^- is reduced in the presence of NCS^- or by substitution of $[TcX_6]^{2-}$ (X = Cl, Br) is now known to be due to $[Tc^{IV}(NCS)_6]^{2-}$. This anion is reduced by hydrazine to the yellow, air-sensitive $[Tc^{III}(NCS)_6]^{3-}$ (Tc(IV)/Tc(III), $E_{1/2}$= 0.18 V vs SCE). The magnetic moment of 4.1 BM for the purple $(AsPh_4)_2[Tc(NCS)_6]$ is consistent with an octahedral d^3 configuration (*230*), and the presence of *N*-bonded thiocyanate is confirmed by the crystal structure of the octahedral $(AsPh_4)_2[Tc(NCS)_6]\cdot CH_2Cl_2$. The Tc–N bond distances are 2.00(1) and 2.01(1) Å and the N–Tc–N angles are exactly 90°. Two Tc–NCS groups are linear and for the remaining four the Tc–N–C and N–C–S angles are 175.9(9)° and 175.3(10)°, respectively (*325*).

B. HALIDE AND RELATED COMPLEXES

The highest binary chloride of technetium is the dark red $TcCl_4$, formed as the major product of the chlorination of Tc metal (*26, 326*). Crystallography reveals a polymeric chain structure of Cl-bridged distorted octahedral $TcCl_6$ units (*327*). Reaction of $TcCl_4$ with Me_3SiBr yields "$TcBr_4$" (*324*). Of great importance and synthetic utility are the stable complex halides $[TcX_6]^{2-}$. Salts of the bright yellow chloro complex $[TcCl_6]^{2-}$ are best prepared by prolonged reflux of TcO_4^- in concentrated HCl in order to ensure complete reduction of the initially formed $[Tc^VOCl_4]^-$. Concentrated HBr rapidly yields the red $[TcBr_6]^{2-}$, whereas the deep purple $[TcI_6]^{2-}$ may be prepared by ligand exchange of the chloro and bromo complexes with HI (*26, 27, 328*). The white fluoro complex $K_2[TcF_6]$ has been prepared by fusion of $K_2[TcBr_6]$ with KHF_2

(*329*); a convenient high-yield synthesis is by ligand exchange with AgF in 40% HF (*330*). All eight possible mixed $[TcCl_nBr_{6-n}]^{2-}$ (n = 1–5) complexes have been separated by ion-exchange chromatography. A notable feature of this work is the use of the greater *trans* effect of Br compared with that of Cl in order to accomplish stereospecific synthesis. Ligand exchange of $[TcBr_6]^{2-}$ with HCl results in the *cis*/*fac* complexes for n = 2, 3, and 4, whereas ligand exchange of $[TcCl_6]^{2-}$ with HBr yields the *trans*/*mer* isomers (*331*). From the LMCT spectra an optical electronegativity value of 2.25 for Tc(IV) is indicated, compared with 2.05 for the less oxidizing Re(IV), and $10Dq$ is 28,400 cm^{-1} for $[TcF_6]^{2-}$ and 32,800 cm^{-1} for $[ReF_6]^{2-}$ (*332, 333*). The force constants for all the $[TcX_6]^{2-}$ complexes have been determined (*334*), and the IR and Raman spectra of the 10 $[TcCl_nBr_{6-n}]^{2-}$ (n = 0–6) species, including the pure geometrical isomers, at 80 K have been completely assigned and supported by normal coordinate analysis. Due to the Cl < Br *trans* influence, the force constants indicate that in asymmetric Cl′–Tc–Br′ axes the Tc–Br′ bonds are strengthened by on average 6% and the Tc–Cl′ bonds weakened by 10% relative to symmetric Br–Tc–Br and Cl–Tc–Cl axes, respectively (*331*). Luminescence spectra for mixed ClBr species have been reported (*335, 336*). Recent μ_{eff} values, utilizing diamagnetic corrections, are in the range 3.34–3.80 BM for $M_2[TcX_6]$ (M = NH_4, K; X = Cl, Br, I), $(NBu_4)_2[TcCl_6]$, and $(NEt_4)_2[TcI_6]$ at 300 K (*150*). In general, EPR spectra are observed only at <5 K (*40*). A surprising number of $[TcX_6]^{2-}$ salts have been studied crystallographically (*38*). The anion may either be regular octahedral (cubic crystal class) or have lower symmetry. Single-crystal structures are available for $M_2[TcCl_6]$ [M = NH_4 (*337*), $AsPh_4$ (*338*)], $H_2[TcCl_6]\cdot 9H_2O$ (*339*), $(NH_2Me_2)(Me_2NHCOMe)[TcCl_6]\cdot OPPh_3$ (*285*), $M_2[TcBr_6]$ [M = NH_4 (*340*), H_3O (*341*)], and $K_2[TcI_6]$ (*342*).

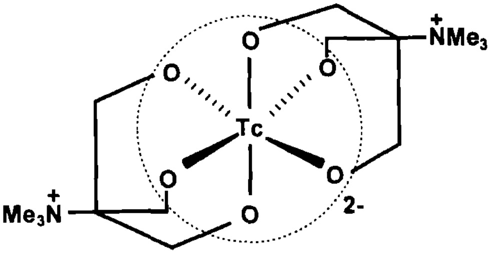
Radiolabeling studies have shown that ligand exchange of $[TcBr_6]^{2-}$ occurs at about 170 times the rate for $[TcCl_6]^{2-}$ and that these complexes undergo ligand exchange at 20 to 50 times the rate of the Re analogs (*343*). The $[TcF_6]^{2-}$ anion is remarkably inert and is hydrolyzed only by hot, concentrated alkali (*329*). Spectroelectrochemical studies show that $[TcX_6]^{2-}$ (X = Cl, Br) undergoes a reversible one-electron reduction in HX/NaX aqueous media (*231*). The aquation of $[TcX_6]^{2-}$ (X = Cl, Br) is promoted by UV and visible light (*344*). Spectrophotometric and paper electrophoretic studies in HX, $HClO_4$, and H_2SO_4 have shown the formation of anionic, neutral, and cationic species together with TcO_4^-, with the proportions depending on the acid (*345–349*). The anionic species is considered most likely to be $[TcX_5(OH_2)]^-$. The octahedral $[TcCl_5(OH_2)]^-$ anion has been identified in the crystal structure of $[(H_3O)(15\text{-crown-}5)][TcCl_5(OH_2)]\cdot(15\text{-crown-}5)$, a product isolated from a solution of $TcCl_4$/15-crown-5/CH_2Cl_2 (*324*). The red $K_2[TcCl_5(OH)]$ precipitates from solution in the reduction of $KTcO_4$ by HCl/I^- (*350*) and the yellow $Zn[TcCl_5(OH)]$ and $La_2[TcCl_5(OH)]_3$ are formed by reduction of the TcO_4^- salts with HCl (*351*). Unlike for rhenium, there is no evidence for the formation of $[Tc_2OCl_{10}]^{4-}$. On heating $(NEt_4)_2[TcBr_6]$ in CF_3COOH, the dimer NEt_4 $[Br_3Tc(\mu\text{-}Br)_3TcBr_3]$ is formed. The vibrational spectra have been assigned in D_{3h} symmetry, with TcBr force constants of 1.045 and 0.80 mdyn $Å^{-1}$ for terminal and bridging bromide (*352*).

C. COMPLEXES WITH OXYGEN LIGANDS AND OXO-BRIDGED COMPLEXES

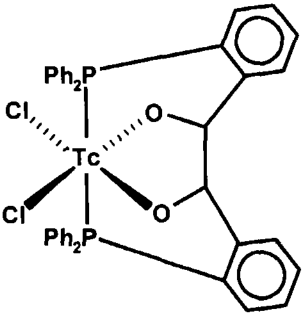
Chemical or electrochemical reduction of TcO_4^- in aqueous solution or hydrolysis of $[TcX_6]^{2-}$ (X = Cl, Br) with aqueous ammonia results in a brown-black precipitate of $TcO_2{\cdot}nH_2O$ ($n \simeq 2$). This precipitate is generally regarded as the "thermodynamic sink" of Tc(IV) chemistry when hydrolysis competes favorably with substitution of Tc(IV) cores. It is, however, a useful starting material (*34*). A Tc(IV) aqua cation is formed when TcO_4^- is reduced in solutions of weakly coordinating acids. The structure is unknown; the usual formulation as $[TcO(OH)]^+$ (*353*) implies the presence of Tc=O and would seem unlikely in the absence of any characterized $Tc^{IV}{=}O$ complexes. In this respect it may be noted that the structure of crystalline TcO_2 consists of linked TcO_6 octahedra in an infinite three-dimensional network (*354*). A spectroelectrochemical study of the reduction of $KTcO_4$ in bicarbonate buffer /CF_3SO_3Na at pH 8 indicates the sequential formation of cationic pink Tc(IV) and blue Tc(III) carbonate species (*355*).

1. Mononuclear Complexes

The unexpectedly high solubility of $K_2[TcBr_6]$ (in contrast to that of the fluoro and chloro complexes) in methanol appears to be due to partial substitution of Br^- by MeO^-. By the use of KOR, salts such as $K_2[Tc(OMe)_6]$ and $K_2[Tc(OCH_2CH_2O)_3]$ may be isolated. These complexes show a ν(TcO) IR absorption at 450–460 cm^{-1} (*356*). A crystal structure of **28**, with the zwitterionic tripod ligand $Me_3N^+C(CH_2O^-)_3$, shows octahedral geometry with Tc–O distances of 1.987(4)–2.005(4) Å. Complex **28** is water soluble and stable at pH > 4 for over 24 hr (*357*).



(28)



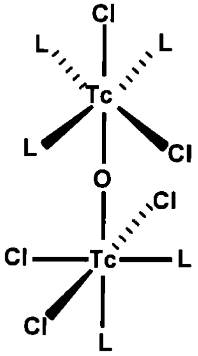
(29)

An unusual phosphine/diolato complex is **29**, formed from $[TcOCl_4]^-$ and *o*-(diphenylphosphino)benzaldehyde. The Tc–O bond distances are 1.95 Å (*358*). Reflux of $(PPh_4)_2[TcCl_6]$ in salicylaldehyde yields $PPh_4[TcCl_4(sal)]$ (μ_{eff} = 3.8 BM), for which the phenolic and aldehyde Tc–O bond distances are 1.98(2) and 2.04(2) Å, respectively (*359*). The pale yellow oxalato complex $(AsPh_4)_2[Tc(C_2O_4)_3]$ is prepared by substitution of $[TcBr_6]^{2-}$ in oxalic acid solution. The crystal structure shows six oxygen atoms in distorted octahedral coordination with pseudo D_3 symmetry and Tc–O distances of 1.978(5)–2.001(4) Å (*360*). The substitution of $[TcX_6]^{2-}$ and the reduction of TcO_4^- in the presence of carboxylic, hydroxycarboxylic, and aminocarboxylic acids has been extensively studied and it appears that, in general, the Tc(IV) species formed are dimeric (*361*).

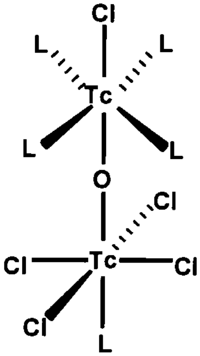
The reaction of acacH with $[TcX_6]^{2-}$ or $[TcX_4(PPh_3)_2]$ (X = Cl, Br) yields products depending on the reaction conditions, and $PPh_4[TcX_4(acac)]$, $[TcX_2(acac)_2]$, and $[TcBr_3(acac)(PPh_3)]$ have been isolated (*242*). The $[TcX_2(acac)_2]$ complexes are stable to acid but in alkaline solution undergo loss of halide followed by loss of the acac anions (*362*). The cationic $[Tc(acac)_3]BF_4$ is formed by oxidation of $[Tc(acac)_3]$ with $[Fe(Cp)_2]^+$ (*363*).

2. *Binuclear Complexes*

A novel series of μ-oxo complexes is formed when a starting material such as $NBu_4[TcOX_4]$, $(NBu_4)_2[TcX_6]$ (X = Cl, Br), *trans*-$[TcO_2(py)_4]Cl$, or TcO_4^-/BH_4^- reacts with pyridine or alkyl pyridines either in neat solution or in a noncoordinating solvent (*364–367*). Crystal structures of the picoline derivatives show that these mixed-valence Tc(III)/Tc(IV) complexes are of the asymmetric $[X_2L_3TcOTcX_3L_2]$ (**30**) and dissymmetric $[XL_4TcOTcX_4L]$ (**31**) type.



(30)



(31)

L = picoline

The reaction of $[TcOCl_4]^-$ with hot picoline results first in the formation of (**30**) and *trans*-$[Tc^VO_2(pic)_4]^+$, with the concentration of the latter remaining nearly constant; this species is not an immediate precursor of the dimeric forms. In the later stages of the reaction the asymmetric form (**30**) is converted to the dissymmetric form (**31**). The formation of picoline *N*-oxide indicates that oxygen atom transfer occurs in the reduction process. Both **30** and **31** are stable in organic solvents at room temperature but undergo equilibration on heating. In *o*-dichlorobenzene, the process is first order in Cl^- and requires the presence of free picoline to prevent decomposition (*365*). In the solid state both forms of μ-oxo pyridine derivatives have small magnetic moments of ~0.9–1.3 BM and ν_{asym}(TcOTc) at 726–698 cm^{-1} in the IR spectra. In the electronic spectra three relatively narrow intervalence CT bands appear at about 10,000 cm^{-1} for both forms. X-ray photoelectron spectroscopic analysis indicates that the Tc ions differ by no more than a single oxidation state in both forms (*366*). The complexes $[\{TcX(bpy)_2\}_2(\mu\text{-}O)]X_2\cdot bpy$ (X = Cl, Br) and $[\{TcCl(phen)_2\}_2(\mu\text{-}O)]Cl_2\cdot 4H_2O$ have been prepared and the crystal structures, determined (*367*). For these complexes the Tc–O–Tc bond angles of 171.6(9)°–173.0(3)° show a slight bending, whereas for **30** (asymmetric) the angle is 176.5(2)° (*366*) and for **31** (dissymmetric) the two independent molecules in the unit cell have angles of 175.7(9)° and 177.1(9)° (*364*).

Reduction of TcO_4^- in the presence of aminocarboxylic and carboxylic acids or substitution of $[TcX_6]^{2-}$ in aqueous solution leads to the formation of bis(μ-oxo) Tc(IV/IV) or Tc(III/IV) dimers. Structural and IR data are listed in Table I and the structure of the oxalato complex is shown in Fig. 10. The four-membered $Tc(\mu\text{-}O)_2Tc$ ring is near planar in all cases and the short Tc–Tc distances are consistent with a multiple

TABLE I

STRUCTURAL AND IR DATA FOR $Tc(\mu\text{-}O)_2Tc$ COMPLEXES

Complex	Tc—Tc (Å)	$Tc—O_{br}$ (Å) (av.)	Tc—O—Tc (°) (av.)	$\nu(TcO_2Tc)$ (IR, cm^{-1}; asym, sym)	Ref.
$K_4[\{Tc^{IV}(C_2O_4)_2\}_2(\mu\text{-}O)_2]\cdot 3H_2O$	2.361(1)	1.913(1)	75.7	730, 401	368
$[\{Tc^{IV}(edtaH_2)\}_2(\mu\text{-}O)_2]\cdot 5H_2O$	2.331	1.913	75.2	725, 404	369, 368
$Na_2[\{Tc^{IV}(nta)\}_2(\mu\text{-}O)_2]\cdot 6H_2O$	2.363(2)	1.919(2)	76.0(1)	715, 410	370, 368
$Ba_2[\{Tc^{III/IV}(tcta)\}_2(\mu\text{-}O)_2]ClO_4\cdot 9H_2O$ **(32)**	2.402(1)	1.936(7)	76.6(3)	734[a]	371

[a] Raman spectrum of sodium salt.

bond. The $edtaH_2$ complex is diamagnetic and extended Hückel calculations have suggested the partly antibonding $\sigma^2\pi^2\delta^{*2}$ configuration of a Tc–Tc single bond for the six metal d electrons, rather than the triply bonded $\sigma^2\pi^2\delta^2$ configuration (*369*). This suggestion has been questioned, and it has been noted that a Tc–Tc triple bond with the δ component weakened to such an extent that its contribution to the overall energy of the Tc–Tc bond is close to zero is consistent with the observed long bond distance (*42*). A characteristic feature of the electronic spectra of the Tc(IV/IV) dimers is an intense visible absorp-

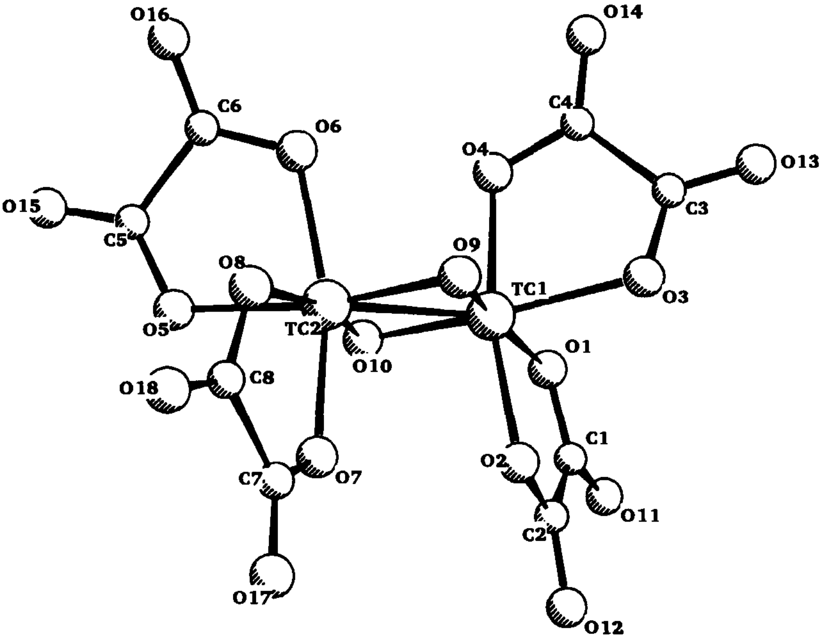


FIG. 10. The structure of the anion in $K_4[\{Tc(C_2O_4)_2\}_2(\mu\text{-}O)_2]\cdot 3H_2O$ (*368*).

tion at about 500 nm. In the IR spectra the asymmetric and symmetric oxygen stretches of the ring system occur at about 725 and 400 cm^{-1}, respectively. Treatment of a solution of $[Tc^{V}O(OCH_2CH_2O)(tcta)]^{2-}$ with BH_4^- yields, on heating, the deep-blue Tc(III/IV) dimeric anion $[\{Tc(tcta)\}_2(\mu\text{-}O)_2]^{3-}$ (**32**) (*371*). The EPR spectrum of the solid shows a broad signal with the hyperfine splitting expected for a single electron coupled equally between two Tc atoms with spin $\frac{9}{2}$. On oxidation by $K_2S_2O_8$, blue **32** is converted to the pink Tc(IV/IV) dimer $[\{Tc(tcta)\}_2(\mu\text{-}O)_2]^{2-}$ and the reaction is reversed on treatment of the pink dimer with hydrazine. For **32**, the Tc–Tc bond distance of 2.402(1) Å is distinctly longer than the Tc–Tc distances of the Tc(IV/IV) dimers in Table I. A polynuclear Tc(IV) citrate complex of uncertain structure has been prepared by substitution of $[TcBr_6]^{2-}$ (*372*).

3. *Phosphonato Complexes*

Of great clinical importance as skeletal imaging agents are the ^{99m}Tc complexes of the phosphonates $CH_2(PO_3H_2)_2$ ($mdpH_4$) and RC(OH)-$(PO_3H_2)_2$ (R = H, Me), which localize in bone due to the affinity of the coordinated diphosphonate for calcium in actively growing bone. The radiopharmaceutical preparations appear to be a mixture of oligomers and polymers with the oxidation state of ^{99m}Tc uncertain but thought to be +4 (*12, 19*). The crystal structure of the polymeric $\{[Li(OH_2)_3][Tc(OH)(mdp)]\cdot\frac{1}{3}H_2O\}_n$, prepared by substitution of $(NH_4)_2[TcBr_6]$ with $mdpH_4$, is shown in Fig. 11. The structure consists of infinite polymeric

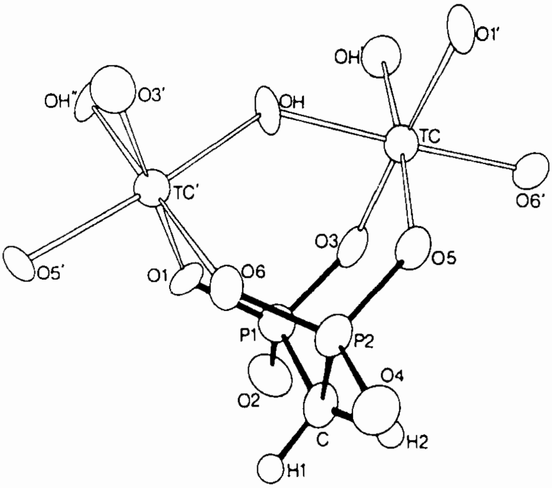


FIG. 11. A portion of the $\{[Li(OH_2)_3][Tc(OH)(mdp)]\cdot\frac{1}{3}H_2O\}_n$ structure (reproduced from Ref. *373* with permission).

chains, with each mdp ligand bridging two symmetry-related Tc atoms and each Tc atom bound to two symmetry-related mdp ligands. The bridging oxo ligand appears to be in the hydroxy form, consistent with a Tc(IV) oxidation state (*373*). An EXAFS study of the Tc-mdp form of the ^{99m}Tc-mdp bone seeking complex in solution indicates a Tc(IV) tetrameric structure, with each Tc having 1.5 ± 0.5 Tc neighbors and surrounded by six singly-bonded oxygen atoms from water or the diphosphonato ligands, and the absence of Tc═O groups (*374*). Raman spectroscopy of Tc-MeC(OH)$(PO_3)_2$ prepared by BH_4^- reduction, however, indicates the presence of Tc═O and O═Tc═O cores (*375*) and thus of Tc(V) components in this preparation.

D. COMPLEXES WITH SCHIFF BASE AND OTHER NITROGEN LIGANDS

A number of Schiff base complexes have been prepared by substitution of $[TcCl_6]^{2-}$ or $[TcCl_4(PPh_3)_2]$ (*376, 269*). The reaction of $TcCl_4$ with bpy yields $[TcCl_4(bpy)]$ (*377*) and thermolysis of $(pyH)_2[TcCl_6]]$ yields $[TcCl_4(py)_2]$, which has been suggested to be the *cis*-isomer on the basis of the far IR spectrum (*378*). Orange-colored $[TcCl_3\{HB(pz)_3\}]$ is formed by the reaction of $[Tc^VOCl_4]^-/KHB(pz)_3/HCl$ and has a magnetic moment of 3.7 BM, consistent with a d^3 configuration (*379*). The reaction of $[TcOCl_4]^-$ with aromatic amines and dppe in refluxing alcohols gives the purple air-stable imido complexes $[TcCl(NAr)(dppe)_2]^+$ in good yield. Paramagnetism is evident in the broadened NMR spectra. The crystal structure of *trans*-$[TcCl(NNMe_2)(dppe)_2]PF_6$ shows that the hydrazido(2-) ligand is bonded as a linear four-electron donor (*278*).

E. COMPLEXES WITH PHOSPHINE AND ARSINE LIGANDS

The emerald-green air-stable *trans*-$[TcCl_4(PPh_3)_2]$ is readily prepared in high yield by the reduction of TcO_4^- with HCl/PPh_3 (*280*). If the reaction is performed in acetone at room temperature, then the salts $R[TcCl_5(PPh_3)]$ (R = PPh_3H, orange; $AsPh_4$, yellow) are formed (*380*). In the case of the more highly reducing PMe_2Ph and PEt_2Ph, *trans*-$[TcCl_4L_2]$ is formed if the Tc:L ratio is 1:5, and *mer*-$[Tc^{III}Cl_3L_3]$ is formed at a 1:15 ratio. On reflux in CCl_4, the Tc(III) complexes are oxidized to $[TcCl_4L_2]$ (*280*). A number of bromo analogs and $[TcCl_4(AsPh_3)_2]$ have been reported (*192, 280, 377*). In all reactions of TcO_4^- with monodentate phosphines the intermediate oxidation states Tc(VI) and Tc(V) are not observed, whereas bidentate phosphines, in general, favor reduction to Tc(III). The magnetic moments of 3.4–3.8 BM for $[Tc^{IV}X_4L_2]$ are consistent with an octahedral d^3 environment

(*280*). Crystal structures have been reported for $(Ph_3PCMe_2CH_2CO\text{-}Me)[TcCl_5(PPh_3)]$ (*380*), $(PEt_3H)[TcCl_5(PEt_3)]$ (*381*), and *trans*-$[TcCl_4L_2]$ [L = PMe_3 (*382*), PMe_2Ph (*383*), $PMePh_2$, PEt_3 (*381*)]. The *trans*-$[TcCl_4(PPh_3)_2]$ complex is a useful starting material for Tc(IV) and Tc(III) chemistry. On heating in coordinating solvents, such as dmso or pyridine, the PPh_3 ligands are displaced to yield $[TcCl_4L_2]$ (L = dmso, py), whereas reaction with pyridine/PPh_3 results in reduction to $[TcCl_3(py)_3]$ (*384*).

F. COMPLEXES WITH SULFUR LIGANDS

The reaction of $[TcOCl_4]^-$ with a dithiocarbamate $(S_2CNC_4H_8O^-)$ results in loss of the oxo group to give neutral $[Tc(S_2CNC_4H_8O)_4]\cdot H_2O$ (*385*), and reaction with 2-mercaptopyrimidine (mcpH) gives the structurally characterized $NBu_4[TcCl_4(mcp)]$ (*386*). A cationic complex is the blue-violet paramagnetic $[Tc(S_2CNEt_2)_3(PMe_2Ph)]PF_6$, formed by air oxidation of $[Tc^{III}(S_2CNEt_2)_3(PMe_2Ph)]$ in the presence of HCl (*387, 388*). Substitution of $[TcBr_6]^{2-}$ with $Na_2(mnt)$ in ethanol yields $(AsPh_4)_2[Tc^{IV}(mnt)_3]$. The crystal structure shows that Tc is coordinated to six S atoms with chelate twist angles of 32.6°–39.0°, which are intermediate between the value of 60° for a regular octahedron and 0° for a trigonal prism (*389*). Reduction of TcO_4^- by 1,2-benzenedithiol /HCl yields on standing the wine-red dimer $[Tc_2(bdt)_4]$ (*390, 391*). The crystal structure (Fig. 12) shows each Tc atom coordinated to a trigonal prismatic array

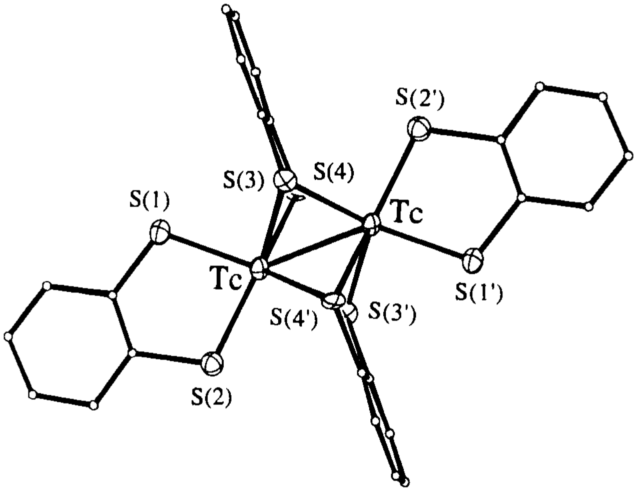


FIG. 12. The structure of $[Tc_2(bdt)_4]$ (*391*).

of six S atoms with a shared quadrilateral face and with the eight S atoms delineating a rhombohedral prism. An arrangement in which two bdt ligands span the rhombohedral faces and two span opposite edges is found rather than a "paddle wheel" with the bdt ligands spanning the four vertical edges. The Tc–Tc distance of 2.591(3) Å and the d^3–d^3 configuration would seem to indicate a multiple bond, but any assignment needs to consider the noninnocent nature of the dithiolene ligands (*391*). The dark-green dimer $[Tc_2(edt)_2(SCHCHS)_2]$ has been isolated from the reaction of 1,2-ethanedithiol with $[TcCl_6]^{2-}$ (*379*). The structure is similar to that of $[Tc_2(bdt)_4]$, with a Tc–Tc distance of 2.610(3) Å. A novel feature is the dehydrogenation of $(SCH_2CH_2S)^{2-}$ to $(SCHCHS)^{2-}$ to give a mixed dithiolate–dithiolene coordination, with each dithiolene ligand coordinated to one Tc atom only and each S atom of the dithiolato ligands coordinated to both Tc atoms.

VIII. Technetium(V)

The chemistry of this oxidation state is dominated by complexes containing oxygen and nitrogen multiple bonds. This is a reflection of both the tendency of high oxidation states to induce deprotonation of aqua or amine ligands and the ability of good π-donors such as O^2 and N^{3-} to stabilize high oxidation states. The greater ease of reduction of Tc in comparison with Re is seen for Tc in the absence of analogs of the large number of $[ReO]^{3+}$ complexes with monodentate phosphines of the type $[ReOX_3(PR_3)_2]$ (*189*). Otherwise, the chemistry of Tc(V) resembles that of Re(V), with the predominance of complexes based on the $[TcO]^{3+}$, $[TcO_2]^+$, $[Tc_2O_3]^{4+}$, and $[TcN]^{2+}$ cores. Tc(V) complexes not containing a multiply bonded oxygen or nitrogen ligand are relatively few. The only binary halide is the yellow TcF_5 (m.p., 50°C), formed as a by-product of the direct fluorination of Tc metal (*392*). The complex fluorides $M[TcF_6]$ (M = Na, K, Rb, Cs) have been prepared by the reduction of TcF_6 in the presence of MCl and IF_5 and the rhombohedral unit cell parameters determined (*393*). In $NO[TcF_6]$, the presence of the free NO^+ cation results in an IR absorption at 2315 cm^{-1} (*394*).

A. MONONUCLEAR $[TcO]^{3+}$ COMPLEXES

The structure and chemistry of the square–pyramidal five-coordinate and pseudo-octahedral six-coordinate $[Tc^VO]^{3+}$ complexes are dominated by the strong tetragonal distortion induced by the multiply bonded oxo ligand. The d orbital energy levels in C_{4v} symmetry are in the order b_2 (d_{xy}) < e (d_{xz}, d_{yz}) < b_1 ($d_{x^2-y^2}$) < a_1 (d_{z^2}) (*35, 395*). The d^2 electrons are paired in the low-energy, essentially nonbonding, b_2 (d_{xy}) orbital, resulting in complexes with a $^1A_1$ ground state, which are either diamagnetic or show only temperature-independent paramagnetism (*150*). The $[TcO]^{3+}$ core may thus be regarded as a "closed shell" electronic configuration and complexes expected to be relatively kinetically inert to substitution, but this is dependent on the nature of the coordinated ligands (*35*). The TcO bond is formally triple with one σ and two π (O p_x, p_y/Tc d_{xz}, d_{yz}) components, but because of the unfavorable charge distribution in $Tc^{-}{\equiv}O^{+}$, the bonding will be intermediate between triple and double. The strong *trans* influence of the oxo ligand results in the *trans* ligand being only weakly bound and often absent and the Tc atom being raised above the square basal or equatorial ligand plane. In complexes in which the *trans* ligand is present, the $Tc-L_{trans}$ distance may be 0.1–0.2 Å longer than that for the same ligand in an equatorial position. An aqua cation of the type $[TcO(OH_2)_n]^{3+}$, or of polymeric forms, is not found because $[TcO]^{3+}$ is unstable to disproportionation to Tc(IV) and TcO_4^- (*35*). When the $[TcO]^{3+}$ core is stabilized by suitable ligands, kinetically stable and substitution inert complexes result. A general route to $[TcO]^{3+}$ complexes is by substitution of $[TcOX_4]^-$ (X = Cl, Br) (*35, 396*). The $NBu_4[TcOCl_4]$ salt is conveniently prepared in 99% yield from TcO_4^-/HCl and is readily soluble in polar organic solvents such as methanol, acetone, or MeCN (*397*). An alternative method is by the reduction of TcO_4^- in the presence of the ligand(s). A variety of reducing agents has been used, of which sodium dithionite is convenient and popular, but reduction to a lower oxidation state may also occur. The *in vitro* stability of $[TcO]^{3+}$ complexes has been related to the solid angle factor sum of the coordinating atoms (*398*).

1. *Cyano and Thiocyanato Complexes*

Green-yellow $K_2[Tc^{V}O(CN)_5]\cdot 4H_2O$ is formed in low yield from the reaction of $TcO_2\cdot nH_2O$ with KCN or from aerobic crystallizations of $K_4[Tc^{III}(CN)_7]\cdot 2H_2O$. In the IR spectrum ν(TcO) occurs at the rather low value of 910 cm^{-1} and three ν(CN) absorptions are observed at 2095, 2080, and 2035 cm^{-1}, which have been assigned to the $2A_1 + E$ modes in C_{4v} symmetry. The lilac $(NBu_4)_2$*trans*-$[TcO(OMe)(CN)_4]$ is formed on substitution of $NBu_4[TcOCl_4]$ with CN^- in MeOH [ν(TcO) at 932 cm^{-1}] (*229*), and (NMe_4)*trans*-$[TcO(OH_2)(CN)_4]\cdot 2H_2O$ has been isolated from the protonation of $[TcO_2(CN)_4]^{3-}$ (*399*). The strong *trans* labilizing effect of the oxo ligand is apparent in the rapid rate of exchange of the *trans* water for NCS^-, for which the forward rate constant is 22 M^{-1} sec^{-1} at 25°C. The crystal structure of $(bpyH)_2$*trans*-[TcO-

$(NCS)(CN)_4]$ shows *N*-bonded thiocyanate and a short Tc=O bond distance of 1.612(8) Å (*399*). Substitution of $[TcOCl_4]^-$ with NCS^- gives a high yield of the bright-red $(AsPh_4)_2[TcO(NCS)_5]$. In the presence of NCS^- this complex is easily reduced to mixtures of $[Tc^{IV}(NCS)_6]^{2-}$ and $[Tc^{III}(NCS)_6]^{3-}$ (*400*).

2. *Halide Complexes*

When TcO_4^- is added to concentrated HCl at room temperature, a yellow solution, thought to contain *fac*-$[Tc^{VII}O_3Cl_3]^{2-}$, is formed and is then converted to an olive-green color on reduction to $[Tc^{V}OCl_4]^-$ (*35*). If the solution is heated, the kinetically controlled product $[TcOCl_4]^-$ undergoes further reduction to the yellow thermodynamic product $[Tc^{IV}Cl_6]^{2-}$. These steps are described by the equations

$$TcO_4^- + 3HCl \rightleftharpoons [TcO_3Cl_3]^{2-} + H_3O^+$$

$$[TcO_3Cl_3]^{2-} + 3HCl + H_3O^+ \longrightarrow [TcOCl_4]^- + 3H_2O + Cl_2$$

$$[TcOCl_4]^- + 3HCl \longrightarrow [TcCl_6]^{2-} + H_3O^+ + 1/2\,Cl_2.$$

With concentrated HBr as the reductant, the preparation of $[TcOBr_4]^-$ is performed at, or below, 0°C to avoid reduction to $[TcBr_6]^{2-}$ (*396*). The reduction of $[TcOBr_{4/5}]^{-/2-}$ in 8.7 *M* HBr proceeds by a combination of first- and zero-order reactions (*401*). The product isolated on addition of cations to solutions of $[TcOX_4]^-$ (X = Cl, Br) in HX is dependent on the nature of the cation. Large cations such as NBu_4^+ result in the precipitation of the five-coordinate $R[TcOX_4]$ (*402*); small cations such as NH_4^+, K^+, or Cs^+ result in the six-coordinate $M_2[TcOX_5]$ (*403, 404*), and with NEt_4^+ the *trans*-aqua complex $NEt_4[TcO(OH_2)Br_4]$ has been isolated (*405*). These results show that the *trans* ligand is labile and indicate that crystal packing forces determine the composition of the solid form. In aqueous HX solution the most likely form is $[TcO(OH_2)X_4]^-$ (but is generally written simply as $[TcOCl_4]^-$). For $[TcOCl_4]^-$ in 12 *M* HCl the equilibrium

$$trans\text{-}[TcO(OH_2)Cl_4]^- + Cl^- \rightleftharpoons [TcOCl_5]^{2-} + H_2O$$

has been demonstrated by Raman spectroscopy and $[TcO(OH_2)Cl_4]^-$ was found to predominate by a factor of about 60. In CH_2Cl_2 solution the equilibrium constant is ca. 400 times larger, indicating the equilibrium

$$[TcOCl_4]^- + Cl^- \rightleftharpoons [TcOCl_5]^{2-},$$

with the *trans* position in $[TcOCl_4]^-$ either vacant or containing an only weakly interacting CH_2Cl_2 molecule (*404*). In water, $[TcOCl_4]^-$ disproportionates to $TcO_2 \cdot nH_2O$ and TcO_4^- in the reaction $3Tc(V) \rightarrow 2Tc(IV) + Tc(VII)$, whereas in 1 *M* *p*-toluenesulfonic acid $Cs_2[TcOCl_5]$ dissolves to give a brown Tc(IV) cation and TcO_4^- (*35, 406*). This disproportionation is very slow in >2 *M* HCl solutions (*35*). Salts such as $NBu_4[TcOX_4]$ (X = Cl, Br) may also be prepared directly from $NBu_4[TcO_4]$ and HX (*407*) and $NBu_4[TcOI_4]$ by ligand exchange of $NBu_4[TcOCl_4]$ with NaI in acetone (*408*). Structural and ν(TcO) data are listed in Table II. The first structural characterization of the $[TcOCl_4]^-$ anion in the $[N(PPh_3)_2]^+$ salt showed only approximate C_{2v} symmetry (*402*). This distortion is a consequence of the presence of the large cation in the crystal because in $AsPh_4[TcOX_4]$ (X = Cl, Br) the anions possess ideal C_{4v} symmetry (*409, 410*) and C_{4v} symmetry for the anions is also indicated by the vibrational spectra of $NBu_4[TcOX_4]$ (X = Cl, Br, I) (*407, 408*). In the square–pyramidal five-coordinate $[TcOX_4]^-$ complexes, the oxo ligand is in the apical position and the Tc=O bond distance is rather short at 1.60–1.62 Å. Structurally, the square–pyramidal five-coordinate and octahedral six-coordinate complex anions are dominated by the *trans* influence of the oxo ligand, which results in the displacement of the Tc atom above the square basal or equatorial plane and, in six-coordinate complexes, the weakening of the bond *trans* to the oxo ligand. This *trans* bond weakening is indicated by the long $Tc{-}OH_2$ bond distance of 2.317(9) Å in (NEt_4)*trans*-$[TcO(OH_2)Br_4]$ (*405*). In the five-coordinate complexes, the *trans* influence may be regarded as sufficiently large to prevent the bonding of a *trans* ligand.

The TcO IR stretching frequency is sensitive to the presence and nature of the *trans* ligand. For $[TcOX_4]^-$ (X = Cl, Br, I) this absorption

TABLE II

STRUCTURAL AND IR DATA FOR $[TcO]^{3+}$ HALIDE COMPLEXES

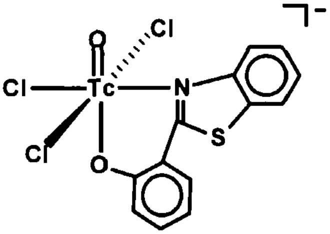
Complex	Tc=O (Å)	Tc—X (Å)	O—Tc—X (°)	δTcX_4[a] (Å)	ν(TcO) (cm^{-1})	Ref.
$\{N(PPh_3)_2\}[TcOCl_4]$	1.610(4)	2.305 av.	103.2, 110.4	0.66	1016	402
$AsPh_4[TcOCl_4]$	1.593(8)	2.309(2)	106.8	0.67	1025	409
$AsPh_4[TcOBr_4]$	1.613(9)	2.460(1)	106.6	0.70	—	410
$NEt_4[TcO(OH_2)Br_4]$	1.618(9)	2.507(1) av.	99.5, 97.6	0.37	1000	405
$Cs_2[TcOCl_5]$[b]	1.65	2.36_{cis} 2.50_{trans}			954	404
$Cs_2[TcOBr_5]$[b]	1.66	2.54_{cis} 2.74_{trans}			952	404

[a] Displacement of Tc above the square basal or equatorial plane.

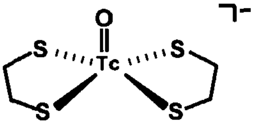
[b] Bond distances from solid-state EXAFS spectra.

occurs at 1025–1000 cm^{-1}, whereas the presence of *trans* halide in $Cs_2[TcOX_5]$ (X = Cl, Br) results in a substantial lowering in energy to 954 cm^{-1} (*404*). The value of 992 cm^{-1} reported for $M_2[TcOCl_5]$ (M = NH_4, K) in the solid state, however, indicates that the nature of the cation is important (*411*). Normal coordinate analysis of $NBu_4[TcOX_4]$ results in force constants of 8.41, 8.39, and 8.04 mdyn $Å^{-1}$ for X = Cl, Br, and I, respectively, (*412*). These values, when compared with 8.61 and 8.55 mdyn $Å^{-1}$ for Ru≡N in $AsPh_4[RuNX_4]$ (X = Cl, Br) (*413*), indicate considerable triple bond character for $[TcO]^{3+}$. A bond order of 2.55–2.59 has been calculated for $M_2[TcOCl_5]$ (*414*) and the value will be higher for $[TcOX_4]^-$. The $NBu_4[TcOX_4]$ (X = Cl, Br, I) and $M_2[TcOCl_5]$ (M = NH_4, K) salts are diamagnetic at 80–300 K, which is consistent with an $^1A_1$ (b_2^2) electronic ground state (*150, 395*). Three d–d bands in the electronic spectrum of $(NH_4)_2[TcOCl_5]$ in HCl at 10,700 (ε = 18), 16,700 (6), and 20,600 (24) cm^{-1} have been assigned to ^1E (b_2e) $\leftarrow$ $^1A_1$, $^1A_2$ (b_2b_1) $\leftarrow$ $^1A_1$, and $^1B_2$ (b_2a_1) $\leftarrow$ $^1A_1$ transitions, respectively (*414*). Recent L-edge spectra of $[MoO]^{3+}$ complexes, however, show that the assignment of $^1B_2 \leftarrow {}^1A_1$ for the 20,600-cm^{-1} peak in $[TcOCl_5]^{2-}$ is most likely incorrect and that this transition is more likely $d_{xy} \rightarrow d_{x^2-y^2}$ in nature (*415*).

Brown, thermally stable $TcOCl_3$ and grey-black $TcOBr_3$ have been prepared by chlorination or bromination of TcO_2. The chloro compound is very readily hydrolyzed by water to $TcO_2{\cdot}nH_2O$ and TcO_4^- in the ratio 2:1 (*416*). Water-sensitive $[TcOX_3(bpy)]$ (X = Cl, Br), $[TcOCl_3(phen)]{\cdot}H_2O$ and $[TcOCl_2(OEt)(bpy)]$ are prepared by substitution of $[TcOX_4]^-$ in ethanol/HX. The ν(TcO) IR absorptions of 910–850 cm^{-1} for $[TcOX_3L]$ and 922 cm^{-1} for the ethoxy complex indicate a somewhat lower TcO bond order than that for $[TcOX_4]^-$ or $[TcOX_5]^{2-}$ (*417*). Another example is $[TcOCl_3(terpy)]$, for which the terpy ligand is thought to be bidentate (*418*). Interesting related complexes are $(AsPh_4)$*mer*-$[TcOX_3(hbt)]$ (X = Cl, Br), prepared by substitution of $[TcOX_4]^-$ [ν(TcO) at 945 cm^{-1}, X = Cl; 940 cm^{-1}, X = Br]. The structure



(33)



(34)

of the chloro complex (**33**) shows a Tc=O bond distance of 1.650(6) Å and a *trans* OTc–O_{phenolic} distance of 1.948(4) Å (*419*).

3. *Complexes Based on the TcO{O_4}, TcO{S_4}, TcO{$O_{4-n}S_n$}, and TcO{Se_4} Cores*

Square–pyramidal complexes of the type $[TcOL_4]^-$, where L is an O, S, or Se ligand, are readily prepared either by substitution of $[TcOCl_4]^-$ or by the reduction of TcO_4^- in the presence of the ligand. A large number of complexes have been reported, mainly with bidentate ligands. Structural data and ν(TcO) values are summarized for representative complexes in Table III. General features are square–pyramidal geometry with the oxo ligand in the apical position, e.g., **34**, a Tc=O bond distance of 1.63–1.67 Å, and a considerable displacement of Tc by 0.70–0.88 Å above the square basal plane. The anionic ligands effectively neutralize the positive charge on $[TcO]^{3+}$ and the position *trans* to the oxo ligand is usually vacant.

The TcO{O_4} complexes such as M[TcO(OCH_2CH_2O)$_2$] (M = Na, NBu_4) are relatively weak and hydrolyze in the absence of excess diol (*420, 433*). The catecholate complex $[TcO(O_2C_6H_4)_2]^-$ is, however, more stable and may be prepared by the addition of a stoichiometric amount of

TABLE III

STRUCTURAL AND IR DATA FOR $[TcO]^{3+}$ COMPLEXES WITH O, S, OR Se LIGANDS

Complex	TcO (Å)	Tc—L (Å) (av.)	δsbp[a] (Å)	ν(TcO) (IR, cm^{-1})	Ref.
TcO{O_4}					
$NBu_4[TcO(o\text{-}O_2C_6H_4)_2]$	1.648(5)	1.957(3)	0.701	970	420
$NBu_4[TcO(o\text{-}O_2C_6H_3NO_2)_2]$	1.634(4)	1.966	0.695	983	421
$NBu_4[TcO(o\text{-}O_2C_6Cl_4)_2]$	1.646(5)	1.955		969	422
$(AsPh_4)_2[TcO(ox)_2(Hox)]\cdot 3H_2O$	1.640(6)	2.016*cis*	0.25	985	423
TcO{S_4}					
$NBu_4[TcO(SAr)_4]$[b]	1.659(11)	2.380	0.846	940	424
$AsPh_4[TcO(edt)_2]$	1.64(1)	2.300	0.761		425
$NBu_4[TcO(SCH_2COS)_2]$	1.672(8)	2.320(3)	0.791	950	426
$AsPh_4[TcO(SCOCOS)_2]$	1.646(4)	2.329(1)	0.759		427
$AsPh_4[TcO(mnt)_2]$	1.655(6)	2.315(1)	0.742	950	428
$NBu_4[TcOL_2]$[c]	1.672(6)	2.316	0.78	940	429
$AsPh_4[TcO(bdt)_2]$	1.658(5)	2.315(2)	0.732	938	430
TcO{S_2O_2}					
$AsPh_4[TcO(SCH_2CH_2O)_2]$	1.662(5)	O 1.950(4) S 2.291(2)	0.720	948	431
TcO{Se_4}					
$NEt_4[TcO\{Se_2CC(CN)_2\}_2]$	1.67(2)	2.471(4)	0.88	965	432

[a] Displacement of Tc above the square basal plane.

[b] Ar = 2,4,6-trimethylphenyl.

[c] L = SCH(COOMe)CH(COOMe)S.

catechol to $[TcOCl_4]^-$ *(420)*. Substitution of $[TcOCl_4]^-$ with oxalic acid yields pale-green crystals of the $AsPh_4^+$ salt of an oxalato complex with $\nu(TcO)$ at 963 cm^{-1}. Recrystallization from acetone–water containing oxalic acid results in the isolation of emerald-green $(AsPh_4)_2[TcO(ox)_2(Hox)]\cdot 3H_2O$ (**35**) with $\nu(TcO)$ at 985 cm^{-1}. The structure (Fig. 13) is unusual, with a monodentate protonated oxalate coordinated *cis* to the oxo ligand *(423)*. Also unusual is the absence of a significant *trans* influence of the oxo ligand, with the oxalate $Tc–O_{trans}$ distance of 2.069(6) Å being similar to 2.016 Å (av.) for $Tc–O_{cis}$. The low susceptibility of oxalate to the *trans* influence has been noted for $[MoO]^{3+}$ complexes but the reason is unclear *(434)*. It is likely that the form in solution is the *trans*-aqua complex and that the crystallization of **35** is the result of crystal packing effects. The gluconate and heptagluconate complexes are of uncertain structure but thought to be $[TcOL_2]^-$ from IR and Raman evidence *(19)*. The ^{99m}Tc complexes, and ^{99m}Tc-diethylenetriaminepentaacetate [of unknown structure but the oxidation state is probably Tc(V)], are useful as kidney and brain imaging agents *(19)*.

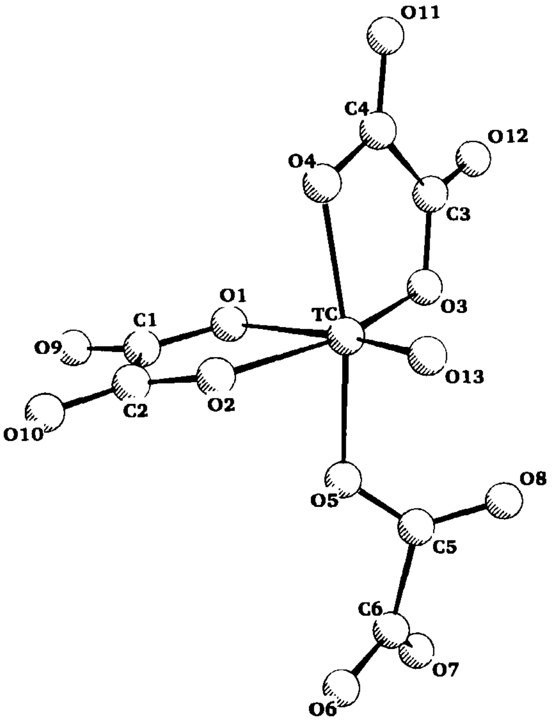


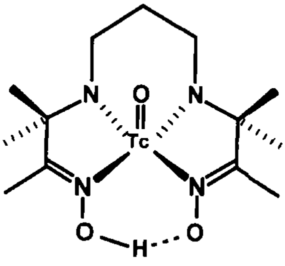
FIG. 13. The structure of the anion in $(AsPh_4)_2[TcO(ox)_2(Hox)]\cdot 3H_2O$ (**35**) *(423)*.

The preparation of a variety of [TcO(β-diketonate)$_2$Cl] complexes has been reported (*435*).

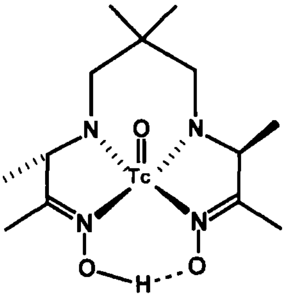
Pertechnetate is reduced by thiols in the presence of acid in a first-order process in TcO_4^- and the thiol (*436, 437*). The kinetic data for a series of *p*-substituted benzenethiols follow the Hammett relationship with a decrease in rate by more electron withdrawing substituents (*438*). TcO{S_4} and related complexes are generally prepared from TcO_4^- by the use of a reducing agent such as $S_2O_4^{2-}$ or by ligand exchange (*439–443*). There is now a considerable variety of TcO{S_4} complexes; structurally characterized examples are listed in Table III. Four thiolato ligands effectively satisfy the charge on the $[TcO]^{3+}$ core to give square–pyramidal complexes that show little or no tendency to bind a sixth *trans* ligand. In general, these complexes are highly stable and substitution inert; for instance, $[TcO(edt)_2]^-$ is unaffected by PPh_3 in refluxing MeCN. Electrochemically, there is no tendency to oxidation to Tc(VI) (*441*). The magnetic moments of a representative series have been shown to be field-strength dependent and lie in the region 0.1–1.5 BM. The frequency of ν(TcO) is ~20 cm^{-1} lower than that in the $[ReO]^{3+}$ analog, and an LMCT band at 330–450 nm in the electronic spectra of TcO{S_4} complexes is at lower energy than that for Re (*441*). An interesting complex is $NBu_4[TcO(SCH_2COS)_2]$, prepared by use of commercial $HSCH_2COOH$, indicating the presence of a significant content of $HSCH_2COSH$ as an impurity (*441*). The complex $NBu_4[TcO(S_4Mo)_2]$ shows a low ν(TcO) at 895 cm^{-1} and undergoes reduction by PPh_3 to give a product formulated as $[Tc^{IV}(PPh_3)_2(S_4Mo)_2(H_2O)]$, but which is possibly a hydrate (*444*). Reduction of TcO_4^- by tetramethylthiourea/HCl yields $[TcO(tmtu)_4](PF_6)_3$, a labile complex useful for ligand-exchange reactions (*445*). From the reaction of $[TcO(tmtu)_4](PF_6)_3$ with dppe in dmf solution one of the products isolated has been shown by crystallography to be $[TcO(tmtu)_2(Me_2NCS_2)](PF_6)_2$, in which the dithiocarbamato ligand is presumably derived from tetramethylthiourea by sulfur transfer and loss of $NHMe_2$ (*196*). A radiopharmaceutical for tumor imaging is $[^{99m}TcO(dmsa)_2]^-$ ($dmsaH_2$ = *meso*-dimercaptosuccinic acid) (*446*). The ^{99m}Tc complex has been shown from ^1H NMR and chromatographic studies with $[TcO(dmsa)_2]^-$ and the dimethyl ester to be a mixture of three stereoisomers (*446, 447*). The crystal structure of the ester $NEt_4[TcO\{SCH(COOMe)CH(COOMe)S\}_2]$ has shown the product isolated in 21% yield to be the *syn-endo* form (*429*). The important ^{99m}Tc-dmsa renal agent is thought to contain Tc in a lower oxidation state, possibly Tc(III), but the structure is unknown (*19, 446*). The potential for different chemical behavior at the ^{99m}Tc and ^{99}Tc concentration levels is illustrated by the mnt ligand, for which the product at macroscopic concentration is $[Tc^{V}O(mnt)_2]^-$, whereas the product at the ^{99m}Tc level is $[^{99m}Tc^{IV}(mnt)_3]^{2-}$ (*448*). The preparations of a variety of $[TcO]^{3+}$ complexes with $^{-}S(CH_2)_2X(CH_2)_2S^{-}$ (X = O, S)/ ^{-}SAr ligands (*449–450*), of TcO-metallothioneins (*451*), and of the three possible $NEt_4[TcO\{XYC{=}C(CN)_2\}_2]$ (X,Y = S or Se) complexes (*452*) have been reported. The oxo ligand in $[TcO\{S(CH_2)_2O(CH_2)_2S\}(SAr)]$ is removed by PPh_3 at room temperature (*450*).

4. *Complexes Based on* $TcO\{N_4\}$, $TcO\{N_{4-n}O_n\}$, *and* $TcO\{N_2P_2\}$ *Cores*

The discovery that the neutral, lipophilic ^{99m}TcO complex **36**, prepared by the reduction of TcO_4^- in the presence of the tetradentate propyleneamine oxime ligand, is able to cross the blood–brain barrier in both directions has stimulated much work in this area (*19*).



(**36**)

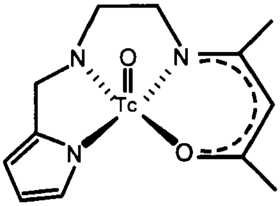


(**37**) (*d, l*)

A large number of variously substituted analogs were prepared and the *d,l* stereoisomer (**37**) was found to be sufficiently retained in the brain due to transformation to a more hydrophilic species, which is then unable to diffuse out of the brain. The ^{99m}Tc complex (**37**) is now an important radiopharmaceutical for cerebral perfusion imaging and the evaluation of stroke (*19*). Crystal structures of **36** and *meso*-**37** and a variety of analogs have been reported (*453–455*).

The $[TcO]^{3+}$ core is sufficiently electron deficient to deprotonate secondary aliphatic amines, and in **36** and analogs neutrality is achieved by loss of both amine protons and one oxime proton, with the remaining oxime proton being intramolecularly hydrogen bonded. Features of the structures are Tc═O bond distances in the range 1.670(4)–1.682(5) Å and the displacement of Tc above the N_4 plane, which for **36** is 0.678(1) Å. Also, for **36** the distance between Tc and the deprotonated N (imino) atoms of 1.913 Å (av.) is considerably shorter than the Tc–N(oxime) distance of 2.090 Å (av.) (*453*). The $\nu(TcO)$ IR absorption in the rather low range of 934–908 cm^{-1} is consistent with the long TcO distances. A study of analogs of **36** with the aliphatic $N(CH_2)_3N$ chain replaced by two, four, and five carbons has shown that for the four- and five-carbon chains both the five-coordinate monooxo and the six-coordinate *trans*-$[TcO_2]^+$ complexes are formed (*455*). Reduction of TcO_4^-/1,2-diaminobenzene ($pdaH_2$) by $S_2O_4^{2-}$ allows the isolation of diamagnetic $NBu_4[TcO(pda)_2]$ (*456*). A single ν(NH) confirms the deprotonated form of the ligands and the low ν(TcO) at 891 cm^{-1} is consistent with coordination by four $^-$NH groups with Tc–N 1.98 Å. The Tc=O distance is 1.668(7) Å and Tc lies 0.67 Å above the N_4 plane. Another complex of this group is [TcO(octaethylporphyrinate)]OAc (*457*).

A variety of five- and six-coordinate structurally characterized complexes with mixed $TcO\{N_{4-n}O_n\}$ and related cores have been reported. The only seven-coordinate complex is $[TcO(edta)]^-$, prepared by the reaction of $[TcOCl_4]^-$ with $edtaH_4$ in anhydrous dmso. A crystal structure of the barium salt shows distorted pentagonal–bipyramidal geometry, with the oxo group and the two N atoms bound equatorially (*458*). The six-coordinate Schiff-base complex *trans*-$[TcO(OH_2)\{(acac)_2en\}]X$ has distorted octahedral geometry, a Tc=O bond distance of 1.648(2) Å, and Tc 0.39 Å above the N_2O_2 plane. As expected, the *trans* influence of the oxo ligand results in a long Tc–OH_2 bond distance of 2.282(2) Å. Similarly, in *trans*-$[TcO\{(sal)_2en\}Cl]$ Tc–Cl is long at 2.527(4) Å and Tc is displaced by ~0.27 Å (*459*). A structurally characterized six-coordinate 8-quinolinolate complex is [TcO(Ophsal)(quin)] (*460*). In the orange phenolic derivative $NBu_4[TcO(epa)]\cdot H_2O$ [$epaH_4$ = *N,N'*-ethylenebis(2-phenoxyacetamide)], both the amide and the phenolic groups are deprotonated and ν(TcO) occurs at 925 cm^{-1}. The average Tc–N distance is 1.977(6) Å and Tc lies 0.65 Å above the N_2O_2 plane (*461*).



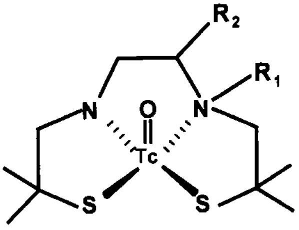
(38)

The novel neutral complex **38** is formed by substitution of $[TcO(OCH_2CH_2O)_2]^-$ or $[TcOCl_4]^-$ (*462, 463*). Triple deprotonation of the starting ligand includes the loss of an amine and pyrrolic proton. The ^{99m}Tc–**38** complex is undergoing clinical evaluation for efficacy in the detection and determination of the severity of stroke and illustrates the degree of ligand design undertaken to achieve the desired *in vivo* behavior. The Tc–$N_{pyrrole}$ bond distance of 1.993(4) Å is, as expected, rather longer than the Tc–N_{imino} distance of 1.897(4) Å. Other structurally characterized six-coordinated complexes are [TcOL] (L = ONNNO Schiff base) (*464*), the unusual [TcO(apa)], where apa represents a pentadentate ONNNO Schiff-base ligand derived from dehydroacetic acid (*465*), and [TcOL(sal)] [L = *N*-salicylidine-D-glucosamine(2-)] (*466*). The last complex precipitates from a methanol solution of the glucose derivative and $[TcOCl_4]^-$. The presence of salicylaldehyde in the product does not appear to be the result of hydrolysis of the Schiff base prior to coordination. The bidentate coordination of the salicylaldehyde(-1) anion is unusual. The preparation of a variety of complexes with heterocyclic *N,O* and other ligands (*467, 468*) and of salicylidine Schiff-base complexes with amino acids has been reported (*469*). Reaction of NBu_4TcO_4 with **25** (R = NH_2) under rigorously controlled conditions in ROH, to avoid further reduction to Tc(III), yields $[Tc^VO(OR)L_2]$ [R = Me, Et; L = **25**(1-)]. The crystal structure of the methoxy complex shows approximate octahedral geometry with an NNPP equatorial plane, a Tc=O bond distance of 1.700(8) Å, a Tc–OMe bond distance of 1.999(8) Å, and an O=Tc–OMe angle of 158.3(3)°. The *trans* alcoxy group accounts for the stability of these complexes and results in low ν(TcO) values of 878 (R = Me) and 857 cm^{-1} (R = Et) (*470*).

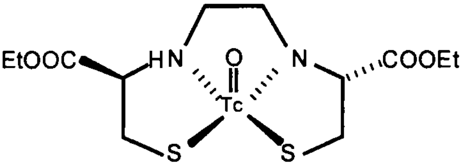
5. *Complexes Based on $TcO\{N_{4-n}S_n\}$ Cores*

The search for neutral, lipophilic ^{99m}Tc cerebral perfusion imaging agents has led to the intensive investigation of the chemistry of $[TcO]^{3+}$ with bisaminedithiolato (BAT) ligands (*17, 19*). The N_2S_2 coordination results in highly stable complexes in which neutrality is achieved by deprotonation of one of the amino groups. A common method of preparation is by the reduction of TcO_4^- with $S_2O_4^{2-}$ in the presence of the ligand.

If one of the amino groups is substituted, then *syn*/*anti* isomerism is possible. For **39** (R_1 = Me, R_2 = H), crystal structures of both isomers have been determined and the major product has been shown to be the *syn* form (with the methyl group pointing in the same direction as TcO). The Tc–N bond distance to the anionic nitrogen is 0.288(9) and 0.198(9) Å shorter in the *syn* and *anti* forms, respectively, than the corresponding Tc–NMe bond distance (*471*). In *syn*-**39** (R_1 = Et, R_2 = H), the Tc–N and Tc–NEt distances are 1.921(2) and 2.224(2) Å, respectively (*472*). A large number of variously imaginatively substituted BAT ligands have been synthesized and the ^{99}Tc and ^{99m}Tc complexes, prepared (*473–478*). In general, ^1H and ^{13}C NMR are useful for stereo-



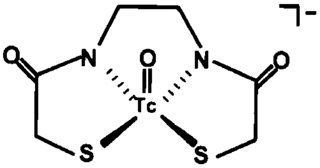
(39)



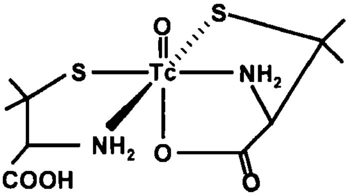
(40)

chemical assignment of the ^{99}Tc complex and the stereochemistry is important in determining the level of brain uptake of the ^{99m}Tc complex (*477*). Complexes include those for which a benzene ring forms part of the ligand skeleton (*474*) and for which R_1 is a steroid moiety (*475*). An interesting example is **39** (R_1 = H, R_2 = CH_2-NC_5H_9Ph), containing a pendant phenylpiperidine group for which the crystal structures of the *syn* and *anti* forms (with respect to R_2) are available and differences in the brain uptake of the ^{99m}Tc complexes are found (*477*). Other crystal structures, including **40** (*478*), have been reported (*474*). The complexities of *in vivo* behavior are illustrated by ^{99m}Tc–**40**, which is retained in the brain on trapping by enzymatic hydrolysis of one ester group to the free acid and the formation of a charged species. The hydrolysis is stereospecific and only the L,L enantiomer is trapped (*19*). Additionally, high brain uptake appears limited to humans and primates, presumably due to the high serum and lower brain esterase levels in lower animal species (*17*). Cationic BAT complexes have been prepared with or without alkylated amine groups and these are of interest as potential myocardial imaging agents (*476*). A number of crystal structures are available (*476, 479–481*). Cationic N_2S_2 complexes such as the six-coordinate *trans*-[TcO(OH_2){(sacac)$_2$en}]Cl are formed with imine nitrogen ligands. The ν(TcO) absorption in this complex occurs at 964 cm^{-1} and the Tc–OH_2 distance is quite long at 2.384(3) Å (*482*).

The greater acidity of the amide protons in diamidedithiols results in the loss of two amide protons, producing anionic complexes for which the ^{99m}Tc preparations are of interest as renal agents (19). Yellow salts of the parent complex (**41**), and derivatives, may be isolated from the *in situ* hydrolysis of the *S*-protected ligand and TcO_4^-/$Na_2S_2O_4$ (*483*). Crystal structures of ($AsMePh_3$)(**41**) and the PPh_4^+ salt of the butanediamine derivative show the usual square–pyramidal geometry, with the Tc atom displaced 0.771 and 0.67 Å, respectively, above the N_2S_2 plane (*484, 485*). The preparation of a variety of substituted analogs of **41** (and the monoamides) and crystal structures have been reported



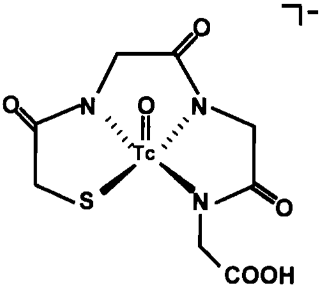
(41)



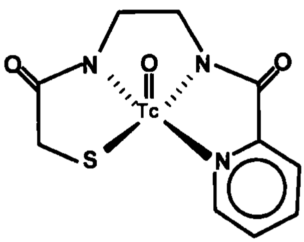
(42)

(*486–489*). In a novel example the CH_2CH_2 bridge in **41** is replaced by a ribonucleoside (*490*). Crystallography and NMR have been used to assign stereoisomers (*487, 491*). In the reaction of $[TcOCl_4]^-$ with excess ligand, the blue lantern dimer $(AsPh_4)_2[(TcO)_2\{SCH_2CONH(CH_2)_2NHCOCH_2S\}_4]$, with each Tc coordinated by four S atoms and an intramolecular Tc···Tc distance of 7.175 Å, is formed. In aqueous basic solution the dimer is immediately and quantitatively converted to 2 eq. of $(AsPh_4)$(**41**) (*492*). If one of the thiolate groups in **41** is substituted by $-CH_2CH_2$-*N*-(piperidinyl), then a neutral complex is formed. This complex readily undergoes $S{-}CH_2$ bond cleavage in solution, assisted by neighboring group participation of the piperidine nitrogen, to reform **41** (*493*). The neutral six-coordinate D-penicillaminato (pen) complex (**42**) contains one bidentate ligand, one tridentate ligand with a $Tc{-}O_{carboxylate}$ distance of 2.214(4) Å, and one free carboxyl group (*494*). The [TcO-(D-pen)(L-pen)]$^-$ anion is fluxional in solution and racemizes by exchange of bonded and free carboxylate groups *trans* to the oxo ligand. Racemization of the Tc complex is faster than that for the Re analog (*495*). Other structurally characterized examples with bidentate NS ligands are $NBu_4[TcO(abt)_2]$ (*496*) and a cationic $[TcOL_2]Cl$ [L = substituted (thiocarbamoyl)benzamidinate] (*497*). The preparations of a variety of Schiff-base dithiocarbazate derivative and *N*-heterocyclic thiolato complexes have been reported (*498–500*).

An N_3S complex is $[TcO(MAG_3)]^-$ (**43**), for which the negative charge is achieved by deprotonation of the three amide groups of the mercaptoacetyltriglycinato ligand. *In vivo* the carboxylic acid group is ionized and $[^{99m}TcO(MAG_3)]^{2-}$ is an important radiopharmaceutical for the assessment of renal function. The presence of the uncoordinated carboxylate group in the dianion is important for efficient renal clearance (*19*). The crystal structure of $AsPh_4[TcO(MAG_3)]$ shows the carboxylic acid group to be distant from the Tc center, and two crystal forms of the methyl ester $AsPh_4[TcO(MAG_3Me)]$ differ with the orientation of the carbomethoxy group being approximately parallel and perpendicular to the Tc=O bond (*501*). Calculations indicate that in solution



(43)



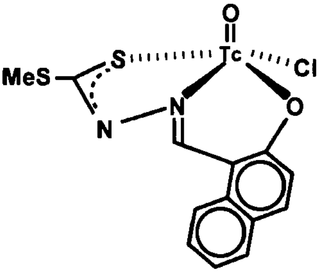
(44)

$[TcO(MAG_3)]^{2-}$ is conformationally flexible (*502*). A variation of N_3S coordination is the inclusion of one pyridine nitrogen in the neutral 44. The Tc═O bond distance is 1.653(4) Å, and $Tc–N_{pyridine}$ at 2.102(4) Å is substantially longer than the $Tc–N_{amide}$ distances [1.965(4) Å (av.)] (*488*). A complex with NS_3 coordination is $[TcO(tmbt)_3(py)]$ (*319*).

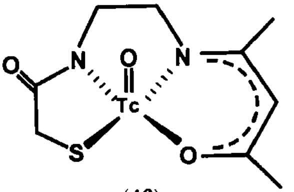
6. *Complexes Based on Other TcO Mixed Ligand Cores*

Numerous five- and six-coordinate TcO complexes containing mixed ligand atom coordination are known and many have been structurally characterized. Examples not containing sulfur are $[TcO(OR)X_2L_2]$ (R = Me, Et; X = Cl, Br; L = $pyNO_2$ or L_2 = bpy, polypyridyl derivative) and $[TcOCl_2(terpy)]TcO_4$ (*503–505, 418*). For *trans*(*N*)-trans(*Br*)-$[TcO(OEt)Br_2(pyNO_2)_2]$, the Tc–OEt distance is short at 1.855(6) Å and Tc═O is 1.684(6) Å. The ethoxy group results in a low ν(TcO) at 938 cm^{-1} (*503*). Reduction of TcO_4^- by HX /KBH_4 in the presence of $HB(pz)_3^-$ yields the lipophilic $[TcOCl_2\{HB(pz)_3\}]$ (*506*), and the bromo complex may be prepared from $[TcOBr_4]^-$ (*396*). In the chloro complex, the three N donor atoms span *fac* positions with $OTc–N_{cis}$ bond distances of 2.086(4) and 2.088(3) Å, and $OTc–N_{trans}$ is markedly longer at 2.259(4) Å (*506*). The neutral six-coordinate $[TcOL_2Cl]$ (L = 2-methyl-8-quinolinolate), prepared by substitution of $[TcOCl_4]^-$, is the *cis*-isomer and hence may be regarded as a $TcO\{N_2OCl\}$ derivative. The $Tc–O_{quinolinolate}$ bond distances *cis* and *trans* to the oxo group are 1.947(3) and 1.994(3) Å, respectively, and Tc–Cl is 2.360(1) Å (*507*). The chloro ligand in this and related complexes undergoes solvolysis in methanol (*507, 508*). Electrochemical studies of $[TcOClL_2]$, where L is a bidentate *N,O*-Schiff base or 8-quinolinolate ligand, have shown reduction to $Tc^{IV}O$ species (*509*). In $[TcOCl(OCH_2CH_2O)(phen)]$ the Cl atom is also *cis* to the oxo group and the OTc–N bond distances are 2.173(4) Å (*cis*) and 2.268(4) Å (*trans*) (*505*). Similar structurally characterized complexes are [TcOClL$_2$] (L = *N*-phenylsalicylidineiminate) (*510*) and [TcOCl$_2$L] (L = *NNO* Schiff base) (*511*). A five-coordinate example is [TcOCl(Ophsal)], in which Tc is displaced by 0.67 Å above the ONOCl plane (*512*).

Crystallography has shown that a product obtained from the reaction of **20** [E = S (SphsalH$_2$)] with [TcOCl$_4$]$^-$ is the octahedral [TcOCl(hbt)$_2$] with equatorial ONNCl coordination. The hbt ligand (see **33**) is formed by an oxidative intramolecular ring closure (*513*). The five-coordinate [TcOCl(Sphsal)] has since been prepared by substitution of [TcOCl$_4$]$^-$, with a stoichiometric amount of the ligand and crystal structures of this complex (*514*) and the related [TcO(Sphsal)(SPh)] (*515*) reported. Crystal structures are also available for the dithiocarbazate derivative (**45**) (*268*), the potential brain imaging agent (**46**) (*516*), *cis*-[TcO{8-hydroxy-3,6-dithiaoctan-1-olate-(*O,S,S,*)}Cl$_2$] (*517*), and the square–pyramidal AsPh$_4$[TcO(MAG$_2$)] [MAG$_2$ = mercaptoacetylglycylglycinate(2-)], with the carboxylate group participating in the ONNS coordination (*518*). The preparation of TcO complexes with a variety of dithiocarbazate derivatives (*519, 520*) and of tridentate Schiff bases with a thiolato coligand (*521*) has been reported.



(**45**)



(**46**)

An interesting structurally characterized complex is the distorted square–pyramidal [Tc^{V}O(SC$_6$H$_2{}^i$Pr$_3$)$_2$(PhNNCON$_2$HPh)] (*522*), which has also been assigned the Tc(III) oxidation state on the basis of structural and spectroscopic features (*523*). In view of the absence of any other Tc=O group in an oxidation state below Tc(V) and Holm's generalization that M=O groups are stabilized at metal centers with an oxidation state of no less than +4 (*524*), the Tc(V) assignment would seem preferable.

B. COMPLEXES OF THE *trans*-[TcO(OH)]$^{2+}$ AND [TcO$_2$]$^+$ CORES

Technetium, in common with rhenium (*189*), forms a considerable number of cationic complexes containing the *trans*-[TcO$_2$]$^+$ core. The poor ability of neutral σ- or weak π-donor equatorial ligands in *trans*-$[TcO(OH_2)L_4]^{3+}$ to neutralize the positive charge on the $[TcO]^{3+}$ core results in enhanced acidity of the *trans* water and the following acid–base equilibria (*525, 35*):

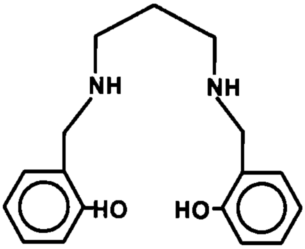
$$[O{=}Tc{-}OH_2]^{3+} \overset{K_{a1}}{\rightleftharpoons} [O{=}Tc{-}OH]^{2+} \overset{K_{a2}}{\rightleftharpoons} [O{=}Tc{=}O]^{+}.$$

Negatively charged ligands do not favor proton loss but an exception is CN^-, which, although a good σ-donor, is also an effective π-acceptor. From neutral solution K_3*trans*-$[TcO_2(CN)_4]$ [$\nu_{asym}(TcO_2)$ at 785 cm^{-1}] is isolated and acidification to pH 1 yields *trans*-$[TcO(OH_2)(CN_4)]^-$ (pK_{a1} 2.90) via the $[TcO(OH)(CN)_4]^{2-}$ intermediate. The π-acceptor nature of the equatorial cyanides in (NMe_4)*trans*-$[TcO(OH_2)(CN)_4]{\cdot}2H_2O$ is apparent in the high value of 1029 cm^{-1} for $\nu(TcO)$ (*399*). The dioxo complex is also formed by the hydrolysis of $K_2[TcO(CN)_5]$ (*229*). In general, cationic *trans*-$[TcO_2]^+$ complexes are prepared by the reaction of $TcO_4^-/Na_2S_2O_4$ (*399*) or $[TcOX_4]^-$ (*526, 527*) and neutral nitrogen or N_2S_2 cyclic thioether ligands. The *trans*-$[TcO_2(py)_4]Cl$ complex is readily prepared by hydrolysis/oxidation of $[TcCl_6]^{2-}$ in neutral conditions or by substitution of $[TcOCl_4]^-$ in the presence of water and serves as a useful starting material for ligand exchange reactions (*528, 399*). Crystal structures have been reported for $[TcO_2(cyclam)]ClO_4{\cdot}H_2O$ (*525*), *trans*-$[TcO_2(en)_2]X$ (X = Cl, I) (*529*), $[TcO_2L_4]Cl{\cdot}nH_2O$ (L = imidazole, $n = 2$; L = 1-methylimidazole, $n = 3$) (*530*), $[TcO_2$(4-*tert*-butylpyridine)$_4]CF_3SO_3{\cdot}H_2O$ (*526*), $[TcO_2$(1,4-dithia-8,11-diazacyclotetradecane)$]PF_6$ (*531*), and a polymeric $\{Li[TcO_2$(1,4,8,11-tetraazaundecane)$](CF_3SO_3)_2\}_n$ (532). There is a brief mention of the structure of $[TcO_2(CN)_4]^{3-}$ (*35*). Characteristic features illustrated by the structure of *trans*-$[TcO_2(en)_2]Cl$ are Tc═O bond distances of 1.752(1) and 1.741(1) Å, a Tc–N bond distance of 2.158 Å (av.) and an O–Tc–O angle of 178.6(3)° (*529*). Interestingly, although **36** exists as the monooxo form, an increase in the hydrocarbon chain to $N(CH_2)_5N$ results in the formation of the neutral dioxo complex (no amine nitrogen deprotonated) with Tc═O, 1.745(3) Å, and the O–Tc–O angle, 170.1(1)° (*455*). The long Tc═O distances and low asymmetric O═Tc═O IR stretching frequencies in the range 850–750 cm^{-1} are indicative of a lower bond order than that in $[TcO]^{3+}$ complexes. Group theoretical analysis predicts that for *trans*-$[TcO_2]^+$ in D_{4h} symmetry the maximum Tc–O bond order is 2 (*533*) and this is consistent with the bond order of 2.10 indicated by the Tc═O stretching force constant of 6.23 mdyn $Å^{-1}$ for *trans*-$[TcO_2(en)_2]Cl$ (*414*). Kinetic studies of pyridine exchange in *trans*-$[TcO_2(py)_4]^+$ indicate a dissociative mechanism and the Tc complex has been found to undergo exchange at ca. 8000 times the rate of the Re analog (*534, 535*). The cationic nature of $[TcO_2]^+$ complexes has attracted considerable radiopharmaceutical interest. A promising myocardial imaging agent that shows good blood and liver clearance is the diphosphine derivative $[^{99m}TcO_2L_2]^+$ [L = $\{CH_2P(CH_2CH_2OEt)_2\}_2$]. The Tc=O bond distance in *trans*-$[TcO_2L_2][Cr(SCN)_4(NH_3)_2]$ is 1.738(17) Å (*536*). With the dmpe ligand the hydroxo complex *trans*-$[TcO(OH)(dmpe)_2](CF_3SO_3)_2$ has been isolated and Tc=O and Tc–OH bond distances of 1.66 and 1.96 Å have been determined by EXAFS (*123*). The *trans*-$[TcO(OH)(CN)_4]^{2-}$ species could not, however, be isolated due to rapid dimerization (*399*), but $(NBu_4)_2$*trans*-$[TcO(OMe)(CN_4)]$, with a nonionizable methoxy group, may be regarded as a trapped form (*229*). The isolation of $K_2[TcO(OH)Cl_4]$, with ν(TcO) at 900 cm^{-1}, has been claimed (*537*), but has not been substantiated. The formation of monoanionic TcO_2 complexes with Schiff bases has also been reported (*538*), but these may be the μ-oxo dimers.

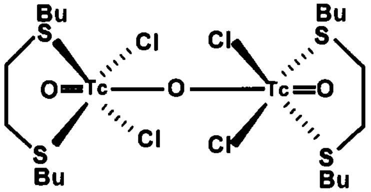
C. OXO-BRIDGED $[Tc_2O_3]^{4+}$ AND OTHER BINUCLEAR COMPLEXES

Protonation of $[TcO_2(CN)_4]^{3-}$ in acidic aqueous solution and rapid dimerization of the initially formed *trans*-$[TcO(OH)(CN)_4]^{2-}$ yield the purple μ-oxo dimer $[Tc_2O_3(CN)_8]^{4-}$ (*399*). Generally, $[Tc_2O_3]^{4+}$ complexes are prepared from substitution reactions of $[TcOCl_4]^-$, for example, $[\{TcO(S_2CNEt_2)_2\}_2(\mu\text{-}O)]$ (*539*), or from reduction of TcO_4^-. The reaction sequence is illustrated by *trans*-[TcOClL], prepared by substitution of $[TcOCl_4]^-$ with $(sacac)_2enH_2$ (H_2L) in dry solvents. In the presence of moisture, the labile chloride is replaced by water to give the cationic $[TcO(OH_2)L]Cl$, which then forms the μ-oxo dimer $[\{TcOL\}_2(\mu\text{-}O)]$ by reaction of [TcOClL] with the intermediate hydroxy complex [TcO(OH)L] (*540*). Crystal structures of $[\{TcOL\}_2(\mu\text{-}O)]$, where L represents a variety of tetradentate ONNO aminephenolato ligands, (*e.g.*, **47**) (*541*), the ONNO Schiff base ligands *N,N'*-2-hydroxypropane-1,3-bis(salicylideneiminate) (*542*) and *N,N'*-propane-1,3-diylbis(salicylideneiminate) (*543*), and **48** (*517*) have shown the presence of either a crystallographically imposed linear or a near-linear (167°–173°) Tc–O–Tc bridge with O=Tc–O angles of 163°–171°, giving an essentially linear $[O{=}Tc{-}O{-}Tc{=}O]^{4+}$ core analagous to the $[Re_2O_3]^{4+}$ core (*189*).

Other features are $Tc{-}O_{bridge}$ bond distances of 1.90–1.92 Å and the near-eclipsed arrangement of the donor atoms of the two Tc centers as shown in **48**, in which the near-eclipsed atoms are Cl and S (*517*). The occurrence of linear d^2–d^2 $[M^V{}_2O_3]^{4+}$ (M = Tc, Re) cores is explained



(47)



(48)

by MO theory. For a [O=ML$_4$–O–L$_4$M=O] complex in D_{4h} symmetry, the π interactions between the two t_{2g} sets from the two metal atoms and the p_x, p_y sets from the three oxygen atoms give rise to two nonbonding molecular orbitals ($b_{2g} + b_{1u}$), which do not correspond to any oxygen π linear combinations. A d^2–d^2 configuration corresponding to the occupation of these nonbonding orbitals satisfies the closed-shell electronic configuration (*544*). In the IR spectra ν_{asym}(Tc–O–Tc) appears as an intense broad band at 625–680 cm^{-1} but ν(Tc=O) is of variable intensity and may not be observed (*541, 543*). A complex formulated as the mixed-valence $K_3[Tc^{V/IV}{}_2O_2Cl_8]$ has been obtained by reflux of $K_3[Tc_2Cl_8]\cdot 2H_2O$ in 2-butanone in air. The IR spectrum indicates the presence of both Tc=O (1020 cm^{-1}) and Tc–O–Tc (680 cm^{-1}), but the structure is uncertain (*42*).

Formation of the novel dimer **49** on reaction of $[TcOCl_4]^-$ with 1.5 eq. of edtH$_2$ may be viewed as the interaction of the Lewis base $[TcO(edt)_2]^-$ with the Lewis acid $[TcO(edt)]^+$ (Fig. 14) (*35, 545*). On reaction with excess edtH$_2$, **49** is converted quantitatively to $[TcO(edt)_2]^-$, but $[(TcO)_2\{S(CH_2)_3S\}_3]$ does not react with further amounts of ligand. Also, although a dimeric intermediate was found to form in the reaction of $[TcO(SCH_2CH_2O)_2]^-$ with 2 eq. of edtH$_2$, no intermediate was detected in the substitution of $[TcO(OCH_2CH_2O)_2]^-$ to $[TcO(edt)_2]^-$ (*546*). An interesting binuclear complex is $[\{TcO(OEt)Cl_2\}_2(\mu\text{-}L)]$, where L is an N$_6$ heterocyclic nitrogen ligand (*547*). Addition of $NBu_4[TcOCl_4]$ to $(NBu_4)_4[H_3PW_{11}O_{39}]$ in MeCN yields purple crystals of the Tc-substituted Keggin polyoxotungstate derivative $(NBu_4)_4[PW_{11}TcO_{40}]$. The silicon derivative $(NBu_4)_5[SiW_{11}TcO_{40}]$ has been prepared by the addition of $Na[TcO(OCH_2CH_2O)_2]$ to $\alpha\text{-}K_8SiW_{11}O_{39}\cdot 12H_2O$ in sodium acetate buffer. Electrochemically, the Tc center of $[PW_{11}TcO_{40}]^{n-}$ appears to exhibit only three accessible oxidation states, Tc(IV) $\rightleftarrows$ Tc(V) $\rightleftarrows$ Tc(VI), in contrast to the five oxidation states, Re(III)–Re(VII), accessible for the analogous Re cluster (*548*).

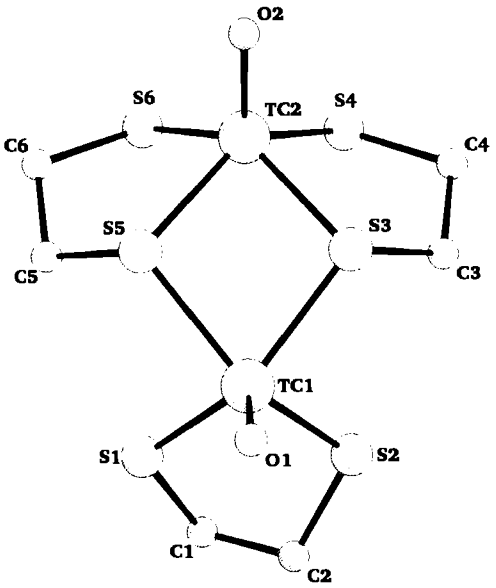


FIG. 14. The structure of $[(TcO)_2(edt)_3]$ (49) (*545*).

D. $[TcS]^{3+}$ COMPLEXES

The diamagnetic sulfido complex $AsPh_4[TcS(edt)_2]$ [$\nu(Tc{=}S)$ at 520 cm^{-1}] is formed from the reaction of $[TcCl_6]^{2-}$ with 1,2-ethanedithiol and $[TcSCl_2\{HB(pz)_3\}]$ from the oxo complex by S atom transfer from B_2S_3 (*379, 549*). The $[TcS]^{3+}$ core is less stable than $[TcO]^{3+}$ and readily undergoes replacement of the sulfido ligand by oxo in solution and under aerobic conditions.

E. NITRIDO COMPLEXES

The nitrido ligand (N^{3-}) is isoelectronic with the oxo ligand (O^{2-}) and is a powerful π-electron donor that effectively stabilizes technetium in the +5 to +7 oxidation states. The first complexes containing the $[Tc^{V}N]^{2+}$ core, $[TcNCl_2(PPh_3)_2]$ and $[TcN(S_2CNEt_2)_2]$, were prepared from the reaction of TcO_4^- /ligand with $NH_2NH_2{\cdot}HCl$ as the reducing agent and source of the nitrido ligand (*550, 551*), but this method is of limited applicability. Two general methods for the synthesis of $[TcN]^{2+}$ complexes are by ligand exchange of $[TcNCl_2(PPh_3)_2]$ and by reduction/exchange of $[Tc^{VI}NX_4]^-$ (X = Cl, Br) (*551, 552, 220*). A characteristic feature is the generally sharp $\nu(TcN)$ IR absorption at 1100–1028 cm^{-1}, which is shifted by ~30 cm^{-1} on ^{15}N labeling (*145*). The TcN bond is formally triple with one σ and two π components and quite short in the range 1.60–1.64 Å. The lower charge on $[TcN]^{2+}$ in comparison with the isoelectronic $[TcO]^{3+}$ results in little tendency to deprotonation of coordinated amine ligands. The TcN bond is very resistant to hydrolysis or removal by other reactions but readily reacts with active sulfur sources such as S_2Cl_2 to yield thionitrosyl complexes (*322*). In general, $[TcN]^{2+}$ complexes are not readily reduced and require agents such as chlorine for oxidation (*553, 554*). Structurally, the strong *trans* influence of the nitrido ligand results in either five-coordinate square–pyramidal complexes or six-coordinate complexes with the *trans* ligand only weakly bound.

The anion in $(AsPh_4)_2$*trans*-$[TcN(OH_2)(CN)_4]\cdot 5H_2O$ has distorted octahedral geometry with a Tc≡N bond distance of 1.60(1) Å, a very long NTc–OH_2 distance of 2.559(9) Å, and the Tc atom 0.35 Å above the equatorial plane. A high ν(TcN) at 1100 cm^{-1} results from the π-acceptor property of the equatorial cyanides. The pK_{a1} value of the coordinated water has not been determined but the long bond distance indicates very low acidity and high kinetic lability (*555*). In the case of $[Re(E)(OH_2)(CN)_4]^{n-}$ (E = O, N) the strong *trans* effect of the nitrido ligand is apparent in the pK_{a1} values of 1.4 and 11.7 for the oxo and nitrido complexes, respectively, and a reaction rate constant some 9×10^5 times greater for the nitrido complex (*556*). The structurally characterized Cs_2Na *trans*-$[TcN(N_3)(CN)_4]\cdot 2H_2O$ is obtained by ligand exchange with N_3^- (*557*), and $Cs_2K[TcN(CN)_5]$ may be isolated in the presence of cyanide (*558*). The IR spectrum of the latter complex shows three well-defined ν(CN) absorptions ($2A_1 + E$) consistent with C_{4v} symmetry. Reaction of NCS^- with $[TcNCl_2(PPh_3)_2]$ yields yellow $[TcN(NCS)_2(PPh_3)_2]$, which on reflux in MeCN is converted to orange-red crystals of *trans,trans*-$[TcN(NCS)_2(PPh_3)_2(MeCN)]\cdot \frac{1}{2}MeCN$. The Tc≡N bond distance is 1.629(4) Å and the weak binding of the MeCN ligand is apparent in the long Tc–NCMe distance of 2.491(4) Å and the formation of the five-coordinate complex on dissolution in $CHCl_3$ (*559*). The thiocyanato ligands are *N*-bonded, as is also the case for the structurally characterized $(NEt_4)_2[TcN(NCS)_4(MeCN)]$, prepared by reaction of $[TcNCl_4]^-$ with NCS^- and crystallization from MeCN (*560*). The preparation of $(AsPh_4)_2[TcN(NCS)_4]$ has been reported (*561*) but crystallography shows the product crystallized from MeCN/EtOH is the *trans*-aqua complex $(AsPh_4)_2[TcN(OH_2)(NCS)_4]\cdot EtOH$ (*557*). Spectroelectrochemical studies at −60°C show a reversible one-electron reduction of $[Tc^{VI}NX_4]^-$ (X = Cl, Br) to $[TcNX_4]^{2-}$, but the colorless reduced species have not been isolated (*562*).

No $Tc^{V}N\{O_4\}$ complex has yet been identified, but five-coordinate $Tc^{V}N\{S_4\}$ complexes are readily prepared by ligand exchange of $[TcNCl_2(PPh_3)_2]$ or reduction/substitution of $[TcNCl_4]^-$ (*552, 563*). Key structural data are summarized in Table IV. Of particular interest is a comparison of the *trans* influence of the nitrido and oxo ligands in the same coordination environment. The three TcN/TcO pairs in Table IV show that, although the nitrido ligand exerts the greater *trans* influence, the oxo ligand exerts the greater structural steric effect (*566*). This is seen in the greater displacement of Tc above the square basal plane in the five-coordinate square–pyramidal complexes in Table IV and the correspondingly greater OTcL angles. The $Tc{\equiv}N$ bonds are shorter than the $Tc{=}O$ bonds and it has been suggested that this may be largely accounted for by σ-electron effects, with nitrogen utilizing an sp hybrid orbital and oxygen, an sp^2 orbital in the TcN/O bond. The Tc–L distances are longer in the nitrido complexes, but this effect largely may be due to the lesser core charge on $[TcN]^{2+}$ (*566*).

Reaction of $[TcNCl_2(PPh_3)_2]$ with $K(S_2COEt)$ and treatment with aqueous ethanol yield the dithiocarbonato complex $K_2[TcN(S_2CO)_2]$ on hydrolysis of the intermediate xanthate (*564*). The mixed-ligand complex $AsPh_4[TcN(S_2CNEt_2)(SCOCOS)]$ is prepared in a controlled fashion by the reduction/substitution of $[Tc^{VI}NCl_2(S_2CNEt_2)]$ with dithiooxalic acid (*565*). Reaction of thiourea with $[TcNCl_4]^-$ yields the orange $[TcN(tu)_4Cl]Cl$, which is a useful starting material for ligand exchange in aqueous solution (*568*). Mass spectrometry has shown that $[TcN(SSeCNEt_2)_2]$ undergoes a thermally induced scrambling to give the S_4, S_3Se, and SSe_3 species (*569*). Chromatographic studies have shown the formation of $[^{99m}TcNL_2]^{2-}$ (L = mnt, dto) on reaction of

TABLE IV

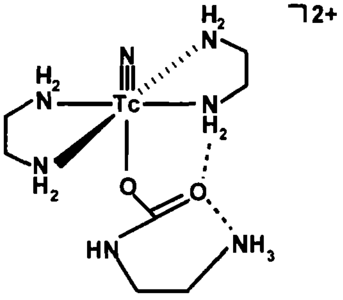
STRUCTURAL DATA FOR $Tc^{V}N\{S_4\}$ COMPLEXES AND $Tc^{V}N\{S_4/Se_4\}/Tc^{V}O\{S_4/Se_4\}$ COMPLEXES WITH THE SAME COORDINATION ENVIRONMENT

Complex	TcN/O (Å)	Tc—L (Å)	NTcL/OTcL (°)	δ-sbp[a] (Å)	Ref.
$[TcN(S_2CNEt_2)_2]$	1.604(6)	2.401 av.	108.1 av.	0.741(5)	550
$K_2[TcN(S_2CO)_2]\cdot 2H_2O$	1.621(6)	2.390 av.	107.3 av.	0.71	564
$AsPh_4[TcN(S_2CNEt_2)(dto)]$	1.54(2)	2.393 av.	106.0 av.	0.66	565
$(AsPh_4)_2[TcN(dto)_2]$	1.613(4)	2.378(2)–2.391(2)	105.4(2)–106.1(3)	0.65	427
$AsPh_4[TcO(dto)_2]$	1.646(4)	2.327(1)–2.330(1)	108.6(2)–109.9(2)	0.76	427
$(AsPh_4)_2[TcN(mnt)_2]$	1.59(1)	2.367(4)–2.419(4)	101.8(8)–106.8(8)	0.59	566
$AsPh_4[TcO(mnt)_2]$	1.655(6)	2.310(2)–2.320(2)	107.4(2)–109.8(2)	0.74	428
$(NBu_4)_2[TcN\{Se_2CC(CN)_2\}_2]$	1.61(1)	2.508(2)–2.528(2)	106.1(4)–109.5(4)	0.768(1)	567
$NEt_4[TcO\{Se_2CC(CN)_2\}_2]$	1.67(2)	2.463(4)–2.476(4)	108.1(6)–112.4(6)	0.88	432

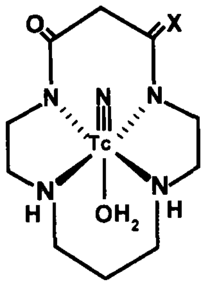
[a] Displacement of Tc above the square basal plane.

$[^{99m}Tc^{VI}NCl_4]^-$ with the ligands (*448*). Exchange of $[^{99m}TcN(dto)_2]^{2-}$ (and the ^{99}Tc complex) with mnt occurs via an intermediate, presumably the mixed complex $[^{99m}TcN(dto)(mnt)]^{2-}$ (*570*). The neutral $[^{99m}TcN\{S_2CNEt(OEt)\}_2]$ is a promising neutral myocardial imaging agent. Cyclic voltammetry of the ^{99}Tc complex has shown no oxidation or reduction in the interval +1.225 to −1.75 V vs SCE, indicating that this complex should be stable *in vivo* (*571*).

A variety of $TcN\{N_4\}$ complexes has been prepared from $[TcNCl_2(PPh_3)_2]$ or from $[TcNCl_4]^-$ (usually in the presence of an auxiliary reducing agent such as KBH_4 or PPh_3) (*572, 573*). The cationic ethylenediamine complex *trans*-$[TcN(en)_2Cl]BPh_4$ is typical, with $\nu(TcN)$ at 1085 cm^{-1}, distorted octahedral geometry, a $Tc{\equiv}N$ bond distance of 1.603(3) Å, and the very marked *trans* influence of the nitrido ligand, resulting in an NTc–Cl bond distance of 2.7320(8) Å. In *trans*-$[TcN(tad)Cl]BPh_4$ (tad = 1,5,8,12-tetraazadodecane) the Tc–Cl distance is 2.663(2) Å (*572*). Crystallography has shown that the product formed from $[TcNCl_2(PPh_3)_2]$ with excess diethylenetriamine in benzene/ethanol under aerobic conditions is the novel dicationic **50**$(BPh_4)_2$. The mechanism of formation of the zwitterionic $NH_3{}^+CH_2CH_2NHCOO^-$ carbamato ligand and the cleavage of the triamine to ethylenediamine is not clear. Under anhydrous conditions in an inert atmosphere, $[TcNCl_2(PPh_3)_2]$ is recovered unchanged, but **50** is readily isolated when a stream of CO_2 is passed into the reaction mixture. The crystal structure shows that the zwitterionic ligand lies in a peculiar "transient state" and is stabilized by strong intramolecular hydrogen bonding (*574*).



(50)



(51)

Other related complexes are $[TcN(cyclam)Cl]Cl$ and **51** (X = O), for which neutrality is achieved by deprotonation of the two amide groups, with the resultant Tc–N bond distance of 2.051 Å significantly shorter than the Tc–NH distance of 2.126 Å (*573*). In the cationic **51**Cl (X = H_2) the $NTc–OH_2$ bond is very long at 2.560(2) Å (*575*). Crystallography has shown the product of the reaction of $[TcNBr_4]^-$ with bpy in ethanol to be $\{cis\text{-}[Tc^{V}NBr(bpy)_2]\}_2[Tc^{II}Br_4]$. The formation of the previously unknown $[TcBr_4]^{2-}$ under mild conditions is unprecedented. With methanol as the solvent the product is *cis*-$[TcNBr(bpy)_2]BPh_4$ (*146, 576*). In *cis*-$[TcNBr_2\{(pyCH_2)_2NCH_2CMe_2SBz\}]$, the Tc–N bond distance of the tertiary amine N atom coordinated *trans* to the nitrido ligand is 2.47(1) Å and that of the pyridine N atoms coordinated *cis* is 2.141 Å (av.). In solution there is an equilibrium between the dibromo form and one in which a bromide ion is expelled, and the thioether sulfur is coordinated (*577*). Other structurally characterized complexes are *cis*-$[TcNCl(phen)_2]PF_6$ (which exhibits a pseudo-twofold symmetry axis that gives rise to reproducible enantiomeric disorder) and *cis*-$[TcNCl(phen)_2]Cl{\cdot}H_2O$ (*578*). The preparations of $[TcNL_4]Cl_2$ (L = py,imidazole) (*579*) and [TcN(phthalocyanine)] (*580*) have been reported. The pyridine ligands in $[TcN(OH)(py)_4]BPh_4$ are labile and undergo exchange with pyridine in solution. The $[TcN(OH)]^+$ core shows similar ^{99}Tc NMR shifts to $[TcO_2]^+$. Reaction with tmbtH gives a quantitative yield of *trans*-$[TcN(tmbt)_2(py)_2]$ (*581*).

The most important phosphine complex is the synthetic intermediate $[TcNCl_2(PPh_3)_2]$, which may be prepared by a variety of routes, including hydrazine·HCl reduction of TcO_4^- in the presence of PPh_3 (*551*), reduction/substitution of $[TcNCl_4]^-$ (*552*), and substitution of $[TcN(tu)_4Cl]Cl$ (*568*). Reaction of PPh_3 or $AsPh_3$ with $[TcNX_4]^-$ gives the five-coordinate $[TcNX_2(EPh_3)_2]$ (X = Cl, Br; E = P, As) in high yield and with the sterically less demanding PMe_2Ph, the six-coordinate *cis*-$[TcNX_2(PMe_2Ph)_3]$. The presence of the *trans* halide ligand in the six-coordinate complexes results in ν(TcN) at 1048 cm^{-1} (X = Cl) and 1028 cm^{-1} (X = Br) compared with 1095–1090 cm^{-1} for the five-coordinate complexes. All these complexes readily undergo ligand-exchange reactions (*582*). Tri(cyanoethyl)phosphine yields the anionic $NBu_4[TcNX_3L]$ (*583*). The reduction of $^{99m}TcO_4^-$ in the presence of $NH_2{-}NR{-}C({=}S)\text{-}SMe/PPh_3/HCl$ and addition of the ligand have been developed for the preparation of ^{99m}TcN radiopharmaceuticals (*584*). The Tc≡N bond distances in $[TcNCl_2(EPh_3)_2]$ (E = P, As) are 1.602(8) and 1.601(5) Å, respectively, and the geometry may be regarded as intermediate between square–pyramidal and trigonal–bipyramidal, as shown in Fig. 15 for the arsine complex (*585, 586*). The six-coordinate *cis-mer*-$[TcNCl_2(PMe_2Ph)_3]$ shows NTc–Cl bond distances of 2.441(1) Å (*cis*) and 2.665(1) Å (*trans*) and a Tc≡N distance of 1.624(4) Å (*587*). For the octahedral *trans*-$[TcNCl(dmpe)_2]BPh_4$, a Tc≡N bond distance of 1.853(6) Å has been reported, but problems in the refinement were noted (*576*). This distance seems unreasonably long and is likely due

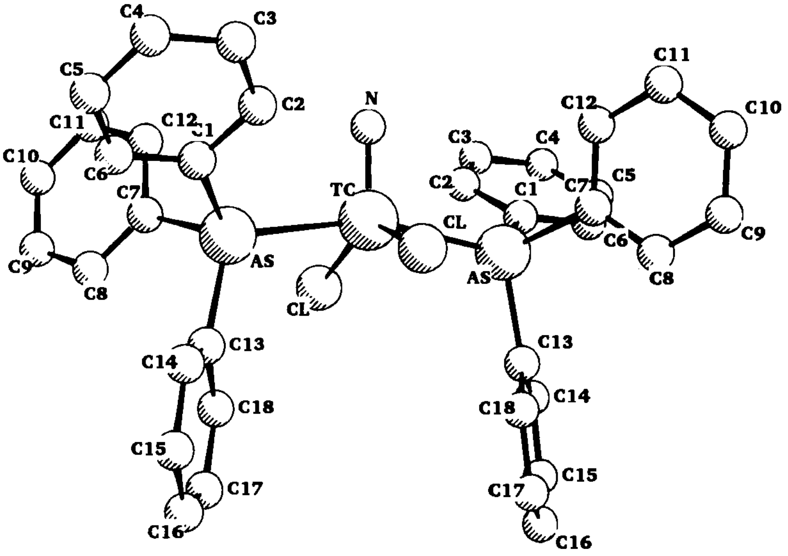
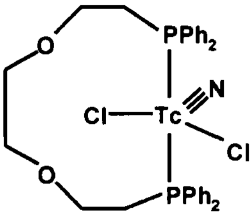
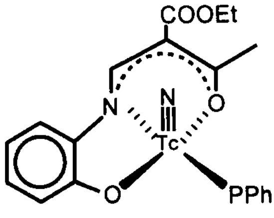


FIG. 15. The structure of $[TcNCl_2(AsPh_3)_2]$ (*586*)

to disorder between the *trans* nitrido and chloro ligands, giving rise to the crystallographic artifact of "distortional isomerism". Cationic $[^{99m}TcN(dppe)_2Cl]^+$ and related complexes undergo *in vivo* reduction and are then washed out of the myocardium (*588*). Cyclic voltammetry has shown that $[TcNCl(dmpe)_2]^+$ undergoes reversible reduction with unexpected ease at −0.02 V vs SCE when compared with the irreversible reduction of $[ReNCl(dppe)_2]^+$ at −1.8 V vs SCE (*184*). Trigonal-bipyramidal geometry is observed for **52**, with Tc≡N, 1.601(4) Å, and a near-linear P–Tc–P angle of 176.5°. The ether oxygens cannot be regarded as coordinated with Tc···O contact distances of 3.190(2) Å. A related $[TcNCl_2L]$ complex with L containing a tertiary amine bridge has square-pyramidal geometry and a $Tc\cdots N_{amine}$ distance of 2.70(1) Å, indicative of incipient coordination (*589*).



(52)



(53)

A variety of complexes containing **25** (R = SH), **27**, or PPh_3 in a mixed coordination sphere has been reported, indicating the versatility of the $[TcN]^{2+}$ core (*308, 310, 590*). The binuclear $[\{Tc_2N_2Cl_4L_2]$(L = $^iPr_2PCH_2CH_2P^iPr_2$) is thought to contain Cl bridges (*576*). Structurally characterized examples are **53** (*591*), [TcNL(PPh_3)] (L = tridentate *S*-methyl dithiocarbazate) (*592*), and [TcNCl(PPh_3){PhN=C(OEt)S}] (*593*). The TcN{O_2S_2} core is found in thio-β-diketonato complexes (*594*). Structurally characterized TcN{N_2S_2} complexes are [TcN$(tox)_2$] (tox = 8-quinolinethiolate) (*552*), [TcN{$(sacac)_2$en}] (*540*), and [TcN(Me_2CNNC(S)SMe$)_2$] (*592*). A novel complex is [TcN$(tmbt)_2L_2$], where L represents what is generally regarded as a "noncoordinating" proton sponge, 1,1,2,2-tetramethylguanidine. The Tc≡N bond distance and ν(TcN) are unexceptional at 1.615(6) Å and 1057 cm^{-1} (*581*). Neutral bisaminedithiolato and *N*-(*N*″-morpholinylthiocarbonyl)-*N*′-phenylbenzamidinato complexes have been prepared (*481, 595*).

F. IMIDO AND HYDRAZIDO COMPLEXES

The reaction of $[TcOX_4]^-$ (X = Cl, Br) with ArNCO in toluene yields the moisture-sensitive blue-black $[Tc(NAr)X_4]^-$ in high yield (*278*). Imido complexes containing phosphine ligands are formed from the reaction of $[TcOCl_4]^-$/organohydrazine or aromatic amine/phosphine (*278, 523*). Alternatively, TcO_4^- may be used as in the reaction with PPh_3/PhNHNHCOMe in methanol containing a minimal amount of HCl to give a good yield of the yellow-green octahedral imido complex [$TcCl_3$(NPh)$(PPh_3)_2$], with the phosphine ligands in trans positions. The Tc=N bond distance of 1.704(4) Å is longer than that in $[TcO]^{3+}$ or $[TcN]^{2+}$ complexes, but the Tc=N–C bond angle of 171.8(4)° confirms that the imido(2-) ligand is in the linear triply bonded form. This bonding mode is also consistent with the ν(TcN) IR absorption at 1090 cm^{-1}. Reaction with py/MeOH gives the mixed-ligand complex [$TcCl_3$(-NPh)(PPh_3)(py)] (*523, 596*). Similarly, in *fac*-[$TcCl_3$(NPh)(dppe)], ν(TcN) occurs at 1110 cm^{-1} and the Tc=N–C bond angle is 175.7(9)° (*523*). The hydrazido(2-) complex [$TcCl_3$(NNMePh)$(PPh_3)_2$] is formed by reaction of $[TcOCl_4]^-$/NH_2N(Me)Ph/PPh_3 in refluxing methanol. With less bulky phosphines, $[TcCl_2(NNMePh)(PMe_2Ph)_3]^+$ and the structurally characterized *trans*-[TcCl($NNMe_2$)$(dppe)_2$]PF_6 cations are formed (*278*). The hydrazido(2-) ligand in the dppe complex is coordinated in the linear (four-electron donor) mode. The reaction of MePhNH$_2$/dppe/$[TcOCl_4]^-$ in methanol, however, yields the cationic oxo-imido complex *trans*-$[TcO(NH)(dppe)_2]^+$, with marked asymmetry of imido complex *trans*-$[TcO(NH)(dppe)_2]^+$, with marked asymmetry of the two axial ligands shown by crystallography (*278*). The structurally characterized trigonal prismatic diazene complex $[Tc(HNNCSPh)_2(S_2CPh)]$ (*597*) and the octahedral hydralazino complex $[TcCl_2(C_8H_5N_4)(PPh_3)_2]$ (*598*) were assigned the Tc(V) oxidation state but an alternative assignment, that of Tc(I) and Tc(III) species, respectively, has been proposed (*523*). The deep-green thiobenzoyldiazene complex $NBu_4[Tc(HNNCSPh)_3]$ is also likely to be trigonal prismatic (*597*). Addition of HCl to $[Tc^{III}Cl(NNAr)_2(PPh_3)_2]$ yields the neutral $[TcCl_2(NNAr)(NNHAr)(PPh_3)_2]$ and addition of HBr yields the cationic doubly protonated $[TcBr_2(NNAr)(NHNHAr)(PPh_3)_2]Br$ (*277*). These complexes and the diazene complex $[Tc(C_8H_5N_2N{=}NH)_3]BPh_4$ have been assigned the Tc(I) oxidation state, but the ^{99}Tc NMR chemical shifts fall in the established Tc(V) region (*277, 599*).

G. COMPLEXES NOT CONTAINING MULTIPLY BONDED LIGANDS

Treatment of the 16-electron $[Tc^{III}(diars)_2Cl_2]Cl$ with chlorine results in oxidative addition, producing the brown 18-electron $[Tc^{V}(diars)_2Cl_4]Cl$ with a magnetic moment of 0.9 BM (*191*). The crystal structure of $[Tc(diars)_2Cl_4]PF_6$ shows D_{2d} dodecahedral eight-coordination geometry, with Tc–As bond distances of 2.578(2) and Tc–Cl bond distances of 2.442(4) Å (*295*). Reaction of $NBu_4[Tc^{V}O(abt)_2]$ with 12 M HCl yields the blue $NBu_4[Tc^{V}Cl_4(abt)]$ by removal of the oxo ligand in a formally nonredox process. The crystal structure and the magnetic moment of 2.86 BM establish the presence of Tc(V) and thus that the abt ligand is in the doubly deprotonated form (*600*). The Tc=O bond in $NBu_4[Tc^{V}O(abt)_2]$ is abnormally long [1.73(2) Å] (*496*) and appears to be susceptible to protonation as indicated by ^1H NMR evidence of an equilibrium between the anionic and the neutral species in wet $CDCl_3$ (*600*). Removal of the nitrido ligand in $AsPh_4[Tc^{VI}NCl_4]$ by 1,2-benzenedithiol and reduction gives a low yield of $AsPh_4[Tc^{V}(bdt)_3]$. The structure of the anion shows only small distortions from ideal trigonal prismatic geometry, with chelate twist angles for the three dithiolene ligands of 1.1°, 16.3°, and 5.8°, compared with the ideal value of 0° (*360*). This complex is more conveniently prepared in quantitative yield by the reduction of TcO_4^- by $bdtH_2$ in refluxing $EtOH/H_2O/HCl$ (*558*). The intermediate $[Tc^{V}O(bdt)_2]^-$ is the kinetically controlled product formed at room temperature. The thermodynamic product $[Tc(bdt)_3]^-$ is then formed by removal of the oxo ligand in a formally nonredox process. A related complex is $[Tc(abt)_3]^-$ (*601*).

IX. Technetium(VI)

The $[Tc^{VI}O]^{4+}$ core is highly susceptible to hydrolysis and disproportionation and unlike $[Tc^{V}O]^{3+}$ is not readily stabilized by coordination. The nitrido ligand is, however, very effective in stabilizing Tc(VI) as $[TcN]^{3+}$. A characteristic feature is the formation of dimeric $[NTcOTcN]^{4+}$ and $[NTc(\mu\text{-}O)_2TcN]^{2+}$ complexes that have no analogs for any other transition metal. Complexes not containing an oxo, nitrido, or imido ligand are relatively few and confined to fluorides and complexes with dithiolene and other noninnocent ligands. Monomeric Tc(VI) (d^1) is easily and reliably detected by EPR spectroscopy (*40*), but the dimeric species are EPR silent due to spin pairing (*602*). The only binary halide, and the highest fluoride for Tc, is the golden-yellow TcF_6, prepared by the reaction of fluorine gas on the metal powder (*603, 392*). Reaction of TcF_6 with NOF and NO_2F yields $(NO)_2[TcF_8]$ and $NO_2[TcF_7]$, respectively. Magnetic moments of 1.72 and 1.67 BM confirm the +6 oxidation state (*394*).

A. OXO COMPLEXES

The TcO_4^{2-} and ReO_4^{2-} anions are rather less stable than MnO_4^{2-}. Pulse radiolysis and cyclic voltammetry have shown that in alkaline aqueous solution TcO_4^{2-} has a lifetime of the order of milliseconds (*604*). In neutral solution TcO_4^{2-} decays by a second-order process, about 100-fold more slowly than ReO_4^{2-} (*605, 606*). The pK_{a1} of H_2TcO_4 is estimated to be ≥ -0.5 (*607*). The paramagnetic, violet $(NMe_4)_2[TcO_4]$ [$\mu_{eff} = 1.60$ BM; ν(TcO) at 780 cm^{-1}] has been prepared by electrochemical reduction of TcO_4^- in MeCN with rigorous exclusion of air and water. The salt is extremely sensitive to air and atmospheric moisture, which cause rapid oxidation and disproportionation (*608, 609*). Fluorination of Tc yields the blue $[TcOF_4]$ (m.p., 134°C) as a by-product (*392*). The blue monoclinic form is isostructural with $ReOF_4$, the structure of which consists of infinite chains of F-bridged octahedra (*610*). A minor product, the green hexagonal form, is the F-bridged cyclic trimer with a Tc=O bond distance of 1.66(3) Å (*611*). The purple, light-sensitive $[TcOCl_4]$ has been prepared from the chlorination of Tc metal (*326*). Reduction of TcO_4^- by HCl in concentrated H_2SO_4 gives a deep-blue solution ($\lambda_{max} = 572$ nm), shown by the EPR spectrum to be a Tc(VI) species, most likely $[TcOCl_5]^-$, although the presence of $[TcOCl_4]$ cannot be totally excluded. The EPR parameters are $g_{\parallel} = 2.057$, $g_{\perp} = 1.938$, $A_{\parallel} = 230 \times 10^{-4}$, and $A_{\perp} = 96 \times 10^{-4}$ cm^{-1}. After 1 hr the blue color vanishes and the EPR signal decreases (*612*). Unstable deep-blue solutions containing Tc(VI) oxochloro complexes are also formed by the reduction of $AsPh_4TcO_4$ in $SOCl_2$ or $POCl_3$ (*613*). The reaction of Tc_2O_7 with $SnMe_4$ gives the sublimable organometallic bis(μ-oxo) dimer (**54**) (*228*). Coordination about each Tc atom is distorted square–pyramidal with Tc═O bond distances of 1.666(2) and 1.647(2) Å and Tc–O_{bridge} distances of 1.900(2)–1.925(2) Å. The dimer has been reported to be paramagnetic on the basis of the absence of ^{99}Tc NMR signals but the Tc–Tc distance of 2.5617(3) Å would seem to indicate a single bond and consequent diamagnetism.

(**54**)

B. Nitrido Complexes

1. *Monomeric* $[TcN]^{3+}$ *Complexes*

The reaction of TcO_4^-/NaN_3 in refluxing HX (X = Cl, Br) gives high yields of orange-red R[$TcNCl_4$] and intensely blue R[$TcNBr_4$] (R = $AsPh_4$, NBu_4] on precipitation with the organic cations (*614*). The structure of the square–pyramidal $[TcNCl_4]^-$ is shown in Fig. 16. These

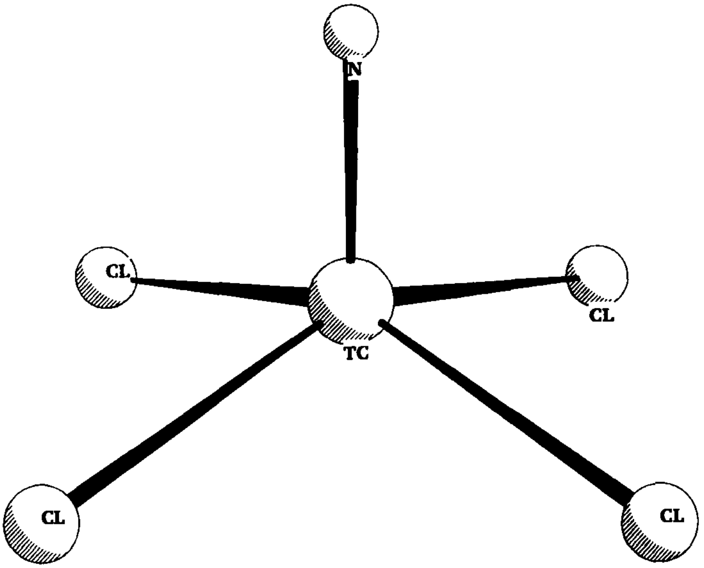


FIG. 16. The structure of the $[TcNCl_4]^-$ anion in $AsPh_4[TcNCl_4]$ (*614*).

salts are air-stable and the remarkable resistance of the $Tc^{VI}N$ bond to acid hydrolysis is apparent from the method of preparation. Evaporation of the MeCN extract of the dried $TcO_4^-/NaN_3/HCl$ reaction mixture and dissolution of the residue in concentrated HCl yield an orange-red solution that probably contains $HTcNCl_4$. Addition of CsCl to this solution gives red crystals of the six-coordinate $Cs_2[TcNCl_5]$ (*552*), whereas NEt_4Cl gives orange crystals of (NEt_4)*trans*-$[TcN(OH_2)Cl_4]$ (*615*). The aqua complex (NEt_4)*trans*-$[TcN(OH_2)Br_4]$ may be prepared in high yield directly from the TcO_4^- $/NaN_3/HBr$ reaction. In concentrated HX solution the major species is most likely $[TcN(OH_2)X_4]^-$ (*615*). The $[TcNCl_4]^-$ anion is also formed by the oxidation of Tc^VN species (*554, 586, 616*) and substitution/oxidation of $[TcOCl_4]^-$ with azide (*617*). The reaction of NH_2OSO_3H with TcO_4^-/HCl also yields $[TcNCl_4]^-$ and shows that a single amine nitrogen attached to a good leaving group may serve as an N^{3-} precursor, but the product is contaminated with nitrosyl species and $[TcCl_6]^{2-}$ (*558*). The structural features observed for the isoelectronic $[Tc^VN]^{2+}/[Tc^VO]^{3+}$ pairs are again apparent in a comparison of the $[Tc^{VI}N]^{3+}/[Tc^VO]^{3+}$ pairs in Table V. The nitrido ligand exerts the greater *trans* influence, in terms of the *trans*-NTc–OH_2 bond distance in the aqua complexes, but the OTcX angles are greater than the NTcX angles and the displacement of Tc above the square basal or equatorial plane is consequently greater for the oxo complexes. Also, the Tc–X bond distances are significantly greater

TABLE V

STRUCTURAL AND IR DATA FOR $[Tc^{VI}N]^{3+}$ HALIDE COMPLEXES AND SOME $[Tc^VO]^{3+}$ ANALOGS

Complex	Tc≡N/=O (Å)	Tc—X (Å)	Tc—OH_2 (Å)	O/N—Tc—X (°)	δ[a] (Å)	ν(TcN)/(TcO) (cm^{-1})	Ref.
$AsPh_4[TcNCl_4]$[b]	1.581(5)	2.3220(9)		103.34(3)	0.54	1076	614
$AsPh_4[TcOCl_4]$	1.593(8)	2.309(2)		106.8(1)	0.67	1025	409
$AsPh_4[TcNBr_4]$	1.596(6)	2.4816(5)		103.04(2)	0.56	1074	618
$AsPh_4[TcOBr_4]$	1.613(9)	2.460(1)		106.59(3)	0.70		410
$NEt_4[TcN(OH_2)Br_4]$	1.559(9)	2.510(1) 2.518(1)	2.443(7)	97.2(2) 98.0(2)	0.33	1063	615
$NEt_4[TcO(OH_2)Br_4]$	1.618(9)	2.505(1) 2.508(1)	2.317(9)	97.6(2) 99.5(3)	0.37	1000	405
$[Rb(15\text{-crown-}5)_2]$ $[TcN(OH_2)Cl_4]$	1.600(3)	2.320(2)	2.43(4)	94.5(2)		1074	619
$Cs_2[TcNCl_5]$	1.600[c]	$2.373(5)_{cis}$ $2.740(5)_{trans}$		99.73(8)	0.401	1027	615

[a] Displacement of Tc above the square basal or equatorial plane.

[b] The $[TcYX_4]^-$ (Y = N, O) anions have ideal C_{4v} symmetry.

[c] Value fixed in the refinement due to the statistical disorder of the ligands in the cubic space group.

for the nitrido complexes. The ν(TcN) IR absorption occurs at higher energy than that of ν($Tc^{V}O$) but this difference may be accounted for, either partially or entirely, by the greater mass of the ^{16}O atom. Thus, the difference betwen ν($Tc^{14}N$) at 1076 cm^{-1} for $AsPh_4[TcNCl_4]$ and ν($Tc^{16}O$) at 1025 cm^{-1} for $AsPh_4[TcOCl_4]$ is less than the 61 cm^{-1} calculated by the simple diatomic oscillator model. The presence of *trans* halide in $Cs_2[TcNX_5]$ (X = Cl, Br) results in the decrease of ν(TcN) to 1027 (X = Cl) and 1028 cm^{-1} (X = Br) from the values of 1076 and 1074 cm^{-1} for $AsPh_4[TcNX_4]$ (*552, 614, 620*). The $NEt_4[TcN(OH_2)Cl_4]$ complex undergoes complete dehydration to $NEt_4[TcNCl_4]$ under vacuum and the aqua complex is reformed on exposure to atmospheric moisture. The small change in ν(TcN) from 1065 to 1070 cm^{-1} on removal of the *trans* water is indicative of very weak binding and of a Tc–OH_2 bond distance in the aquachloro complex that is longer than that in $NEt_4[TcN(OH_2)Br_4]$, which does not undergo dehydration under the same conditions (*615*). The $[Rb(15\text{-crown-}5)_2][TcN(OH_2)Cl_4]$ salt contains $[Rb(15\text{-crown-}5)_2]^+$ sandwich cations and isolated anions, with an NTc–OH_2 bond distance of 2.43(4) Å and ν(TcN) at 1074 cm^{-1}. Because this salt is prepared from $SOCl_2$ solution, the coordinated water presumably arises from atmospheric moisture (*619*).

The $4d^1$ ($S = \frac{1}{2}$) configuration of Tc(VI) results in readily observed EPR spectra at temperatures of >77 K (*40, 41*). The spectra of $[TcNX_4]^-$ (X = Cl, Br) have been examined in detail (*620, 621*), including single-crystal EPR, electron nuclear double resonance (ENDOR), and electron spin echo envelope modulation (ESEEM) studies of ^{15}N-enriched $AsPh_4$-$[TcNCl_4]$ doped into the diamagnetic $AsPh_4[TcOCl_4]$ host (*622, 623*), as well as single-crystal EPR and ^{15}N powder ENDOR studies of $NBu_4[TcNBr_4]/[TcOBr_4]$ (*624*). The molecular orbital of the unpaired electron is a combination of the Tc d_{xy} and equatorial ligand p orbitals. Analysis of the hyperfine data for $AsPh_4[TcNCl_4]$ indicates 20% of the spin density is localized in the 3p orbitals of the Cl atoms (*622*), but a polarized neutron diffraction study has shown exceptionally high covalence of the Tc–Cl bonds, with 46(5)% of the spin density located on the Cl atoms (*625*). Interestingly, $AsPh_4(CF_3SO_3)$ may also serve as a host lattice for $AsPh_4[TcNCl_4]$, giving an extremely well-resolved spectrum at 130 K (*619*). EPR spectroscopy has proven particularly useful for the identification of $[TcN]^{3+}$ species in solution and the monitoring of ligand-exchange reactions. Mixed-ligand $[TcNBr_{4-n}Cl_n]^-$ (n = 1–3) species have been identified in mixtures of $[TcNCl_4]^-$ and $[TcNBr_4]^-$ and equilibrium constants, determined (*579, 626, 627*). Mixed species are readily assigned because the EPR parameters are nearly linearly dependent on the spin–orbit coupling constants of the equatorial donor ligands (*40, 579, 626, 628*). A 0.002 M solution of $Cs_2[TcNCl_5]$ in 28.6 *M* HF shows the presence of the five $[TcNF_{4-n}Cl_n]^-$ ($n = 0$–4) species, presumably due to the low activity of fluoride ion in the solution. Partial removal of Cl^- by the addition of 1 eq. of AgF results in the disappearance of signals due to $[TcNCl_4]^-$ and $[TcNFCl_3]^-$, and after the addition of 3 eq. of AgF only signals due to $[TcNF_3Cl]^-$ and $[TcNF_4]^-$ remain. The $[TcNF_4]^-$ species may be prepared in solution by the dissolution of "$TcN(OH)_3$" in 50% HF but has not been isolated. The EPR parameters for $[TcNF_4]^-$ are $g_\parallel = 1.895$, $g_\perp = 1.990$, $A_\parallel = 377 \times 10^{-4}$, and $A_\perp = 179 \times 10^{-4}\ cm^{-1}$ (*628*). EPR studies of $AsPh_4[TcNX_4]$ (X = Cl, Br) in organic solvents in the presence of a large molar ratio of X^- and of $Cs_2[TcNX_5]$ (X = Cl, Br) in HX solution show no evidence for the equilibrium (*620*)

$$[TcNX_4]^- + X^- \rightleftharpoons [TcNX_5]^{2-}$$

The mixed-ligand species $[TcNCl_3(CN)]^-$ and $[TcNCl_2(CN)_2]^-$ have been identified by EPR in the reaction of $[\{TcN(CN)_2\}_2(\mu\text{-}O)_2]^{2-}$ with HCl (*565*), $[TcNBr_3(NCS)]^-$ and $[TcNBr_2(NCS)_2]^-$ in the reaction of $[TcNBr_4]^-$ with NCS^- (*579*), and $[TcNX_n(N_3)_{4-n}]^-$ (X = Cl, Br; $n = 1$–4) in the reaction of $NBu_4[TcNX_4]$ with azide in acetone (*629*). Also, a variety of $[TcN]^{3+}$ species such as $[TcN(HSO_4)_4]^-$ and $[TcN(H_2PO_4)_4]^-$ have been identified in concentrated acid solution (*630*). The oxidation of $[Tc^VNCl_2(EPh_3)_2]$ (E = P, As) to $[TcNCl_4]^-$ by $SOCl_2$ has been shown by EPR to proceed via the Tc(VI) species $[TcNCl_3(EPh_3)]$ (*586*).

Substitution of $R[TcNX_4]$ in organic solvents occurs readily but generally results in reduction and the $[Tc^VN]^{2+}$ substituted product. Thus, reaction with PPh_3, KNCS, $Na(S_2CNEt_2)$, and 8-quinolinethiol yields $[TcNCl_2(PPh_3)_2]$, $(NEt_4)_2[TcN(NCS)_4(MeCN)]$, $[TcN(S_2CNEt_2)_2]$, and $[TcN(C_9H_6NS)_2]$, respectively (*552*). Reduction also occurs upon substitution by nonreducing ligands such as bpy or phen (*146, 578*). Substitution reactions in which the Tc(VI) oxidation state is retained are the reaction of $AsPh_4[TcNCl_4]$ with LiBr in acetone to give $AsPh_4[TcNBr_4]$ and of $NBu_4[TcNBr_4]$ with $(sal)enH_2$ to form $[TcN\{(sal)en\}]Cl$ (*552, 631*). Attempts to prepare $R[TcNI_4]$ by ligand exchange with LiI in acetone result in oxidation of iodide to iodine. The ease of reduction of $[TcNX_4]^-$ (X = Cl, Br) and the inability to prepare $[TcNI_4]^-$ may be understood in terms of the lowest energy $\pi X \rightarrow Tc$ LMCT transitions at 18,975 cm^{-1} (X = Cl) and 13,100 cm^{-1} (X = Br) for $NBu_4[TcNX_4]$ in MeCN (*632*). According to the theory of charge-transfer spectra and the optical electronegativity difference of 0.5 between Cl^- (π) and I^- (π), substitution of iodide for chloride is expected to result in a red shift of ~15,000

cm^{-1} for the lowest energy Laporte-allowed LMCT transition (*633*). An LMCT transition may be regarded as the transfer of an electron from a predominantly ligand orbital to a predominantly metal orbital and, if the energy difference is less than about 10,000 cm^{-1}, then, commonly, there will be total electron transfer, resulting in reduction of the metal and oxidation of the ligand (*634*). For $[TcNI_4]^-$ in organic solvents the first LMCT band is calculated to be at ~4000 cm^{-1} and a facile redox reaction is apparent. The $[TcNL_4]^-$ (L = HSO_4, H_2PO_4) species are colorless and show only an intense absorption at 33,800 and 37,600 cm^{-1}, respectively, which has been assigned to a $\pi N \rightarrow$ Tc LMCT transition (*630*).

The formation of $[^{99m}TcNCl_4]^-$ on reaction of $^{99m}TcO_4^-/NaN_3/HCl$ has been established (*635*). After removal of HCl the residue is stable to oxidation under acidic conditions but undergoes oxidation to $^{99m}TcO_4^-$ at pH > 4 (*636*). Addition of ligand solutions results in the formation of ^{99m}TcN complexes with biological distributions different from those of ^{99m}Tc complexes prepared from $^{99m}TcO_4^-$ and the ligand by use of Sn^{2+} or other reducing agents. In general, the ^{99m}TcN complexes are cleared from the blood more slowly, indicating greater *in vivo* reactivity and the exchange of ^{99m}TcN with serum proteins. Although reaction of $[^{99m}TcNCl_4]^-$ with thiolato ligands leads to reduction to Tc(V), the oxidation state with ligands such as gluconate or phosphonates is unclear (*635*).

2. *Dimeric and Polymeric* $[TcN]^{3+}$ *Complexes*

The very moisture-sensitive neutral $TcNCl_3$ may be prepared by the reaction of $TcCl_4$ with IN_3 or $NBu_4[TcNCl_4]$ with $GaCl_3$. The IR spectrum indicates a polymeric structure with TcNTc and $TcCl_nTc$ bridges. $TcNCl_3$ is insoluble in CH_2Cl_2 but dissolves on addition of $AsPh_4Cl$ due to the formation of $AsPh_4[TcNCl_4]$ (*637*). Addition of 18-crown-6 to a suspension of $Cs_2[TcNCl_5]$ in $SOCl_2$ results in the formation of an orange-red solution, which on slow evaporation of the solvent yields crystals of $[Cs(18\text{-crown-}6)][TcNCl_4]$ (*619, 638*). The structure consists of the unprecedented "infinite sandwich" M^+/crown ether configuration with ordered and disordered infinite chains of $[TcNCl_4]^-$ anions arranged in an antiparallel fashion (Fig. 17a). In the ordered $Tc{\equiv}N\cdots Tc{\equiv}N\cdots$ chain the $Tc{\equiv}N$ and $N\cdots Tc$ bond distances are 1.561(36) and 2.714(36) Å, respectively. An unusual aspect of the structure is that the nearest neighbors of each Cs^+ cation are two Cs^+ cations at 4.275 Å, whereas the Tc atoms of the four nearest anions are at 7.95 Å and the nearest $Cs^+\cdots Cl$ contacts are 6.4–6.6 Å. Also, although each Cs^+ cation has neighbors at 4.275, 8.55, and 12.825 Å along each vertical column,

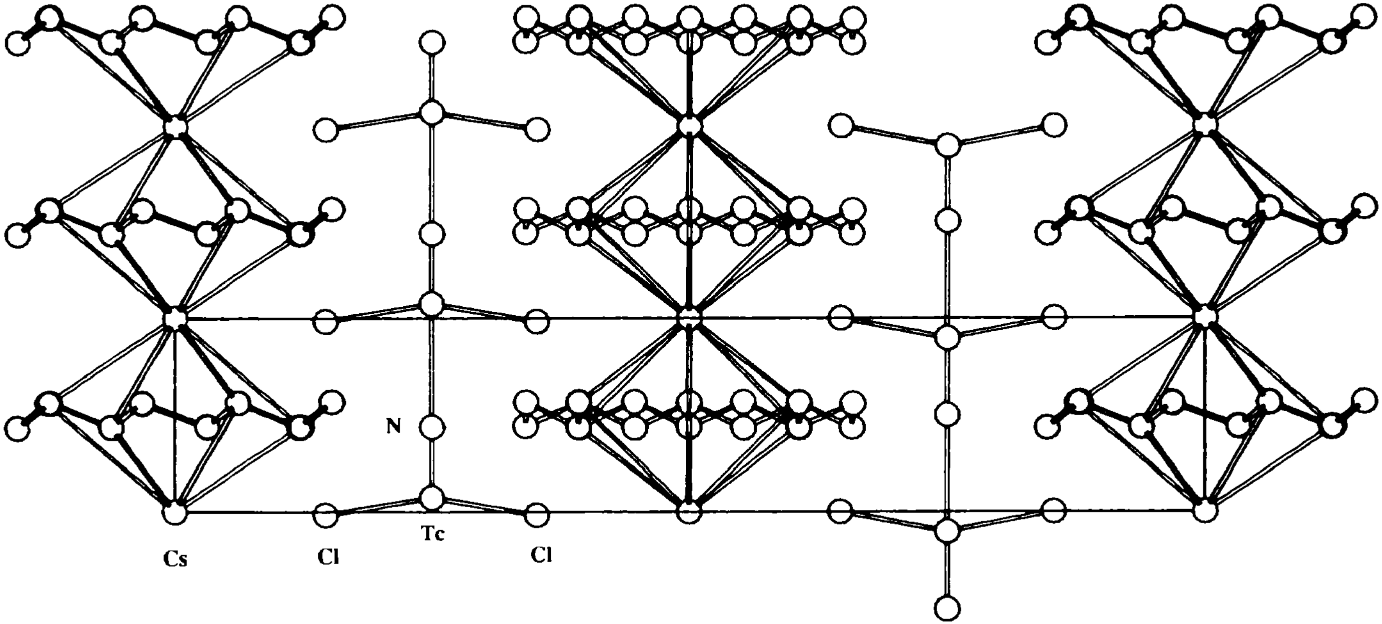


FIG. 17a. The structure of polymeric [Cs(18-crown-6)][$TcNCl_4$] viewed down the *b* axis (*619*).

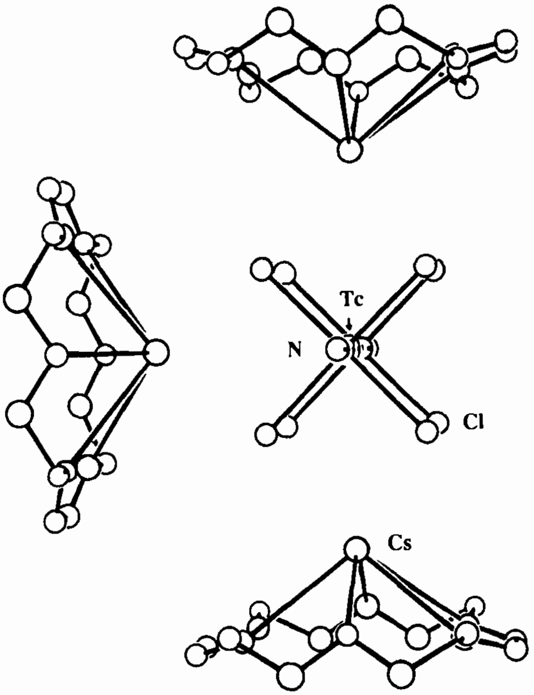
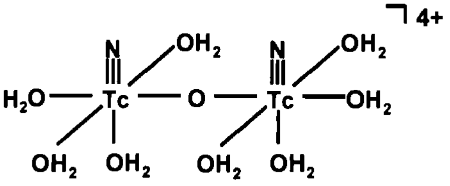


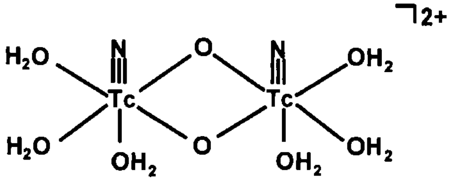
FIG. 17b. A portion of the structure of $[Cs(18\text{-crown-}6)]_4[(TcNCl_4)_4(OH_2)_3]$ *(639)*.

in the horizontal plane the nearest Cs^+ neighbors are at 11.23 Å. The IR spectrum shows a single $\nu(TcN)$ absorption at 1041 cm^{-1}, but partial ^{15}N labeling results in complex behavior due to the coupling of TcN oscillators in the infinite $[TcNCl_4]^-$ chains and is diagnostic for this arrangement. At a 12.5% ^{15}N content the spectrum shows essentially two peaks, at 1042 and 1025 cm^{-1}, with the latter peak being predominantly due to $^{14}NTc\cdots{}^{15}NTc\cdots{}^{14}NTc$ groupings. With 50% ^{15}N content, the major ^{15}NTc absorption at 1015 cm^{-1} is strong but the ^{14}NTc absorptions are reduced to two weak shoulders at 1053 and 1045 cm^{-1}. The EPR spectra over the temperature range 130–290 K indicate the presence of exchange interactions along the $\cdots TcN\cdots TcN\cdots$ chains *(619)*. Recrystallization of the infinite sandwich $[Cs(18\text{-crown-}6)][TcNCl_4]$ from MeCN, acetone, or ethanol, or the reaction of $Cs_2[TcNCl_5]$ with 18-crown-6 in 6 *M* HCl, yields $[Cs(18\text{-crown-}6)]_4[(TcNCl_4)_4(OH_2)_3]$ with two $\nu(TcN)$ absorptions at 1055 and 1046.5 cm^{-1}, which are shifted to 1023 and 1016 cm^{-1} on ^{15}N labeling. Ether diffusion into an MeCN solution of the aqua complex may result in the crystallization of either the infinite sandwich or a mixture of the infinite sandwich and the aqua complex. The crystal structure of the aqua complex shows dimeric $[N{\equiv}TcCl_4{\cdots}N{\equiv}Tc(OH_2)Cl_4]^{2-}$ units inside a square cage formed by four $[Cs(18\text{-crown-}6)]^{+}$ cations, with two monomeric $[TcN(OH_2)Cl_4]^{-}$ units present in the lattice (Fig. 17b) (*639*). The $[(H_3O)(18\text{-crown-}6)]_2[(TcNCl_4)_2(OH_2)]$ complex has also been isolated and shown by crystallography to contain only dimeric $[N{\equiv}TcCl_4{\cdots}N{\equiv}Tc(OH_2)Cl_4]^{2-}$ units (*639*). Reaction of $NBu_4[TcNCl_4]$ with $(NBu_4)_4[H_3PW_{11}O_{39}]$ in MeCN results in the incorporation of TcN to give dark crystals of the Keggin polyoxotungstate derivative $(NBu_4)_4[PW_{11}TcNO_{39}]$, for which the Tc(VI) oxidation state is thought to be retained (*548*).

A characteristic feature of the chemistry of $[TcN]^{3+}$ is the formation of dimeric complexes based on the $[NTc\text{-}O\text{-}TcN]^{4+}$ and $[NTc(\mu\text{-}O)_2TcN]^{2+}$ cores (*423, 565, 630, 640*). Analogous nitrido complexes are not known for any other transition metal but the chemistry and structural aspects of the $Tc^{VI}N$ dimers parallel those of the well-known isoelectronic $[OMo^{V}\text{-}O\text{-}Mo^{V}O]^{4+}$ and $[OMo^{V}(\mu\text{-}O)_2Mo^{V}O]^{2+}$ dimers (*640, 641*). Hydrolysis of $Cs_2[TcNCl_5]$ in an ample quantity of water gives a brown precipitate of "$TcN(OH)_3$," which has been formulated as the bis(μ-oxo) dimer $[\{TcN(OH)(OH_2)\}_2(\mu\text{-}O)_2]$ (**55**) on the basis of its reactions and the presence of ν(TcOTc) absorptions in the IR spectrum (*628, 640*). This precipitate is the isoelectronic analog of "$MoO(OH)_3$," a compound of unknown structure (*641*). Solutions of **55** in 7.5 *M* CF_3SO_3H (a very weakly coordinating medium) are orange (λ_{max} = 474 nm) and EPR silent, showing the absence of monomeric species. The monomeric aqua cation $[TcN(OH_2)_5]^{3+}$ is thus not a viable species even in strongly acid solution and appears to spontaneously dimerize to the μ-oxo aqua cation $[\{TcN(OH_2)_4\}_2(\mu\text{-}O)]^{4+}$ (**56**) (*630*).



(**56**)



(**57**)

Solutions of **55** in 1 *M* *p*-toluenesulfonic acid, CF_3SO_3H, or $MeSO_3H$ are pale yellow and shown by paper electrophoresis to contain a single cationic species (*630, 640*). Also, dilution of a solution of **56** in 7.5 *M* CF_3SO_3H leads to the slow formation of the yellow species. That this species is the bis(μ-oxo) aquanitrido cation $[\{TcN(OH_2)_3\}_2(\mu\text{-}O)_2]^{2+}$ (**57**) is indicated by the similarity of the electronic spectrum to that of the well-established $[\{MoO(OH_2)_3\}_2(\mu\text{-}O)_2]^{2+}$ cation, the absence of EPR signals, and the isolation of $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ on reaction with

$Na(S_2CNEt_2)$ (*602*). Structure **57** has been confirmed in solution by EXAFS studies, but the actual number of coordinated water molecules is uncertain (*642*). Addition of ethanol to a solution of **55** in aqueous CsOH precipitates the yellow $Cs_2[\{TcN(OH)_2\}_2(\mu\text{-}O)_2]$ with ν(TcN) at 1046 cm^{-1} and ν(TcOTc) at 734 cm^{-1}. On treatment with HCl this salt is converted to $[TcNCl_4]^-$ (*640*).

The only μ-oxo complex to have been isolated and structurally characterized is the cyclic tetramer $(AsPh_4)_4[Tc_4N_4(O)_2(ox)_6]$ prepared by the reaction of $AsPh_4[TcNCl_4]$ with oxalic acid in aqueous acetone (*423*). The centrosymmetric structure consists of two [(ox)TcN–O–TcN(ox)] units joined by two tetradentate oxalates (Fig. 18). The Tc≡N bond distances are 1.639(17) and 1.606(17) Å and the Tc–O–Tc bridges are only approximately linear,with angles of 150.4(8)° and Tc–O_{bridge} distances of 1.840(13) and 1.869(13) Å. A marked asymmetry due to the *trans* influence of the nitrido ligand is apparent in the Tc–O bond distances of the bridging oxalates, with NTc–O_{trans}, 2.410(11) and 2.369(12) Å, and NTc–O_{cis}, 2.076(11) and 2.061(11) Å. The μ-oxo structure of the oxalato complex with the nitrido ligands *cis* to the oxygen

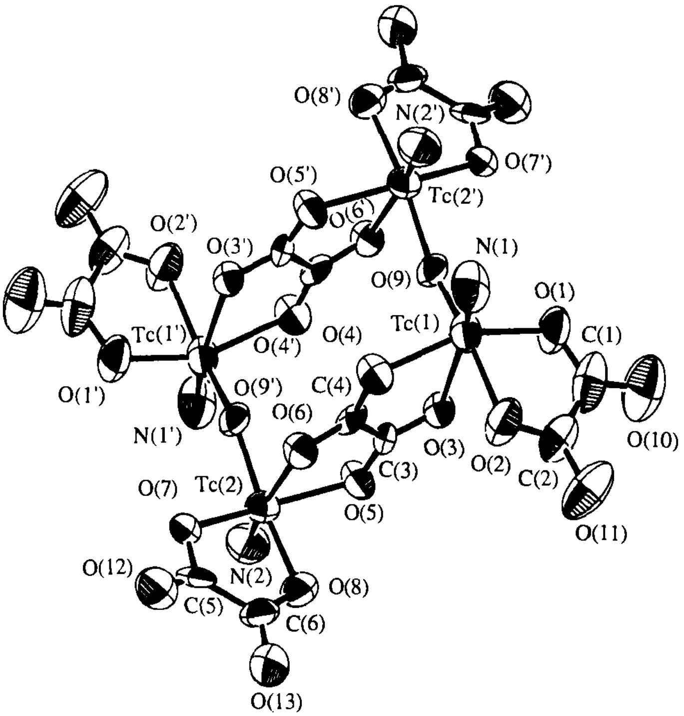


FIG. 18. The structure of the anion in $(AsPh_4)_4[Tc_4N_4(O)_2(ox)_6]$ (*423*).

bridge may be contrasted to the linear (or near linear) $[OTc^{V}–O–Tc^{V}O]^{4+}$ $d^2–d^2$ dimers, in which the oxo ligands are *trans* to the oxygen bridge. This difference in geometry is explained in terms of closed-shell electronic structures. In the *syn* conformer (C_{2v} symmetry) shown in **56** and **60** [and also for an *anti* conformer (C_{2h} symmetry)], only one molecular orbital is available for the metal d electrons and the Tc(VI) $d^1–d^1$ configuration will thus satisfy the closed-shell requirement (*544*).

Addition of $AsPh_4Cl$ and then HCl to a solution of $Cs_2[TcNCl_5]$ in water with sufficient $MeSO_3H$ added to dissolve the initial precipitate gives a high yield of the yellow $(AsPh_4)_2[(TcNCl_2)_2(\mu\text{-}O)_2]$, and the bromo complex may be similarly prepared (*643*). Dithiocarbamato, cyano, and ethanedithiolato complexes have been prepared by the addition of the ligand to solutions of $Cs_2[TcNCl_5]$ in aqueous $Na_4P_2O_7$ (*565*). The structure of the $[(TcNCl_2)_2(\mu\text{-}O)_2]^{2-}$ anion (*643*) in Fig. 19 shows the features of the TcO_2Tc ring system and structural data are given in Table VI. The geometry of the $[Tc_2N_2O_2]^{2+}$ complexes may be described as two square pyramids sharing the bridging oxygens to give a bent Tc_2O_2 ring. Each Tc atom is displaced above the plane of the four basal donor atoms by 0.50–0.67 Å. A comparison of the isostructural $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ and $[\{MoO(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ (*644*) again shows the greater effect of the oxo ligand, with the Mo atoms displaced by 0.73 Å above the square basal planes compared with 0.65 Å for the Tc atoms (*565*). The Tc–Tc distances of 2.542(2)–2.591(1) Å correspond to a $d_{xy}{}^1–d_{xy}{}^1$ single bond and account for the absence of EPR spectra. The two nitrogen atoms in $[Tc_2N_2O_2]^{2+}$ complexes are

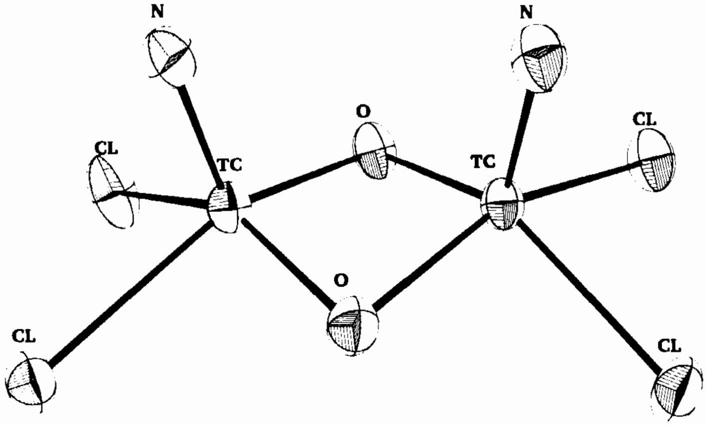


FIG. 19. The structure of the $[(TcNCl_2)_2(\mu\text{-}O)_2]^{2-}$ anion (*643*).

TABLE VI

STRUCTURAL DATA FOR $[NTc(\mu\text{-}O)_2TcN]^{2+}$ DIMERS

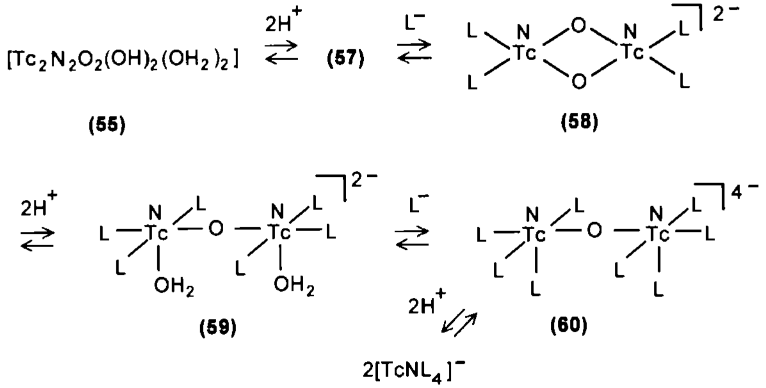
Complex	Tc≡N (Å)	Tc—Tc (Å)	Tc—O_{bridge} (Å)	δ-sbp[a] (Å)	Ref.
$(AsPh_4)_2[\{TcNCl_2\}_2(\mu\text{-}O)_2]$	1.648(8) 1.650(8)	2.579(1)	1.896(7)–1.953(5)	0.54(1) 0.52(1)	632
$(AsPh_4)_2[\{TcNBr_2\}_2(\mu\text{-}O)_2]$	1.610(13)	2.575(1)	1.93(1)–1.95(1)	0.59(1)	632
$(AsPh_4)_2[\{TcN(CN)_2\}_2(\mu\text{-}O)_2]$	1.70(1)	2.560(2)	1.921(9)–1.924(9)	0.50	557
$[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$	1.623(4) 1.624(4)	2.543(1)	1.935(3)–1.942(3)	0.65(1) 0.65(1)	565
$[\{TcN(S_2CNC_4H_8)\}_2(\mu\text{-}O)_2]$	1.65(2) 1.59(2)	2.542(2)	1.934(13)–1.947(12)	0.65(1) 0.67(1)	565

[a] Displacement of Tc atom above the square basal plane.

bent back from each other to an N···N contact distance of 3.3–3.5 Å. In the absence of this bending the N···N distance would be the same as the Tc–Tc bond distance and rather shorter than the van der Waals contact distance of about 3.1 Å (*632*). The TcO_2Tc ring system is readily detected in the IR spectrum by the presence of a strong asymmetric stretching mode at 710–700 cm^{-1} and a weaker symmetric mode at 515–450 cm^{-1}. These assignments have been confirmed by ^{18}O labeling (*565, 632*). All dimers have the *syn* stereochemistry shown in Fig. 19 and show two ν(TcN) absorptions as a result of the in-phase and out-of-phase vibration of the coupled TcN oscillators. For $(AsPh_4)_2[(TcNX_2)_2(\mu\text{-}O)_2]$ these absorptions occur at 1063 and 1054 cm^{-1} (X = Cl) and 1059 and 1051 cm^{-1} (X = Br) (*632*). Surprisingly, $(AsPh_4)_2[\{TcN(CN)_2\}_2(\mu\text{-}O)_2]$ does not show significant ν(CN) IR absorptions (*565*). The crystal structure, however, shows the CN bond distances to be normal, at 1.12–1.18 Å (*643*).

The formation of bis(μ-oxo) dimers greatly reduces the susceptibility of $Tc^{VI}N$ to reduction. Thus, reaction of $(AsPh_4)_2[(TcNCl_2)_2(\mu\text{-}O)_2]$ with $Na(S_2CNEt_2)$ in MeCN gives $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ in good yield, whereas reaction of $[TcNCl_4]^-$ in the same solvent gives only the reduced $[Tc^VN(S_2CNEt_2)_2]$ (*565*). The TcO_2Tc bridge is readily cleaved by HCl in organic solvents. This reaction allows the preparation of Tc(VI) species such as $[TcNCl_2(S_2CNEt_2)]$, which are not accessible by partial substitution of $[TcNCl_4]^-$. The electronic spectra of the bis(μ-oxo) dimers do not show pronounced visible absorptions (*565, 632*).

The interconversions and equilibria of $[TcN]^{3+}$ species in solutions of inorganic and organic acids have been studied by UV–visible and EPR spectroscopy (*630, 643, 645*) and are described by Scheme 1. Monomeric species are identified by their EPR spectra. The μ-oxo dimers

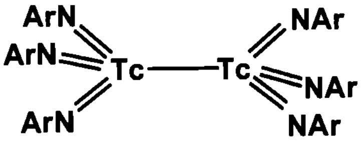


SCHEME 1. L = monoanionic ligand.

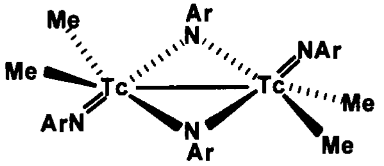
are readily distinguished from bis(μ-oxo) dimers by the intense visible absorption at 470–580 nm, which arises from a transition in the three-center $Tc\overset{\cdot\cdot}{-}O\overset{\cdot\cdot}{-}Tc$ π-bond system. High acidity and the presence of coordinating anions such as Cl^- favor the monomeric species. The reaction sequence may occur in either direction, depending on whether **55** or $Cs_2[TcNCl_5]$ is dissolved in the acid. Solutions of $Cs_2[TcNCl_5]$ in 3.33 *M* HCl show only the presence of $[TcNCl_4]^-$ whereas in 0.5 *M* HCl a pink species (λ_{max} = 538 nm) is formed. If $Cs_2[TcNCl_5]$ is first hydrolyzed and then HCl added to 3.33 *M*, an intensely blue species (λ_{max} = 566 nm) that is converted to $[TcNCl_4]^-$ by first-order kinetics is formed. The pink and blue species have been formulated as **59** and **60** (L = Cl), respectively (*632, 643*). At low acid concentrations the interconversions are slow and paper electrophoresis is a useful technique for the separation of species. Thus, when $Cs_2[TcNCl_5]$ is dissolved in 0.5 *M* H_2SO_4 an orange anionic species and a colorless slow moving cationic species (with some SO_4^{2-} coordination) may be separated (*630*). The presence of μ-oxo and bis(μ-oxo) dimers in HCl and H_2SO_4 solutions has been confirmed by EXAFS studies (*642*).

C. IMIDO AND HYDRAZIDO COMPLEXES

The reaction of $[Tc(NAr)_3I]$ with Na/THF at room temperature yields the homoleptic diamagnetic dimer $[Tc_2(NAr)_6]$ (Ar = 2,6-diisopropylphenyl). The dimer is air-stable in solution and adopts an unprecedented "ethane-like" structure (**61**), with the six imido ligands symmetry equivalent in a staggered arrangement.



(61)



(62)

The unsupported Tc–Tc single bond distance is 2.744(1) Å and the Tc═N bond distances are 1.758(2) Å (*646*). Reduction of [Tc(NAr)$_3$I] (Ar = 2,6-dimethylphenyl) with 1 eq. of Na gives the dimer [Tc$_2$-(NAr)$_4$(μ-NAr)$_2$], which on reaction with MeMgCl undergoes the unprecedented substitution of imido by methyl groups to give successively [TcMe$_2$(NAr)(μ-NAr)$_2$Tc(NAr)$_2$] and tetramethyl derivative (**62**) (*647*). The Tc–Tc bond distances in the dimethyl and tetramethyl derivatives of 2.673(2) and 2.733(1) Å, respectively, are similar to the bond distance in **61** and consistent with a d^1–d^1 single bond. For the tetramethyl derivative only the "Z-type" isomer (**62**) is observed in the solid state.

Reaction of the tetrachlorocatecholate complex NBu$_4$[TcO(C$_6$Cl$_4$O$_2$)$_2$] with NH$_2$NPh$_2$ in CH$_2$Cl$_2$ followed by addition of methanol yields purple crystals of the unusual paramagnetic Tc(V)/(VI) mixed-valence complex NBu$_4$[Tc$_2$(NNPh$_2$)$_2$(C$_6$Cl$_4$O$_2$)$_4$]·CH$_2$Cl$_2$·2MeOH. The crystal structure of the dimeric anion shows the presence of bridging hydrazido(2-) ligands and a Tc–Tc bond distance of 2.612(2) Å. The complex is EPR silent in various solvents to 196 K but at lower temperatures shows a broad line centered at $g \simeq 2.015$. In the electronic spectrum a weak absorption at 12,000 cm^{-1} is consistent with an intervalence charge-transfer band (*422*).

D. DITHIOLENE AND RELATED COMPLEXES

Green [Tc(tdt)$_3$] is formed in about 5% yield from the reaction of TcO$_4^-$ with Zn(tdt) in 7.5 *M* H$_2$SO$_4$. Electrochemically, [Tc(tdt)$_3$] is oxidized to [Tc^{VII}(tdt)$_3$]$^+$ and readily reduced to [Tc^V(tdt)$_3$]$^-$ and with more difficulty to [Tc^{IV}(tdt)$_3$]$^{2-}$ (*648*). The deep-green [Tc(bdt)$_3$] may be prepared quantitatively by the oxidation of [Tc^V(bdt)$_3$]$^-$ with iodine (*558*). The green [Tc(abt)$_3$] complex is formed on allowing a mixture of TcO$_4^-$/2-aminobenzenethiol/HCl to stand overnight (*649*). The coordination sphere is a tapered trigonal prism, with the three N and S atoms occupying the triangular faces and Tc–N and Tc–S bond distances of 1.982(9)–2.004(8) Å and 2.339(3)–2.359(3) Å, respectively (*650*). The EPR spectrum of [Tc(abt)$_3$] has been analyzed (*649, 651*) and the effect of concentration and solvent composition on the spectra of frozen solutions, interpreted in terms of the breakdown of molecular aggregates to the monomeric species (*651*). Dark-blue [Tc(dbcat)$_3$] (λ_{max} = 594 nm; ε = 19,000) is formed in high yield from NH_4TcO_4 and 3,5-di-*tert*-butylcatechol (dbcatH$_2$) in methanol. A well-resolved 10-line EPR spectrum is observed in solution at room temperature. Reversible electrochemical oxidation yields the Tc(VII) species with surprising ease and there are two reversible reductions to Tc(V) and Tc(IV) species. The coordination geometry of [Tc(dbcat)$_3$] is approximately octahedral with the twist angle of 41.7° much closer to the ideal octahedral value of 60° than to the ideal trigonal primatic value of 0°. The Tc–O bond distances are in the range 1.945(6)–1.974(6) Å (*652*).

X. Technetium(VII)

The aqueous solution chemistry of Tc(VII) is dominated by the stability of the TcO_4^- anion. Strong oxidizing agents such as HNO_3 or H_2O_2 ultimately, but at varying rates, oxidize all technetium compounds to TcO_4^- (*12*). Technetium, unlike rhenium, does not form a heptafluoride (*7*). The coordination chemistry of Tc(VII) has been regarded as rather limited but recent results show it to be potentially extensive and novel.

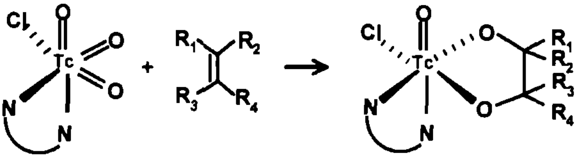
A. Oxo and Sulfido Complexes

The only product formed when Tc metal is burned in an excess of oxygen at 500°C is the volatile, crystalline, yellow Tc_2O_7 (m.p. 119.5°C) (*7*). In the solid state the structure of Tc_2O_7 consists of isolated centrosymmetric molecules with tetrahedral coordination about Tc and a linear Tc–O–Tc bridge with Tc–O_{bridge} bond distances of 1.840 Å (*653*). The oxide dissolves in water to give a colorless solution of the strong acid $HTcO_4$. Concentrated solutions of the acid are red and on evaporation dark-red crystals of hygroscopic anhydrous $HTcO_4$ are obtained (*7*). The TcO_4^- anion absorbs strongly in the UV region at 244 and 287.5 nm (*654*) and the red color of $HTcO_4$ is thought to be due to a disturbance from tetrahedral symmetry, resulting in the movement of the edge of the 287-nm absorption band into the visible region (*27*). The alkali metal salts are very stable; $KTcO_4$ sublimes at about 1000°C without decomposition (*7*). A considerable number of TcO_4^- salts have been prepared and structurally characterized (*655–659*). In $KTcO_4$ the TcO_4^- anion is tetrahedral with Tc–O bond distances of 1.711(3) Å (or 1.724 Å if corrected for librational oscillation) (*659*) but in NMe_4TcO_4

the anion has approximate C_{3v} symmetry with Tc–O bond distances of 1.589(11) Å and 1.696(6)–1.719(9) Å (*656*). The TcO_4^- anion shows no tendency to form polyanions and, unlike ReO_4^- (*660*), appears to have little tendency to act as a ligand, although it may be present as a counteranion. The E° values for the MO_4^-/MO_2 couples of 1.695, 0.738, and 0.510 V for Mn, Tc, and Re, respectively, show that TcO_4^- is a stronger oxidizing agent than ReO_4^-, but very much weaker than MnO_4^- (*654*). Many technetium complexes in lower oxidation states may be prepared directly from TcO_4^- in the presence of the ligand and a suitable reducing agent. Key starting materials such as $[TcOCl_4]^-$ and $[TcCl_6]^{2-}$ are readily prepared by the reduction of TcO_4^- by 12 *M* HCl in the cold and under reflux, respectively, and $[TcNCl_4]^-$ by HCl reduction in the presence of azide (*35, 614*). A kinetic study of the reduction of TcO_4^- by HBr shows that the first-step $TcO_4^- \rightarrow [Tc^VOBr_4]^-$ is a pseudo-first-order process and the second-step $[TcOBr_4]^- \rightarrow [TcBr_6]^{2-}$ is a combination of a first-order with a zero-order process (*661*). Pertechnetate is an effective catalyst in the oxidation of hydrazine by NO_3^- or ClO_4^- (*662*). A unique property of TcO_4^- is the remarkable inhibition of the corrosion of soft iron or carbon steels at concentrations as low as 5×10^{-5} *M*. The ReO_4^- anion is inactive in this respect (*654*). Brown-black Tc_2S_7 may be prepared by H_2S precipitation from 2–4 *M* HCl or H_2SO_4 (*7*). There is some evidence for the presence of the $[TcO_3S]^-$ anion in solution (*663*) but the formation of thiopertechnetates needs further investigation.

Reaction of Tc_2O_7 with $SnMe_4$ yields $MeTcO_3$, the dimer $[(Me_2TcO)_2(\mu\text{-}O)_2]$ (**54**), and the polymeric ester $\{Me_3SnOTcO_3\}_n$ (*228, 664*). The structure of the polymer consists of infinite zigzag chains with Tc=O bond distances of 1.655(13) and 1.676(15) Å and a $Tc–O_{bridge}$ distance of 1.72(1) Å (*664*). The oxide $MeTcO_3$ is a much stronger Lewis acid than $MeReO_3$ and reacts with olefins such as cyclohexene to form a Tc(V) glycolato complex, which decomposes in the presence of water and acids to stereospecifically produce the *cis*-diol and the disproportionation products $TcO_2 \cdot nH_2O$ and TcO_4^- (*228*). The ester $[TcO_3(OSiMe_3)]$ is a useful synthetic intermediate (*665, 666*).

Yellow crystals of $[TcO_3F]$ (m.p., 18.3°C) are formed from the reaction of fluorine with TcO_2 at 150°C (*667*) or by the dissolution of NH_4TcO_4 in anhydrous HF (*668*). In the presence of water, $[TcO_3F]$ hydrolyzes to TcO_4^- and HF (*667*). The pale-yellow liquid $[TcO_3Cl]$ (b.p., 25°C) is formed quantitatively on heating $TcCl_4$ in oxygen at 450°C (*326*). The vibrational spectra of $[TcO_3X]$ (X = F, Cl) have been assigned in C_{3v} symmetry (*669, 670*). The equilibrium $TcO_3F + HF \rightleftharpoons TcO_3^+ + HF_2^-$ has been demonstrated by ^{99}Tc and ^{17}O NMR and confirmed by the addition of AsF_5 to a solution of TcO_4^- in HF. NMR has also identified the species $[Tc_2O_5F_4]$ and $[TcO_2F_3]$ in the reaction of XeF_6 with $[TcO_3F]$/HF (*671*). Pure $[TcO_2F_3]$ (m.p., 200 ± 1°C) has been isolated from the reaction of $Tc_2O_7/HF/XeF_6$ and consists of open chains of F-bridged *cis*-TcO_2F_4 octahedral units, with Tc=O bond distances of 1.646(9) Å, a Tc–F terminal bond distance of 1.834(7) Å, and a bridging bond distance of 2.080(5) Å (*672*). The yellow transitory intermediate formed on addition of TcO_4^- to 12 *M* HCl is thought, by analogy with the reaction of ReO_4^-, to be *fac*-$[Tc^{VII}O_3Cl_3]^{2-}$ but attempts to isolate the NBu_4^+ salt result in reduction to $[TcOCl_4]^-$ or hydrolysis to TcO_4^- (*35*). The presence of choline chloride appears to stabilize $[TcO_3Cl_3]^{2-}$ and the solution remains bright yellow for several hours (*673*). In the presence of bpy or phen the reaction of TcO_4^- with ethanolic 12 *M* HCl yields a yellow precipitate of $[TcO_3ClL]$ and with HBr yields orange $[TcO_3Br(bpy)]$. These complexes are hydrolyzed by water to TcO_4^- and are reduced by reflux in ethanolic HX to $[Tc^VOX_3L]$. In the IR spectra there are three ν(TcO) bands in the range 910–850 cm^{-1} (*417*). Slurries of $[TcO_3ClL]$ (**63**) (L = phen, bpy, Me_4-phen, NO_2-phen) in acetone or CH_2Cl_2 cleanly oxidize olefins at 22°C to give high yields (>70%) of the stereospecific Tc^VO diolato complexes (**64**).



(**63**) (**64**)

Hydrolysis of **64** with concentrated HCl yields $[TcOCl_3L]$ and the stereospecific diol. Thus, reaction of *cis*-4-octene with $[TcO_3Cl(phen)]$ and hydrolysis gives only the *meso*-diol, whereas *trans*-4-octene gives 80% of the DL and 20% of the *meso* isomers, indicating some racemization during the hydrolysis process (*674*). The binuclear $[(TcO_3X)_2(\mu\text{-}L)]$ (L = polynitrogen heterocycle; X = Cl, OR) has been prepared from TcO_4^- or $[TcOCl_4]^-$ (*547*).

Reaction of TcO_4^-, the tripodal ligand $[(\eta^5\text{-}Cp)Co\{PO(OR)_2\}_3]^-$, and concentrated HNO_3 gives $[LTcO_3]$ in 97% yield. This complex may also be prepared, but in low yield, from the oxidation of $[LTcOCl_2]$ (*675*). The structure of the rhenium analog indicates that in $[LTcO_3]$ the geometry is distorted octahedral with coordination by three facial oxygens from the tripodal ligand and three technetyl oxo ligands (*676*). Similarly, HNO_3 oxidation of $[Tc^VOCl_2\{HB(pz)_3\}]$ yields $[TcO_3\{HB$-

$(pz)_3\}]$, which may also be prepared from $TcO_4^-/HB(pz)_3^-$ in ethanol containing concentrated H_2SO_4. Bubbling ethylene through a CH_2Cl_2 solution of $[TcO_3\{HB(pz)_3\}]$ yields the glycolato complex $[Tc^VO(OCH_2 CH_2O)\{HB(pz)_3\}]$. Notably, $[ReO_3\{HB(pz)_3\}]$ does not react with ethylene due to the greater difficulty of reducing Re(VII) to Re(V) (*677*).

B. NITRIDO AND IMIDO COMPLEXES

In view of the stability of the Tc≡N bond and the preparation of $K_2[Re(N)O_3]$, it would seem likely that nitridotechnetic(VII) acid $[Tc(N)O_3H_2]$, or its salts, could be prepared from the reaction of Tc_2O_7 with liquid ammonia or NH_2^-/NH_3, but these reactions have not been attempted (*640*). Slow evaporation of a solution of $Cs_2[TcNCl_5]$ in 10% H_2O_2 yields yellow-orange crystals of the explosive nitridoperoxo complex $Cs[TcN(O_2)_2Cl]$ (Fig. 20). The coordination geometry is a distorted pentagonal pyramid with the nitrido ligand in the apical position [Tc≡N, 1.63(2) Å] and η^2 peroxo ligands with O–O bond distances of 1.41(2) and 1.46(2) Å (*678*). The $AsPh_4[TcN(O_2)_2X]$ (X = Cl, Br) complexes are prepared from $AsPh_4[TcNX_4]/H_2O_2$ and are thermally more stable. Addition of bpy, phen, or oxalic acid to the pale-yellow solution of "$TcN(OH)_3$" in 10% H_2O_2 yields $[TcN(O_2)_2L]$ (L = bpy, phen) and the dimeric $(AsPh_4)_2[\{TcN(O_2)_2\}_2(ox)]$ (*679*). The crystal structure of the oxalate dimer shows the anion to consist of two $TcN(O_2)_2$ units bridged by a tetradentate sideways-bound oxalate with distorted pen-

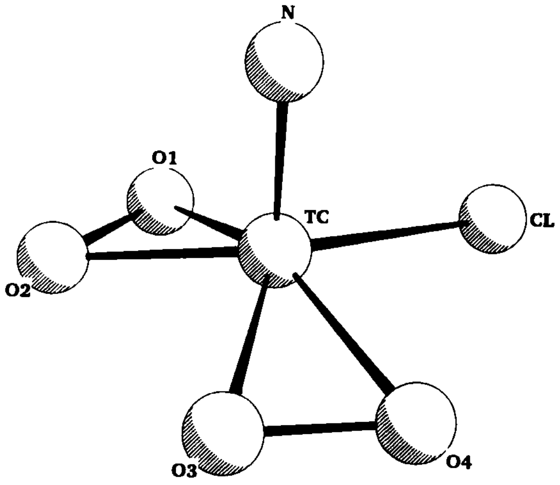
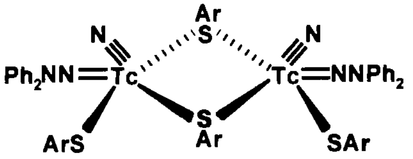


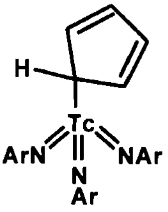
FIG. 20. The structure of the anion in $Cs[TcN(O_2)_2Cl]$ (*678*).

tagonal–bipyramidal geometry about each Tc atom (*680*). In the IR spectra of the nitridoperoxo complexes, ν(TcN) occurs at 1069–1035 cm^{-1}, ν(O–O) at 912–894 cm^{-1}; and $\nu_{sym}(TcO_2)$ at 665–647 cm^{-1} (*679*). These complexes are the only examples of nitridoperoxo complexes and rare examples of peroxo complexes of a metal in the +7 oxidation state. The $[TcN(O_2)_2]$ core is isoelectronic with the well-known $[MO(O_2)_2]$ (M = Cr, Mo, W) cores and emphasizes the analogy between isoelectronic [MoO] and [TcN] complexes noted for $[Tc^{VI}N]^{3+}$ dimeric species. Oxidation of $[TcOCl_4]^-$ by H_2O_2 gives TcO_4^-, with no evidence for the formation of transitory peroxo species (*678*).

The reaction of $NBu_4[TcOCl_4]$ with Ph_2NNH_2 and 2,4,6-triisopropylbenzenethiol yields yellow crystals of the novel nitrido-hydrazido(2-), formally Tc(VII), binuclear complex **65**·$0.5Et_2O$. The geometry about each Tc atom is distorted square–pyramidal with long $Tc{=}NNPh_2$ bond distances of 1.88(1) Å, $Tc{\equiv}N$ bond distances of 1.64(1) Å, and $Tc{-}N{-}NPh_2$ angles of 140.2(11)° and 141.7(11)°. The Tc–S (bridging) distance of 2.470(7) Å is significantly longer than the average Tc–S (terminal) distance of 2.379(6) Å. The nitrido ligands result from N–N bond cleavage of the organohydrazine (*681*).



(**65**)



(**66**)

The reaction of ArNCO (Ar = 2,6-dimethyl- or 2,6-diisopropylphenyl) with $[TcO_3(OSiMe_3)]$ yields the imido complex $[Tc(NAr)_3(OSiMe_3)]$. Tetrahydrofuran solutions of $[Tc(NAr)_3(OSiMe_3)]$ react readily with Grignard reagents to form deep blue-green $[Tc(NAr)_3R]$ (R = Me, Et, η^1-allyl) and with F^- to give the oxoimido complex $[(Ph_3P)_2N][TcO(NAr)_3]$. Reaction with $ISiMe_3$ in toluene yields $[Tc(NAr)_3I]$. Crystal structures of $[Tc(NAr)_3(OSiMe_3)]$ and $[Tc(NAr)_3I]$ (Ar = 2,6-diisopropylphenyl) show approximate tetrahedral geometry and, for the iodo complex, $Tc{=}N$ bond distances of 1.740(7)–1.763(6) Å and Tc–N–C bond angles of 164.8(6)°–169.4(6)°. The presence of three imido ligands imparts a high degree of stability to the Tc(VII) center. Electrochemical studies show that the complexes are difficult to reduce and are also moderately air stable. NMR spectra indicate free rotation about the N–C(Ar) bonds (*666*). The reaction of KCp with $[Tc(NAr)_3I]$ rapidly forms the green, air- and water-stable η^1-Cp complex (**66**). Two of the Tc═N bond distances in **66** are similar, at 1.748(2) and 1.753(2) Å, but the third is significantly longer, at 1.761(2) Å. With an excess of KCp, the air-sensitive $K[Cp_2Tc(NAr)_3]$ is formed and a symmetrical structure is indicated by the ^1H NMR spectrum (*682*).

C. COMPLEXES NOT CONTAINING MULTIPLY BONDED LIGANDS

Treatment of NH_4TcO_4 with K/en/EtOH yields the classic hydrido complex $K_2[TcH_9]$, isostructural with $K_2[ReH_9]$ (*683*). The structure of the $[TcH_9]^{2-}$ anion is thus a trigonal prism capped on the three rectangular faces (*684*). The chemical behavior of $[ReH_9]^{2-}$ and $[TcH_9]^{2-}$ is similar but the Tc complex is more reactive. In solution, $[TcH_9]^{2-}$ has been shown by ^1H and ^{99}Tc NMR to be stereochemically nonrigid (*671*). The preparation of $[TcH_7(PEt_2Ph)_2]$ has been reported (*685*). The green $[Tc(pda)_3]TcO_4$ is formed on reflux of a solution of TcO_4^- and 1,2 diaminobenzene ($pdaH_2$) in methanol. The geometry of the $[Tc(pda)_3]^+$ cation is trigonal prismatic with the pda ligands in the paddle wheel arrangement and the six Tc–NH bond distances in the range 1.98(1)–2.03(2) Å. The presence of a single ν(NH) IR absorption at 3235 cm^{-1} confirms that the ligands are in the deprotonated dianionic form (*456*).

XI. Appendix: Abbreviations

abtH	2-aminobenzenethiol
acacH	acetylacetone
$(acac)_2enH_2$	*N,N'*-ethylenebis(acetylacetoneimine)
AcO	acetate
atm	atmosphere
av.	average value
$bdtH_2$	1,2-benzenedithiol
bpy	2,2'-bipyridine
Bu	*n*-butyl
^{t}Bu	*tert*-butyl
Bz	benzyl
$cdoH_2$	cyclohexane-1,2-dioxime
Cp	cyclopentadienyl
15-crown-5	1,4,7,10,13-pentaoxacyclopentadecane
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
cyclam	1,4,8,11-tetraazacyclotetradecane
depe	1,2-bis(diethylphosphino)ethane

diars	1,2-phenylenebis(dimethylarsine)
dmf	dimethylformamide
$dmgH_2$	dimethylglyoxime
dmpe	1,2-bis(dimethylphosphino)ethane
dmso	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
$dtoH_2$	dithiooxalic acid
ε	molar extinction coefficient (M^{-1} cm^{-1})
$edtH_2$	1,2-ethanediethiol
$edtaH_4$	ethylenediaminetetraacetic acid
en	1,2-ethanediamine
EPR	electron paramagnetic resonance
Et	ethyl
EXAFS	extended X-ray absorption fine structure
FABMS	fast atom bombardment mass spectrometry
$HB(pz)_3$	hydrotris(pyrazol-1-yl)borate (1-)
hbt	2-(2-hydroxyphenyl)benzothiazolate(1-)
HPLC	high-performance liquid chromatography
LMCT	ligand-to-metal charge transfer
Me	methyl
MLCT	metal-to-ligand charge transfer
$mntH_2$	maleonitriledithiol
$ntaH_3$	nitrilotriacetic acid
$OphsalH_2$	*N*-(2-hydroxyphenyl)salicylideneimine
ox	oxalate(2-)
Ph	phenyl
phen	1,10-phenanthroline
pic	4-methylpyridine
^{i}Pr	*iso*-propyl
py	pyridine
quinH	8-hydroxyquinoline
$(sacac)_2enH_2$	*N,N'*-ethylenebis(thioacetylacetoneimine)
salH	salicylaldehyde
$(sal)_2enH_2$	bis(salicylidine)ethylenediamine
$SphsalH_2$	*N*-(2-sulfidophenyl)salicylideneimine
tan	1,4,7-triazacyclononane
$tctaH_3$	1,4,7-triazacyclononane-*N,N',N''*-triacetic acid
tdtH	3,4-toluenedithiol
terpy	2,2 : 6',2''-terpyridine
THF	tetrahydrofuran
tmbtH	2,3,5,6-tetramethylbenzenethiol
tmp	trimethylphosphite
tmtu	tetramethylthiourea
tu	thiourea

ACKNOWLEDGMENTS

I thank Dr. S. F. Colmanet for preparing the structural figures.

REFERENCES

1. Perrier, C., and Segrè, E., *Rend. Accad. Naz. Lincei* **25,** 723 (1937).
2. Perrier, C., and Segrè, E., *Nature* **140,** 193 (1937).
3. Schwochau, K., *Radiochim. Acta* **32,** 139 (1983).
4. Kenna, B. T., and Kuroda, P. K., *J. Inorg. Nucl. Chem. Lett.* **23,** 142 (1961).
5. Coursey, B. M., Gibson, J. A. B., Heitzmann, M. W., and Leak, J. C. *Int. J. Appl. Radiat. Isot.* **35,** 1103 (1984).
6. Wapstra, A. H., and Audi, G., *Nucl. Phys. A* **432,** 1 (1985).
7. Kotegov, K. V., Pavlov, O. N., and Shvedov, V. P., *Adv. Inorg. Chem. Radiochem.* **11,** 1 (1968).
8. Rard, J. A., Rand, M. H., Thornback, J. R., and Wanner, H., *J. Chem. Phys.* **94,** 6336 (1991).
9. Deutsch, E., Libson, K., Vanderheyden, J.-L., Ketring, A. R., and Maxon, H. R., *Nucl. Med. Biol.* **13,** 465 (1986).
10. Boag, N. M., and Kaesz, H. D. *in* Wilkinson, G., (Ed.), "Comprehensive Organometallic Chemistry" (G. Wilkinson, Ed.), Vol. 4, p. 161. Pergamon, New York, 1982.
11. Clarke, M. J., and Fackler, P. H., *Struct. Bonding* **50,** 57 (1982).
12. Deutsch, E., Libson, K., Jurisson, S., and Lindoy, L. F., *Prog. Inorg. Chem.* **30,** 75 (1983).
13. Deutsch, E., and Libson, K., *Comments Inorg. Chem.* **3,** 83 (1984).
14. Saha, G. B., "Fundamentals of Nuclear Pharmacy," 3rd ed. Springer-Verlag, New York, 1992.
15. Clarke, M. J., and Podbielski, L., *Coord. Chem. Rev.* **78,** 253 (1987).
16. Johannsen, B., and Spies, H., *Isotopenpraxis* **24,** 449 (1988).
17. Dewanjee, M. K., *Semin. Nucl. Med.* **20,** 5 (1990).
18. Steigman, J., and Eckelman, W. C., "The Chemistry of Technetium in Medicine." National Academy Press, Washington, D.C., 1992.
19. Jurisson, S., Berning, D., Jia, W., and Ma, D., *Chem. Rev.* **93,** 1137 (1993).
20. Richards, P., Tucker, W. D., and Srivastava, S. C., *Int. J. Appl. Radiat. Isot.* **33,** 793 (1982).
21. Boyd, R. E., *Int. J. Appl. Radiat. Isot.* **33,** 801 (1982).
22. Deutsch, E., Heineman, W. R., Zodda, J. P., Gilbert, T. W., and Williams, C. C. *Int. J. Appl. Radiat. Isot.* **33,** 843 (1982).
23. Bonnyman, J., *Int. J. Appl. Radiat. Isot.* **34,** 901 (1983).
24. Deutsch, E., and Hirth, W., *J. Nucl. Med.* **28,** 1491 (1987).
25. Eckelman, W. C., and Volkert, W. A., *Int. J. Appl. Radiat. Isot.* **33,** 945 (1982).
26. Colton, R., "The Chemistry of Rhenium and Technetium." Interscience Publishers, London, 1965.
27. Peacock, R. D., "The Chemistry of Technetium and Rhenium." Elsevier, Amsterdam, 1966.
28. Spitsyn, V. I., and Kuzina, A. F., "Technetium." Nauka Publishers, Moscow, 1981 (in Russian).

29. "Gmelin Handbook of Inorganic Chemistry; Tc, Technetium," 8th ed., Suppl. Vol. 1. Springer-Verlag, Berlin, 1982; Suppl. Vol. 2. Springer-Verlag, Berlin, 1983.
30. Deutsch, E., Nicolini, M., and Wagner, H. N., Jr. (Eds.), "Technetium in Chemistry and Nuclear Medicine" Cortina International, Verona/Raven Press, New York, 1983.
31. Nicolini, M., Bandoli, G., and Mazzi, U. (Eds.), "Technetium in Chemistry and Nuclear Medicine 2" Cortina International, Verona/Raven Press, New York, 1986.
32. Nicolini, M., Bandoli, G., and Mazzi, U. (Eds.), "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" Cortina International, Verona/Raven Press, New York, 1990.
33. Peacock, R. D., *in* "Comprehensive Inorganic Chemistry" (Bailar, J. C., Emeléus, H. J., Nyholm, R., and Trotman-Dickenson, A. F., Eds., Vol. 3, p. 877. Pergamon, Oxford, 1973.
34. Jones, A. G., and Davison, A., *Int. J. Appl. Radiat. Isot.* **33,** 867 (1982).
35. Davison, A., and Jones, A. G., *Int. J. Appl. Radiat. Isot.* **33,** 875 (1982).
36. Davison, A., *in* "Technetium in Chemistry and Nuclear Medicine" (Deutsch, E., Nicolini, M., and Wagner, H. N., Eds.), p. 3. Cortina International, Verona/Raven Press, New York, 1983.
37. Bandoli, G., Mazzi, U., Roncari, E., and Deutsch, E., *Coord. Chem. Rev.* **44,** 191 (1982).
38. Melník, M., and Van Lier, J. E., *Coord. Chem. Rev.* **77,** 275 (1987).
39. Abram, U., and Kirmse, R., *J. Radioanal. Nucl. Chem., Articles* **122,** 311 (1988).
40. Kirmse, R., and Abram, U., *Isotopenpraxis* **26,** 151 (1990).
41. Raynor, J. B., Kemp, T. J., and Thyer, A. M., *Inorg. Chim. Acta* **193,** 191 (1992).
42. Spitsyn, V. I., Kuzina, A. F., Oblova, A. A., and Kryuchkov, S. V., *Russ. Chem. Rev. (Engl. Transl.)* **54,** 373 (1985).
43. Schwochau, K., *Fortschr. Chem. Forsch.* **96,** 109 (1981).
44. O'Connell, L. A., Pearlstein, R. M., Davison, A., Thornback, J. R., Kronauge, J. F., and Jones, A. G., *Inorg. Chim. Acta* **161,** 39 (1989).
45. Hileman, J. C., Huggins, D. K., and Kaesz, H. D., *Inorg. Chem.* **4,** 933 (1962).
46. Michels, G. D., and Svec, H. J., *Inorg. Chem.* **20,** 3445 (1981).
47. Lindauer, M. W., Evans, G. O., and Sheline, R. K., *Inorg. Chem.* **7,** 1249 (1968).
48. Hileman, J. C., Huggins, D. K., and Kaesz, H. D., *J. Am. Chem. Soc.* **83,** 2953 (1961).
49. Hieber, W., and Herget, C., *Angew. Chem.* **73,** 579 (1961).
50. Calderazzo, F., Mazzi, U., Pampaloni, G., Poli, R., Tisato, F., and Zanazzi, P. F., *Gazz. Chim. Ital.* **119,** 241 (1989).
51. Bailey, M. F., and Dahl, L. F., *Inorg. Chem.* **4,** 1140 (1965).
52. Bor, G., and Sbrignadello, G., *J. Chem. Soc., Dalton Trans.,* 440 (1974).
53. Findeisen, M., Kaden, L., Lorenz, B., Rummel, S., and Wahren, M., *Inorg. Chim. Acta* **128,** L15 (1987).
54. Muto, T., and Ebihara, H., *J. Inorg. Nucl. Chem.* **43,** 2617 (1981).
55. Sbrignadello, G., Tomat, G., Magon, L., and Bor, G., *Inorg. Nucl. Chem. Lett.* **9,** 1073 (1973).
56. Sbrignadello, G., *Inorg. Chim. Acta* **48,** 237 (1981).
57. Kaesz, H. D., and Huggins, D. K., *Can. J. Chem.* **41,** 1250 (1963).
58. Grimm, C. C., and Clark, R. J., *Organometallics* **9,** 1123 (1990).
59. Grimm, C. C., Clark, R. J., and Rosanske, R., *Inorg. Chim. Acta* **159,** 137 (1989).
60. Klimov, V. D., Mamchenko, A. V., and Babichev, A. P., *Radiokhimiya* **33**(5), 33 (1991).

61. Fawcett, J. P., and Poë, A., *J. Chem. Soc., Dalton Trans.* 2039 (1976).
62. Kanellakopulos, B., Nuber, B., Raptis, K., and Ziegler, M. L., *Z. Naturforsch. B* **46,** 55 (1991).
63. Kaden, L., Lorenz, B., Schmidt, K., Sprinz, H., and Wahren, M., *Z. Chem.* **19,** 305 (1979).
64. Struchkov, Yu. T., Bazanov, A. S., Kaden, L., Lorenz, B., Wahren, M., and Meyer, H., *Z. Anorg. Allg. Chem.* **494,** 91 (1982).
65. Hieber, W., Lux, F., and Herget, C., *Z. Naturforsch. B* **20,** 1159 (1965).
66. Borisova, I. V., Miroslavov, A. E., Sidorenko, G. V., and Suglobov, D. N., *Radiokhimiya* **33**(6), 1 (1991).
67. Knight Castro, H. H., Hissink, C. E., Teuben, J. H., Vaalburg, W., and Panek, K., *Rec. Trav. Chim. Pays-Bas* **111,** 105 (1992).
68. Borisova, I. V., Miroslavov, A. E., Sidorenko, G. V., Suglobov, D. N., and Shcherbakova, L. L., *Radiokhimiya* **33**(4), 27 (1991).
69. Kaden, L., Lorenz, B., Rummel, S., Schmidt, K., and Wahren, M., *Inorg. Chim. Acta* **142,** 1 (1988).
70. Lorenz, B., Findeisen, M., Olk, B., and Schmidt, K., *Z. Anorg. Allg. Chem.* **566,** 160 (1988).
71. Borisova, I. V., Miroslavov, A. E., Sidorenko, G. V., and Suglobov, D. N., *Radiokhimiya* **33**(3), 1 (1991).
72. Mazzi, U., Bismondo, A., Kotsev, N., and Clemente, D. A., *J. Organomet. Chem.* **135,** 177 (1977).
73. Joachim, J. E., Apostolidis, C., Kanellakopulos, B., Maier, R., Marques, N., Meyer, D., Müller, J., Pires de Matos, A., Nuber, B., Rebizant, J., and Ziegler, M. L., *J. Organomet. Chem.* **448,** 119 (1993).
74. Alberto, R., Herrmann, W. A., Kiprof, P., and Baumgärtner, F., *Inorg. Chem.* **31,** 895 (1992).
75. Findeisen, M., Kaden, L., Lorenz, B., and Wahren, M., *Inorg. Chim. Acta* **142,** 3 (1988).
76. Grigoriev, M. S., and Kryutchkov, S. V., *Radiochim. Acta* **63,** 187 (1993). and Utilization of Technetium '93, Sendai, Japan," p. 23. [Abstr.]
77. Kaden, L., Findeisen, M., Lorenz, B., Schmidt, K., and Wahren, M., *Isotopenpraxis* **27,** 265 (1991).
78. Lorenz, B., Findeisen, M., and Schmidt, K., *Isotopenpraxis* **27,** 266 (1991).
79. Biagini Cingi, M., Clemente, D. A., Magon, L., and Mazzi, U., *Inorg. Chim. Acta* **13,** 47 (1975).
80. Marchi, A., Rossi, R., Duatti, A., Zucchini, G. L., and Magon, L., *Transition Met. Chem.* **11,** 164 (1986).
81. Rossi, R., Marchi, A., Magon, L., Duatti, A., Casellato, U., and Graziani, R., *Inorg. Chim. Acta* **160,** 23 (1989).
82. Marchi, A., Rossi, R., Duatti, A., Magon, L., Bertolasi, V., Ferretti, V., and Gilli, G., *Inorg. Chem.* **24,** 4744 (1985).
83. Rossi, R., Marchi, A., Magon, L., Casellato, U., and Graziani, R., *J. Chem. Res.* (*S*), 78, (1990).
84. Mazzi, U., Roncari, E., Seeber, R., and Mazzocchin, G. A., *Inorg. Chim. Acta* **41,** 95 (1980).
85. Kaden, L., Findeisen, M., Lorenz, B., Schmidt, K., and Wahren, M., *Inorg. Chim. Acta* **193,** 213 (1992).
86. Miroslavov, A. E., Sidorenko, G. V., Borisova, I. V., Legin, E. K., Lychev, A. A., and Suglobov, D. N., *Radiokhimiya* **32**(6), 14 (1990).

87. El-Sayed, M. A., and Kaesz, H. D., *Inorg. Chem.* **2,** 158 (1963).

88. Miroslavov, A. E., Sidorenko, G. V., Borisova, I. V., Legin, E. K., Lychev, A. A., Suglobov, D. N., and Adamov, V. M., *Radiokhimiya* **32**(4), 6 (1990).

89. Miroslavov, A. E., Borisova, I. V., Sidorenko, G. V., and Suglobov, D. N., *Radiokhimiya* **33**(6), 14 (1991).

90. Hieber, W., Opavsky, W., and Rohm, W., *Chem. Ber.* **101,** 2244 (1968).

91. Hieber, W., and Opavsky, W., *Chem. Ber.* **101,** 2966 (1968).

92. Borisova, I. V., Miroslavov, A. E., Sidorenko, G. V., and Suglobov, D. N., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (Nicolini, M., Bandoli, G., and Mazzi, U., Eds.), p. 337. Cortina International Verona/Raven Press, New York, 1990.

93. Adamov, V. M., Belyaev, B. N., Borisova, I. V., Miroslavov, A. E., Sidorenko, G. V., and Suglobov, D. N., *Radiokhimiya* **33**(4), 38 (1991).

94. Herrmann, W. A., Alberto, R., Bryan, J. C., and Sattelberger, A. P., *Chem. Ber.* **124,** 1107 (1991).

95. Miroslavov, A. E., Sidorenko, G. V., Borisova, I. V., Legin, I. K., Lychev, A. A., and Suglobov, D. N., *Radiokhimiya* **31**(6), 33 (1989).

96. Copp, S. B., Subramanian, S., and Zaworotko, M. J., *Angew, Chem. Int. Ed. Engl.* **32,** 706 (1993).

97. Tsutsui, M., Hrung, C. P., Ostfeld, D., Srivastava, T. S., Cullen, D. L., and Meyer, E. F., *J. Am. Chem. Soc.* **97,** 3952 (1975).

98. Tsutsui, M., and Hrung, C. P., *J. Am. Chem. Soc.* **95,** 5777 (1973).

99. Palm, C., Fischer, E. O., and Baumgärtner, F., *Naturwiss.* **49,** 279 (1962).

100. Knight Castro, H. H., Meetsma, A., Teuben, J. H., Vaalburg, W., Panek, K., and Ensing, G., *J. Organomet. Chem.* **410,** 63 (1991).

101. Raptis, K., Dornberger, E., Kanellakopulos, B., Nuber, B., and Ziegler, M. L., *J. Organomet. Chem.* **408,** 61 (1991).

102. Fischer, E. O., and Fellmann, W., *J. Organomet. Chem.* **1,** 191 (1963).

103. Wenzel, M., and Saidi, M., *J. Labelled Comp. Radiopharm.* **33,** 77 (1993).

104. Raptis, K., Kanellakopulos, B., Nuber, B., and Ziegler, M. L., *J. Organomet. Chem.* **405,** 323 (1991).

105. Palm, C., and Fischer, E. O., *Tetrahedron Lett.*, 253 (1962).

106. Fischer, E. O., and Schmidt, M. W., *Chem. Ber.* **102,** 1954 (1969).

107. Wester, D. W., Coveney, J. R., Nosco, D. L., Robbins, M. S., and Dean, R. T., *J. Med. Chem.* **34,** 3284 (1991).

108. Schwochau, K., and Herr, W., *Z. Anorg. Allg. Chem.* **319,** 148 (1962).

109. Krasser, W., Bohres, E. W., and Schwochau, K., *Z. Naturforsch. A* **27,** 1193 (1972).

110. Holman, B. L., Jones, A. G., Lister-James, J., Davison, A., Abrams, M. J., Kirshenbaum, J. M., Tumeh, S. S., and English, R. J., *J. Nucl. Med.* **25,** 1350 (1984).

111. Abrams, M. J., Davison, A., Faggiani, R., Jones, A. G., and Lock, C. J. L., *Inorg. Chem.* **23,** 3284 (1984).

112. Abrams, M. J., Davison, A., Jones, A. G., Costello, C. E., and Pang, H., *Inorg. Chem.* **22,** 2798 (1983).

113. Findeisen, M., Lorenz, B., and Abram, U., *Z. Chem.* **29,** 29 (1989).

114. Tulip, T. H., Calabrese, J., Kronauge, J. F., Davison, A., and Jones, A. G., *in* "Technetium in Chemistry and Nuclear Medicine 2" (Nicolini, M., Bandoli, G., and Mazzi, U., Eds.), p. 119. Cortina International, Verona/Raven Press, New York, 1986.

115. Kronauge, J. F., Kawamura, M., Lepisto, E., Holman, B. L., Davison, A., Jones, A. G., Costello, C. E., and Zeng, C.-H., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (Nicolini, M., Bandoli, G., and Mazzi, U., Eds.), p. 677. Cortina International, Verona/Raven Press, New York, 1990.

116. Kronauge, J. F., Davison, A., Roseberry, A. M., Costello, C. E., Maleknia, S., and Jones, A. G., *Inorg. Chem.* **30,** 4265 (1991).

117. Abram, U., Beyer, R., Münze, R., Findeisen, M., and Lorenz, B., *Inorg. Chim. Acta* **160,** 139 (1989).

118. O'Connell, L. A., and Davison, A., *Inorg. Chim. Acta* **176,** 7 (1990).

119. Abram, U., Abram, S., Beyer, R., Muenze, R., Kaden, L., Lorenz, B., and Findeisen, M., *Inorg. Chim. Acta* **148,** 141 (1988).

120. O'Connell, L. A., Dewan, J., Jones, A. G., and Davison, A., *Inorg. Chem.* **29,** 3539 (1990).

121. Farr, J. P., Abrams, M. J., Costello, C. E., Davison, A., Lippard, S. J., and Jones, A. G., *Organometallics* **4,** 139 (1985).

122. Joachim, J. E., Apostolidis, C., Kanellakopulos, B., Maier, R., Meyer, D., Rebizant, J., and Ziegler, M. L., *J. Organomet. Chem.* **455,** 137 (1993).

123. Vanderheyden, J.-L., Ketring, A. R., Libson, K., Heeg, M. J., Roecker, L., Motz, P., Whittle, R., Elder, R. C., and Deutsch, E., *Inorg. Chem.* **23,** 3184 (1984).

124. Ichimura, A., Heineman, W. R., Vanderheyden, J.-L., and Deutsch, E., *Inorg. Chem.* **23,** 1272 (1984).

125. Roodt, A., Sullivan, J. C., Meisel, D., and Deutsch, E., *Inorg. Chem.* **30,** 4545 (1991).

126. Doyle, M. N., Libson, K., Woods, M., Sullivan, J. C., and Deutsch, E., *Inorg. Chem.* **25,** 3367 (1986).

127. Libson, K., Woods, M., Sullivan, J. C., Watkins, J. W., Elder, R. C., and Deutsch, E., *Inorg. Chem.* **27,** 999 (1988).

128. Abram, U., Beyer, R., Münze, R., Stach, J., Kaden, L., Lorenz, B., and Findeisen, M., *Polyhedron* **8,** 1201 (1989).

129. Wester, D. W., White, D. H., Miller, F. W., Dean, R. T., *Inorg. Chem.* **23,** 1501 (1984).

130. Abram, U., and Abram, S., *Z. Chem.* **26,** 181 (1986).

131. Wester, D. W., White, D. H., Miller, F. W., Dean, R. T., Schreifels, J. A., and Hunt, J. E., *Inorg. Chim. Acta* **131,** 163 (1987).

132. Davison, A., Kronauge, J. F., Jones, A. G., Pearlstein, R. M., and Thornback, J. R., *Inorg. Chem.* **27,** 3245 (1988).

133. Linse, K. H., Kremer, C., Su, Z. F., and Schwochau, K., *in* "Topical Symposium on the Behavior and Utilization of Technetium '93, Sendai, Japan," p. 59 [Abstr.]

134. Eakins, J. D., Humphreys, D. G., and Mellish, C. E., *J. Chem. Soc.*, 6012 (1963).

135. Armstrong, R. A., and Taube, H., *Inorg. Chem.* **15,** 1904 (1976).

136. Radonovich, L. J., and Hoard, J. L., *J. Phys. Chem.* **88,** 6711 (1984).

137. Roseberry, A. M., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **176,** 179 (1990).

138. Linder, K. E., Davison, A., Dewan, J. C., Costello, C. E., and Maleknia, S., *Inorg. Chem.* **25,** 2085 (1986).

139. Orvig, C., Davison, A., and Jones, A. G., *J. Labelled Comp. Radiopharm.* **18,** 148 (1981).

140. Archer, C. M., Dilworth, J. R., Jobanputra, P., Thompson, R. M., McPartlin, M., and Hiller, W., *J. Chem. Soc., Dalton, Trans.* 897 (1993).

141. Baldas, J., Colmanet, S. F., Raptis, R. G., and Williams, G. A., unpublished results.

142. Chatt, J., and Dilworth, J. R., *J. Chem. Soc., Chem. Comm.*, 508 (1974).

143. Hiller, W., Hübener, R., Lorenz, B., Kaden, L., Findeisen, M., Stach, J., and Abram, U., *Inorg. Chim. Acta* **181,** 161 (1991).

144. Lu, J., and Clarke, M. J., *Inorg. Chem.* **29,** 4123 (1990).

145. Lorenz, B., Schmidt, K., Kaden, L., and Wahren, M., *Isotopenpraxis* **22,** 444 (1986).

146. Archer, C. M., Dilworth, J. R., Kelly, J. D., and McPartlin, M., *J. Chem. Soc., Chem. Comm.*, 375 (1989).

147. Kryuchkov, S. V., Kuzina, A. F., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **266,** 127 [Engl. 304] (1982).

148. Kryuchkov, S. V., Grigor'ev, M. S., Kuzina, A. F., Gulev, B. F., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **288,** 389 [Engl. 147] (1986).

149. Cotton, F. A., Daniels, L. M., Falvello, L. R., Grigoriev, M. S., and Kryuchkov, S. V., *Inorg. Chim. Acta* **189,** 53 (1991).

150. Kryuchkov, S. V., Rakitin, Yu. V., Kazin, P. E., Zhirov, A. I., and Konstantinov, N. Yu., *Koord. Khim.* **16,** 1230 [Engl. 660] (1990).

151. Cotton, F. A., and Bratton, W. K., *J. Am. Chem. Soc.* **87,** 921 (1965).

152. Bratton, K. W., and Cotton, F. A., *Inorg. Chem.* **9,** 789 (1970).

153. Koz'min, P. A., and Novitskaya, G. N., *Russ. J. Inorg. Chem. (Engl. Transl.)* **17,** 1652 (1972).

154. Cotton, F. A., and Shive, L. W., *Inorg. Chem.* **14,** 2032 (1975).

155. Cotton, F. A., Davison, A., Day, V. W., Fredrich, M. F., Orvig, C., and Swanson, R., *Inorg. Chem.* **21,** 1211 (1982).

156. Grigor'ev, M. S., Kryuchkov, S. V., Struchkov, Yu. T., and Yanovskii, A. I., *Koord. Khim.* **16,** 90 (1990).

157. Kryutchkov, S. V., Grigoryev, M. S., and German, K. E., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (Nicolini, M., Bandoli, G., and Mazzi, U., Eds.), p. 253. Cortina International, Verona/Raven Press, New York, 1990.

158. Cotton, F. A., and Pedersen, E., *Inorg. Chem.* **14,** 383 (1975).

159. Cotton, F. A., and Walton, R. A., "Multiple Bonds between Metal Atoms." Wiley, New York, 1982.

160. Cotton, F. A., and Kalbacher, B. J., *Inorg. Chem.* **16,** 2386 (1977).

161. Cotton, F. A., Fanwick, P. E., Gage, L. D., Kalbacher, B., and Martin, D. S., *J. Am. Chem. Soc.* **99,** 5642 (1977).

162. Kryuchkov, S. V., Kuzina, A. F., and Spitsyn, V. I., *Russ. J. Inorg. Chem. (Engl. Transl.)* **28,** 1124 (1983).

163. Spitsyn, V. I., Kuzina, A. F., Kryuchkov, S. V., and Simonov, A. E., *Russ. J. Inorg. Chem. (Engl. Transl.)* **32,** 1278 (1987).

164. Peters, G., Skowronek, J., and Preetz, W., *Z. Naturforsch. A* **47,** 591 (1992).

165. Spitsyn, V. I., Baierl, B., Kryuchkov, S. V., Kuzina, A. F., and Varen, M., *Dokl. Akad. Nauk SSSR* **256,** 608 [Engl. 30] (1981).

166. Cotton, F. A., Fanwick, P. E., and Gage, L. D., *J. Am. Chem. Soc.* **102,** 1570 (1980).

167. Koz'min, P. A., Larina, T. B., and Surazhskaya, M. D. *Koord. Khim.* (a) **9,** 1114 (1983); (b) **7,** 1719 (1981); (c) **8,** 851 (1982).

168. Rakitin Yu. V., and Nefedov, V. I., *Russ. J. Inorg. Chem. (Engl. Transl.)* **29,** 294 (1984).

169. Rakitin, Yu. V., Kryuchkov, S. V., Aleksandrov, A. I., Kuzina, A. F., Nemtsev, N. V., Ershov, B. G., and Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **269,** 1123 [Engl. 253] (1983).

170. Kryuchkov, S. V., Kuzina, A. F., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **287,** 1400 [Engl. 112] (1986).

171. German, K. E., Kryuchkov, S. V., Kuzina, A. F., and Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **288,** 381 [Engl. 139] (1986).

172. Spitzin, V. I., Kryutchkov, S. V., Grigoriev, M. S., and Kuzina, A. F., *Z. Anorg. Allg. Chem.* **563,** 136 (1988).

173. Kryutchkov, S. V., Kuzina, A. F., and German, K. E., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 275. Cortina International, Verona/Raven Press, New York, 1990.
174. Koz'min, P. A., Surazhskaya, M. D., and Larina, T. B., *Koord. Khim.* **11,** 1559 (1985).
175. Kryuchkov, S. V., Grigor'ev, M. S., Yanovskii, A. I., Struchkov, Yu. T., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **297,** 867 [Engl. 520] (1987).
176. Kryuchkov, S. V., Grigor'ev, M. S., Kuzina, A. F., Gulev, B. F., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **290,** 866 [Engl. 396] (1986).
177. Koz'min, P. A., Surazhskaya, M. D., and Larina, T. B. *Dokl. Akad. Nauk SSSR* **265,** 1420 [Engl. 656] (1982).
178. Kryuchkov, S. V., Grigor'ev, M. S., Kuzina, A. F., Gulev, B. F., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **288,** 893 [Engl. 172] (1986).
179. Kryuchkov, S. V., Grigor'ev, M. S., Yanovskii, A. I., Struchkov, Yu. T., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **301,** 618 [Engl. 219] (1988).
180. Gerasimov, V. N., Kryutchkov, S. V., German, K. E., Kulakov, V. M., and Kuzina, A. F. *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 231. Cortina International, Verona/Raven Press, New York, 1990.
181. Kryutchkov, S. V., Kuzina, A. F., and Spitzin, V. I. *Z. Anorg. Allg. Chem.* **563,** 153 (1988).
182. Wheeler, R. A., and Hoffmann, R., *J. Am. Chem. Soc.* **108,** 6605 (1986).
183. Bronger, W., Kanert, M., Loevenich, M., Schmitz, D., and Schwochau, K., *Angew. Chem. Int. Ed. Engl.* **32,** 576 (1993).
184. Archer, C. M., Dilworth, J. R., Kelly, J. D., and McPartlin, M., *Polyhedron* **8,** 1879 (1989).
185. Archer, C. M., Dilworth, J. R., Thompson, R. M., McPartlin, M., Povey, D. C., and Kelly, J. D., *J. Chem. Soc., Dalton Trans.,* 461 (1993).
186. Kirmse R., and Abram, U., *Z. Anorg. Allg. Chem.* **608,** 184 (1992).
187. Wilcox, B. E., Ho, D. M., and Deutsch, E., *Inorg. Chem.* **28,** 3917 (1989).
188. Thomas, J. A., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **184,** 99 (1991).
189. Conner, K. A., and Walton, R. A., *in* "Comprehensive Coordination Chemistry" (G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Eds.), Vol. 4, p. 125. Pergamon Press, Oxford, 1987.
190. Fergusson, J. E., and Nyholm, R. S., *Nature* **183,** 1039 (1959).
191. Fergusson, J. E., and Nyholm, R. S., *Chem. Ind.,* **347** (1960).
192. Fergusson, J. E., and Hickford, J. H., *Aust. J. Chem.* **23,** 453 (1970).
193. Libson, K., Doyle, M. N., Thomas, R. W., Nelesnik, T., Woods, M., Sullivan, J. C., Elder, R. C., and Deutsch, E., *Inorg. Chem.* **27,** 3614 (1988).
194. Bandoli, G., Mazzi, U., Ichimura, A., Libson, K., Heineman, W. R., and Deutsch, E., *Inorg. Chem.* **23,** 2898 (1984).
195. Okamoto, K.-I., Chen, B., Kirchhoff, J. R., Ho, D. M., Elder, R. C., Heineman, W. R., and Deutsch, E., *Polyhedron* **12,** 1559 (1993).
196. Rochon, F. D., Melanson, R., and Kong, P.-C., *Inorg. Chim. Acta* **194,** 43 (1992).
197. Seifert, S., Muenze, R., Leibnitz, P., Reck, G., and Stach, J., *Inorg. Chim. Acta* **193,** 167 (1992).
198. Mazzi, U., Clemente, D. A., Bandoli, G., Magon, L., and Orio, A. A., *Inorg. Chem.* **16,** 1042 (1977).
199. Konno, T., Heeg, M. J., and Deutsch, E., *Inorg. Chem.* **28,** 1694 (1989).
200. Konno, T., Heeg, M. J., Stuckey, J. A., Kirchhoff, J. R., Heineman, W. R., and Deutsch, E., *Inorg. Chem.* **31,** 1173 (1992).

201. White, D. J., Küppers, H.-J., Edwards, A. J., Watkin, D. J., and Cooper, S. R., *Inorg. Chem.* **31,** 5351 (1992).

202. Kirmse, R., Stach, J., Abram, U., and Marov, I. N., *Z. Anorg. Allg. Chem.* **518,** 210 (1984).

203. Baldas, J., Boas, J. F., Bonnyman, J., and Williams, G. A., *J. Chem. Soc., Dalton Trans.*, 827 (1984).

204. Brown, D. S., Newman, J. L., Thornback, J. R., and Davison, A., *Acta Cryst. C* **43,** 1692 (1987).

205. Newman, J. L., Thornback, J. R., and Nowotnik, D. P., *J. Labelled Comp. Radiopharm.* **26,** 24 (1989).

206. Kirmse, R., Lorenz, B., and Schmidt, K., *Polyhedron* **2,** 935 (1983).

207. Pearlstein, R. M., Davis, W. M., Jones, A. G., and Davison, A., *Inorg. Chem.* **28,** 3332 (1989).

208. Brown, D. S., Newman, J. L., Thornback, J. R., Pearlstein, R. M., Davison, A., and Lawson, A., *Inorg. Chim. Acta* **150,** 193 (1988).

209. Brown, D. S., Newman, J. L., and Thornback, J. R., *Acta Cryst. C* **44,** 973 (1988).

210. Cheah, C. T., Newman, J. L., Nowotnik, D. P., and Thornback, J. R., *Nucl. Med. Biol.* **14,** 573 (1987).

211. Abram, U., Hübener, R., Wollert, R., Kirmse, R., and Hiller, W., *Inorg. Chim. Acta* **206,** 9 (1993).

212. Kaden, L., Lorenz, B., Kirmse, R., Stach, J., Behm, H., Beurskens, P. T., and Abram, U., *Inorg. Chim. Acta* **169,** 43 (1990).

213. Abram, U., Kirmse, R., Köhler, K., Lorenz, B., and Kaden, L., *Inorg. Chim. Acta* **129,** 15 (1987).

214. Abram, U., Hartung, J., Beyer, L., Kirmse, R., and Köhler, K., *Z. Chem.* **27,** 101 (1987).

215. Kirmse, R., Stach, J., and Abram, U., *Polyhedron* **4,** 1275 (1985).

216. Yang, G. C., Heitzmann, M. W., Ford, L. A., and Benson, W. R., *Inorg. Chem.* **21,** 3242 (1982).

217. Kirmse, R., and Abram, U., *Z. Anorg. Allg. Chem.* **573,** 63 (1989).

218. Bandoli, G., Clemente, D. A., and Mazzi, U., *J. Chem. Soc., Dalton Trans.*, 373 (1978).

219. Baldas, J., Bonnyman, J., Pojer, P. M., Williams, G. A., and Mackay, M. F., *J. Chem. Soc., Dalton Trans.*, 451 (1982).

220. Abram, U., and Spies, H., *Inorg. Chim. Acta* **94,** L3 (1984).

221. Bonnyman, J., personal communication.

222. Baldas, J., and Bonnyman, J., *Nucl. Med. Biol.* **19,** 741 (1992).

223. de Vries, N., Dewan, J. C., Jones, A. G., and Davison, A., *Inorg. Chem.* **27,** 1574 (1988).

224. Fischer, E. O., and Schmidt, M. W., *Angew. Chem. Int. Ed. Engl.* **6,** 93 (1967).

225. Apostolidis, C., Kanellakopulos, B., Maier, R., Rebizant, J., and Ziegler, M. L., *J. Organomet. Chem.* **396,** 315 (1990); **411,** 171 (1991).

226. Kanellakopulos, B., Nuber, B., Raptis, K., and Ziegler, M. L., *Angew. Chem. Int. Ed. Engl.* **28,** 1055 (1989).

227. Chan, A. W. E., Hoffmann, R., and Alvarez, S., *Inorg. Chem.* **30,** 1086 (1991).

228. Herrmann, W. A., Alberto, R., Kiprof, P., and Baumgärtner, F., *Angew. Chem. Int. Ed. Engl.* **29,** 189 (1990).

229. Trop, H. S., Jones, A. G., and Davison, A., *Inorg. Chem.* **19,** 1993 (1980).

230. Trop, H. S., Davison, A., Jones, A. G., Davis, M. A., Szalda, D. J., and Lippard, S. J., *Inorg. Chem.* **19,** 1105 (1980).

231. Huber, E. W., Heineman, W. R., and Deutsch, E., *Inorg. Chem.* **26,** 3718 (1987).

232. Preetz, W., and Peters, G., *Z. Naturforsch. B.* **35,** 797 (1980).

233. Cotton, F. A., Daniels, L., Davison, A., and Orvig, C., *Inorg. Chem.* **20,** 3051 (1981).

234. Cotton, F. A., and Gage, L. D., *Nouv. J. Chem.* **1,** 441 (1977).

235. Kryuchkov, S. V., and Simonov, A. E., *Koord. Khim.* **16,** 339 (1990).

236. Skowronek, J., and Preetz, W., *Z. Naturforsch. B* **47,** 482 (1992).

237. Skowronek, J., Preetz, W., and Jessen, S. M., *Z. Naturforsch. B* **46,** 1305 (1991).

238. Zaitseva, L. L., Kotel'nikova, A. S., and Rezvov, A. A., *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **25,** 1449 (1980).

239. Baturin, N. A., German, K. E., Grigor'ev, M. S., and Kryuchkov, S. V., *Koord. Khim.* **17,** 1375 (1991).

240. Skowronek, J., and Preetz, W., *Z. Anorg. Allg. Chem.* **615,** 73 (1992).

241. Hashimoto, M., Wada, H., Omori, T., and Yoshihara, K., *J. Radioanal. Nucl. Chem., Lett.* **153,** 283 (1991).

242. Mazzi, U., Roncari, E., Bandoli, G., and Magon, L., *Transition Met. Chem.* **4,** 151 (1979).

243. Patterson, G. S., Davison, A., Jones, A. G., Costello, C. E., and Maleknia, S. D., *Inorg. Chim. Acta* **114,** 141 (1986).

244. Leesmeister, K., and Schwochau, K., *Nucl. Med. Biol.* **19,** 73 (1992).

245. Mutalib, A., Omori, T., and Yoshihara, K., *J. Radioanal. Nucl. Chem., Lett.* **165,** 19 (1992).

246. Hashimoto, K., Kabuto, C., Omori, T., and Yoshihara, K., *Chem. Lett.,* 1379 (1988).

247. Bandoli, G., Clemente, D. A., and Mazzi, U., *J. Chem. Soc., Dalton Trans.,* 1837 (1977).

248. Bandoli, G., Clemente, D. A., Mazzi, U., and Roncari, E., *Acta Cryst. B* **34,** 3359 (1978).

249. Kido, H., and Hatakeyama, Y., *Inorg. Chem.* **27,** 3623 (1988).

250. Mutalib, A., Omori, T., and Yoshihara, K., *J. Radioanal. Nucl. Chem., Articles* **170,** 67 (1993).

251. Spies, H., Abram, U., Uhlemann, E., and Ludwig, E., *Inorg. Chim. Acta* **109,** L3 (1985).

252. Bandoli, G., Mazzi, U., Spies, H., Münze, R., Ludwig, E., Ulhemann, E., Scheller, D., *Inorg. Chim. Acta* **132,** 177 (1987).

253. Linder, K. E., Jurisson, S., Francesconi, L., Nowotnik, D. P., Eckelman, W. C., and Nunn, A. D., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 195. Cortina International, Verona/Raven Press, New York, 1990.

254. Treher, E. N., Francesconi, L. C., Gougoutas, J. Z., Malley, M. F., and Nunn, A. D., *Inorg. Chem.* **28,** 3411 (1989).

255. Linder, K. E., Malley, M. F., Gougoutas, J. Z., Unger, S. E., and Nunn, A. D., *Inorg. Chem.* **29,** 2428 (1990).

256. Jurisson, S. S., Hirth, W., Linder, K. E., Di Rocco, R. J., Narra, R. K., Nowotnik, D. P., and Nunn, A. D., *Nucl. Med. Biol.* **18,** 735 (1991).

257. Jurisson, S., Linder, K. E., Hirth, W., Feld, T., Nowotnik, D. P., Nunn, A. D., and Eckelman, W. C., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 189. Cortina International, Verona/Raven Press, New York, 1990.

258. Thompson, M., Nunn, A. D., and Treher, E. N., *Anal. Chem.* **58,** 3100 (1986).

259. Cyr, J. E., Linder, K. E., and Nowotnik, D. P., *Inorg. Chim. Acta* **206,** 97 (1993).

260. Su, Z. F., Linse, K. H., Steinmetz, H. J., and Schwochau, K., *J. Labelled Comp. Radiopharm.* **31,** 61 (1992).

261. Deutsch, E., Elder, R. C., Lange, B. A., Vaal, M. J., and Lay, D. G., *Proc. Natl. Acad. Sci. USA* **73,** 4287 (1976).

262. Linder, K. E., Nowotnik, D. P., Malley, M. F., Gougoutas, J. Z., and Nunn, A. D., *Inorg. Chim. Acta* **190,** 249 (1991).

263. Jurisson, S., Francesconi, L., Linder, K. E., Treher, E., Malley, M. F., Gougoutas, J. Z., and Nunn, A. D., *Inorg. Chem.* **30,** 1820 (1991).

264. Jurisson, S. S., Dancey, K., McPartlin, M., Tasker, P. A., and Deutsch, E., *Inorg. Chem.* **23,** 4734 (1984).

265. Ichimura, A., Heineman, W. R., and Deutsch, E., *Inorg. Chem.* **24,** 2134 (1985).

266. Vavouraki, H., Papadopoulos, M., Mastrostamatis, S., Varvarigou, A. D., Psilla, M., and Chiotellis, E., *J. Labelled Comp. Radiopharm.* **33,** 249 (1993).

267. Mazzi, U., Refosco, F., Tisato, F., Bandoli, G., and Nicolini, M., *J. Chem. Soc., Dalton Trans.,* 847 (1988).

268. Marchi, A., Rossi, R., Magon, L., Duatti, A., Pasqualini, R., Ferretti, V., and Bertolasi, V., *J. Chem. Soc., Dalton Trans.,* 1411 (1990).

269. Duatti, A., Marchi, A., Luna, S. A., Bandoli, G., Mazzi, U., and Tisato, F., *J. Chem. Soc., Dalton Trans.,* 867 (1987).

270. Tisato, F., Refosco, F., Mazzi, U., Bandoli, G., and Nicolini, M., *Inorg. Chim. Acta* **157,** 227 (1989).

271. Lu, J., Yamano, A., and Clarke, M. J., *Inorg. Chem.* **29,** 3483 (1990).

272. Breikss, A. I., Nicholson, T., Jones, A. G., and Davison, A., *Inorg. Chem.* **29,** 640 (1990).

273. Wilcox, B. E., Ho, D. M., and Deutsch, E., *Inorg. Chem.* **28,** 1743 (1989).

274. Wilcox, B. E., and Deutsch, E., *Inorg. Chem.* **30,** 688 (1991).

275. Abrams, M. J., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **82,** 125 (1984).

276. Kremer, C., and Kremer, E., *J. Radioanal. Nucl. Chem., Lett.* **175,** 445 (1993).

277. Nicholson, T., de Vries, N., Davison, A., and Jones, A. G., *Inorg. Chem.* **28,** 3813 (1989).

278. Archer, C. M., Dilworth, J. R., Jobanputra, P., Thompson, R. M., McPartlin, M., Povey, D. C., Smith, G. W., and Kelly, J. D., *Polyhedron* **9,** 1497 (1990).

279. Dilworth, J .R., Jobanputra, P., Thompson, R. M., Archer, C. M., Kelly, J. D., and Hiller, W., *Z. Naturforsch. B* **46,** 449 (1991).

280. Mazzi, U., De Paoli, G., Di Bernardo, P., and Magon, L., *J. Inorg. Nucl. Chem.* **38,** 721 (1976).

281. Fergusson, J. E., and Heveldt, P. F., *J. Inorg. Nucl. Chem.* **38,** 2231 (1976).

282. Bandoli, G., Clemente, D. A., and Mazzi, U., *J. Chem. Soc., Dalton Trans.,* 125 (1976).

283. Mazzocchin, G. A., Seeber, R., Mazzi, U., and Roncari, E., *Inorg. Chim. Acta* **29,** 1 (1978); 5 (1978).

284. Watson, P. L., Albanese, J. A., Calabrese, J. C., Ovenall, D. W., and Smith, R. G., *Inorg. Chem.* **30,** 4638 (1991).

285. Rochon, F. D., Melanson, R., and Kong, P.-C., *Can. J. Chem.* **69,** 397 (1991).

286. Deutsch, E., Bushong, W., Glavan, K. A., Elder, R. C., Sodd, V. J., Scholz, K. L., Fortman, D. L., and Lukes, S. J., *Science* **214,** 85 (1981).

287. Libson, K., Barnett, B. L., and Deutsch, E., *Inorg. Chem.* **22,** 1695 (1983).

288. Hurst, R. W., Heineman, W. R., and Deutsch, E., *Inorg. Chem.* **20,** 3298 (1981).

289. Kirchhoff, J. R., Heineman, W. R., and Deutsch, E., *Inorg. Chem.* **26,** 3108 (1987).

290. Vanderheyden, J.-L., Heeg, M. J., and Deutsch, E., *Inorg. Chem.* **24,** 1666 (1985).

291. Roodt, A., Sullivan, J. C., Meisel, D., and Deutsch, E., *Inorg. Chem.* **30,** 4545 (1991).
292. Kaden, L., Lorenz, B., Schmidt, K., Sprinz, H., and Wahren, M., *Z. Chem.* **21,** 232 (1981).
293. Cohen, A. I., Glavan, K. A., and Kronauge, J. F., *Biomed. Mass Spectrom.* **10,** 287 (1983).
294. Unger, S. E., *Anal. Chem.* **56,** 363 (1984).
295. Glavan, K. A., Whittle, R., Johnson, J. F., Elder, R. C., and Deutsch, E., *J. Am. Chem. Soc.* **102,** 2103 (1980).
296. Elder, R. C., Whittle, R., Glavan, K. A., Johnson, J .F., and Deutsch, E., *Acta Cryst. B* **36,** 1662 (1980).
297. Konno, T., Heeg, M. J., and Deutsch, E., *Inorg. Chem.* **27,** 4113 (1988).
298. Abram, U., Beyer, R., Mäding, P., Hoffmann, I., Münze, R., and Stach, J., *Z. Anorg. Allg. Chem.* **578,** 229 (1989).
299. Konno, T., Seeber, R., Kirchhoff, J. R., Heineman, W. R., Deutsch, E., and Heeg, M. J., *Transition Met. Chem.* **18,** 209 (1993).
300. Okamoto, K.-I., Kirchhoff, J. R., Heineman, W. R., and Deutsch, E., *Polyhedron* **12,** 749 (1993).
301. Chang, L., Deutsch, E., and Heeg, M. J., *Transition Met. Chem.* **18,** 335 (1993).
302. Stach, J., Abram, U., and Münze, R., *Z. Chem.* **29,** 249 (1989).
303. Konno, T., Kirchhoff, J. R., Heineman, R. W., and Deutsch, E., *Inorg. Chem.* **28,** 1174 (1989).
304. Konno, T., Kirchhoff, J. R., Heeg, M. J., Heineman, W. R., and Deutsch, E., *J. Chem. Soc., Dalton Trans.,* 3069 (1992).
305. Münze, R., Abram, U., Stach, J., and Hiller, W., *Inorg. Chim. Acta* **196,** 151 (1991).
306. Refosco, F., Bandoli, G., Deutsch, E., Duatti, A., Mazzi, U., Moresco, A., Nicolini, M., and Tisato, F., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 221. Cortina International, Verona/Raven Press, New York, 1990.
307. Bolzati, C., Refosco, F., Tisato, F., Bandoli, G., and Dolmella, A., *Inorg. Chim. Acta* **201,** 7 (1992).
308. Dilworth, J. R., Hutson, A. J., Morton, S., Harman, M., Hursthouse, M. B., Zubieta, J., Archer, C. M., and Kelly, J. D., *Polyhedron* **11,** 2151 (1992).
309. Refosco, F., Bolzati, C., Moresco, A., Bandoli, G., Dolmella, A., Mazzi, U., and Nicolini, M., *J. Chem. Soc., Dalton Trans.,* 3043 (1991).
310. Dilworth, J. R., Griffiths, D. V., Hughes, J. M., Morton, S., Archer, C. M., and Kelly, J. D., *Inorg. Chim. Acta* **195,** 145 (1992).
311. Rochon, F. D., Melanson, R., and Kong, P. C., *Acta Cryst. C* **46,** 571 (1990).
312. Pietzsch, H.-J., Spies, H., Leibnitz, P., Reck, G., Beger, J., and Jacobi, R., *Polyhedron* **11,** 1623 (1992).
313. Batsanov, A. S., Struchkov, Yu. T., Lorenz, B., and Wahren, M., *Z. Anorg. Allg. Chem.* **510,** 117 (1984).
314. Lorenz, B., Schmidt, K., Hiller, W., Abram, U., and Hübener, R., *Inorg. Chim. Acta* **208,** 195 (1993).
315. Nicholson, T., Thornback, J., O'Connell, L., Morgan, G., Davison, A., and Jones, A. G. *Inorg. Chem.* **29,** 89 (1990).
316. Lorenz, B., and Schmidt, K., *Z. Chem.* **23,** 423 (1983).
317. Abram, U., and Abram, S., *Z. Chem.* **23,** 228 (1983).
318. Davison, A., de Vries, N., Dewan, J., and Jones, A., *Inorg. Chim. Acta* **120,** L15 (1986).
319. de Vries, N., Jones, A. G., and Davison, A., *Inorg. Chem.* **28, 3728** (1989).

320. de Vries, N., Cook, J., Jones, A. G., and Davison, A., *Inorg. Chem.* **30,** 2662 (1991).

321. de Vries, N., Cook, J., Davison, A., Nicholson, T., and Jones A. G., *Inorg. Chem.* **29,** 1062 (1990).

322. Baldas, J., Bonnyman, J., Mackay, M. F., and Williams, G. A., *Aust. J. Chem.* **37,** 751 (1984).

323. Baldas, J., Colmanet, S. F., and Williams, G. A., *Aust. J. Chem.* **44,** 1125 (1991).

324. Abram, U., Wollert, R., and Hiller, W., *Radiochim. Acta* **63,** 145 (1993). and Utilization of Technetium '93, Sendai, Japan," p. 58. [Abstr.]

325. Williams, G. A., Bonnyman, J., and Baldas, J., *Aust. J. Chem.* **40,** 27 (1987).

326. Guest, A., and Lock, C. J. L., *Can. J. Chem.* **50,** 1807 (1972).

327. Elder, M., and Penfold, B. R., *Inorg. Chem.* **5,** 1197 (1966).

328. Dalziel, J., Gill, N. S., Nyholm, R. S., and Peacock, R. D., *J. Chem. Soc.,* 4012 (1958).

329. Schwochau, K., and Herr, W., *Angew. Chem.* **75,** 95 (1963).

330. Alberto, R., and Anderegg, G., *Polyhedron* **4,** 1067 (1985).

331. Preetz, W., and Wendt, A., *Z. Naturforsch. B* **46,** 1496 (1991).

332. Jørgensen, C. K., and Schwochau, K., *Z. Naturforsch. A* **20,** 65 (1965).

333. Schenk, H. J., and Schwochau, K., *Z. Naturforsch. A* **28,** 89 (1973).

334. Schwochau, K., and Krasser, W., *Z. Naturforsch. A* **24,** 403 (1969).

335. Flint, C. D., and Lang, P. F., *J. Chem. Soc., Dalton Trans.,* 921 (1986).

336. Wendt, A., and Preetz, W., *Z. Naturforsch. A* **47,** 882 (1992).

337. Elder, R. C., Estes, G. W., and Deutsch, E., *Acta. Cryst. B* **35,** 136 (1979).

338. Baldas, J., Bonnyman, J., Samuels, D. L., and Williams, G. A., *Acta Cryst. C* **40,** 1343 (1984).

339. Koz'min, N. A., Novitskaya, G. N., and Kuzina, A. F., *J. Struct. Chem. (Engl. Transl.)* **13,** 878 (1972).

340. Shepel'kov, S. V., Konarev, M. I., Chebotarev, N. T., Zaitseva, L. L., and Vinogradov, I. V., *Russ. J. Inorg. Chem. (Engl. Transl.)* **20,** 1828 (1975).

341. Kryuchkov, S. V., Grigor'ev, M. S., Kuzina, A. F., and Spitsyn, V. I., *Russ. J. Inorg. Chem. (Engl. Transl.)* **32,** 1714 (1987).

342. Kryuchkov, S. V., Grigor'ev, M. S., Kuzina, A. F., and Spitsyn, V. I., *Russ. J. Inorg. Chem. (Engl. Transl.)* **32,** 1708 (1987).

343. Schwochau, K., *Z. Naturforsch. A* **20,** 1286 (1965).

344. Koyama, M., Kanchiku, Y., and Fujinaga, T., *Coord. Chem. Rev.* **3,** 285 (1968).

345. Kanchiku, Y., *Bull. Chem. Soc. Japan* **42,** 2831 (1969).

346. Kawashima, M., Koyama, M., and Fujinaga, T., *J. Inorg. Nucl. Chem.* **38,** 819 (1976).

347. Ianovici, E., Kosinski, M., Lerch, P., and Maddock, A. G., *J. Radioanal. Chem.* **64,** 315 (1981).

348. Colin, M., Ianovici, E., Lerch, P., and Maddock, A. G., *J. Radioanal. Nucl. Chem., Articles* **92,** 283 (1985).

349. Colin, M., Ianovici, E., and Lerch, P., *J. Radioanal. Nucl. Chem., Articles* **120,** 175 (1988).

350. Elder, M., Fergusson, J. E., Gainsford, G. J., Hickford, J. H., and Penfold, B. R. *J. Chem. Soc. A,* 1423 (1967).

351. Zaitseva, L. L., Kruglov, A. A., Romanov, A. V., Samsonov, V. E., and Teterin, E. G., *Russ. J. Inorg. Chem. (Engl. Transl.)* **32,** 1716 (1987); **33,** 1452 (1988).

352. Wendt, A., and Preetz, W., *Z. Anorg. Allg. Chem.,* **619,** 1669 (1993).

353. Sundrehagen, E., *Int. J. Appl. Radiat. Isot.* **30,** 739 (1979).

354. Magneli, A., and Andersson, G., *Acta Chem. Scand.* **9,** 1378 (1955).

355. Paquette, J., and Lawrence, W. E., *Can. J. Chem.* **63,** 2369 (1985).

356. Alberto, R., Anderegg, G., and May K., *Polyhedron* **5,** 2107 (1986).

357. Alberto, R., Albinati, A., Anderegg, G., and Huber, G., *Inorg. Chem.* **30,** 3568 (1991).

358. Refosco, F., Bandoli, G., Mazzi, U., Tisato, F., Dolmella, A., and Nicolini, M., *Inorg. Chem.* **29,** 2179 (1990).

359. Mazzi, U., Roncari, E., Bandoli, G., and Clemente, D. A., *Transition Met. Chem.* **7,** 163 (1982).

360. Colmanet, S. F., Williams, G. A., and Mackay, M. F., *J. Chem. Soc., Dalton Trans.,* 2305 (1987).

361. Kennedy, C. M., and Pinkerton, T. C., *Appl. Radiat. Isot.* **39,** 1159 (1988).

362. Omori, T., Yamada, Y., and Yoshihara, K., *Inorg. Chim. Acta* **130,** 99 (1987).

363. Abrams, M. J., Davison, A., Jones, A. G., and Costello, C. E., *Inorg. Chim. Acta* **77,** L235 (1983).

364. Kastner, M. E., Fackler, P. H., Podbielski, L., Charkoudian, J., and Clarke, M. J., *Inorg. Chim. Acta* **114,** L11 (1986).

365. Lu, J., and Clarke, M. J., *Inorg. Chem.* **27,** 4761 (1988).

366. Clarke, M. J., Kastner, M. E., Podbielski, L. A., Fackler, P. H., Schreifels, J., Meinken, G., and Srivastava, S. C., *J. Am. Chem. Soc.* **110,** 1818 (1988).

367. Lu, J., Hiller, C. D., and Clarke, M. J., *Inorg. Chem.* **32,** 1417 (1993).

368. Alberto, R., Anderegg, G., and Albinati, A., *Inorg. Chim. Acta* **178,** 125 (1990).

369. Bürgi, H. B., Anderegg, G., and Bläuenstein, P., *Inorg. Chem.* **20,** 3829 (1981).

370. Anderegg, G., Müller, E., Zollinger, K., and Bürgi, H.-B., *Helv. Chim. Acta* **66,** 1593 (1983).

371. Linder, K. E., Dewan, J. C., and Davison, A., *Inorg. Chem.* **28,** 3820 (1989).

372. Muenze, R., *Radiochem. Radioanal. Lett.* **48,** 281 (1981).

373. Libson, K., Deutsch, E., and Barnett, B. L., *J. Am. Chem. Soc.* **102,** 2476 (1980).

374. Martin, J. L., Yuan, J., Lunte, C. E., Elder, R. C., Heineman, W. R., and Deutsch, E., *Inorg. Chem.* **28,** 2899 (1989).

375. Mikelsons, M. V., and Pinkerton, T. C., *Appl. Radiat. Isot.* **38,** 569 (1987).

376. Hunter, G., and Kilcullen, N., *J. Chem. Soc., Dalton Trans.,* 2115 (1989).

377. Fergusson, J. E., and Hickford, J. H., *J. Inorg. Nucl. Chem.* **28,** 2293 (1966).

378. Levanda, O. Yu., Oblova, A. A., Kuzina, A. F., Belyaeva, L. I., and Spitsyn, V. I., *Russ. J. Inorg. Chem. (Engl. Transl.)* **30,** 522 (1985).

379. Tisato, F., Bolzati, C., Duatti, A., Bandoli, G., and Refosco, F., *Inorg. Chem.* **32,** 2042 (1993).

380. Bandoli, G., Clemente, D. A., Mazzi, U., and Roncari, E., *J. Chem. Soc., Dalton Trans.,* 1381 (1982).

381. Rochon, F. D., Melanson, R., and Kong, P.-C., *Acta Cryst. C* **47,** 732 (1991).

382. Rochon, F. D., and Melanson, R., *Acta Cryst. C* **49,** 1259 (1993).

383. Cotton, F. A., Day, C. S., Diebold, M. P., and Roth, W. J., *Acta Cryst. C* **46,** 1623 (1990).

384. Breikss, A. I., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **170,** 75 (1990).

385. du Preez, J. G. H., Gerber, T. I. A., and Knoesen, O., *Inorg. Chim. Acta* **109,** L17 (1985).

386. Bush, C. D., Hamor, T. A., Hussain, W., Jones, C. J., McCleverty, J. A., and Rothin, A. S., *Acta Cryst. C* **43,** 2088 (1987).

387. Lorenz, B., and Schmidt, K., *Z. Chem.* **24,** 443 (1984).

388. Findeisen, M., Lorenz, B., and Olk, B., *Z. Chem.* **27,** 447 (1987).

389. Colmanet, S. F., and Mackay, M. F., *Aust. J. Chem.* **41,** 1127 (1988).

390. Colmanet, S. F., and Mackay, M. F., *J. Chem. Soc., Chem. Comm.,* 705 (1987).

391. Colmanet, S. F., and Mackay, M. F., *Aust. J. Chem.* **41,** 269 (1988).

392. Edwards, A. J., Hugill, D., and Peacock, R. D., *Nature* **200,** 672 (1963).

393. Hugill, D., and Peacock, R. D., *J. Chem. Soc. A* 1339 (1966).

394. Holloway, J. H., and Selig, H., *J. Inorg. Nucl. Chem.* **30,** 473 (1968).

395. Jeżowska-Trzebiatowska, B., and Natkaniec, L., *J. Struct. Chem. (Engl. Transl.)* **8,** 460 (1967).

396. Thomas, R. W., Davison, A., Trop, H. S., and Deutsch, E., *Inorg. Chem.* **19,** 2840 (1980).

397. Davison, A., Trop, H. S., DePamphilis, B. V., and Jones, A. G., *Inorg. Synth.* **21,** 160 (1982).

398. Kung, H. F., Liu, B.-L., Wei, Y., and Pan, S., *Appl. Radiat. Isot.* **41,** 773 (1990).

399. Roodt, A., Leipoldt, J. G., Deutsch, E. A., and Sullivan, J. C., *Inorg. Chem.* **31,** 1080 (1992).

400. Davison, A., Jones, A. G., Müller, L., Tatz, R., and Trop, H. S., *Inorg. Chem.* **20,** 1160 (1981).

401. Caron, S., Ianovici, E., Lerch, P., and Maddock, A. G., *Inorg. Chim. Acta* **109,** 209 (1985).

402. Cotton, F. A., Davison, A., Day, V. W., Gage, L. D., and Trop, H. S., *Inorg. Chem.* **18,** 3024 (1979).

403. Jeżowska-Trzebiatowska, B., and Bałuka, M., *Bull. Acad. Polon. Sci., Ser. Chim.* **13,** 1 (1965).

404. Thomas, R. W., Heeg, M. J., Elder, R. C., and Deutsch, E., *Inorg. Chem.* **24,** 1472 (1985).

405. Mantegazzi, D., Ianoz, E., Lerch, P., and Tatsumi, K., *Inorg. Chim. Acta* **167,** 195 (1990).

406. Baldas, J., Boas, J. F., Bonnyman, J., and Colmanet, S. F., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 63. Cortina International, Verona/Raven Press, New York, 1990.

407. Preetz, W., and Peters, G., *Z. Naturforsch. B* **35,** 1355 (1980).

408. Peters, G., and Preetz, W., *Z. Naturforsch. B* **36,** 138 (1981).

409. Baldas, J., and Colmanet, S. F., *Aust. J. Chem.* **42,** 1155 (1989).

410. Hübener, R., and Abram, U., *Z. Anorg. Allg. Chem.* **617,** 96 (1992).

411. Hanuza, J., Bałuka, M., Machner, W., and Jeżowska-Trzebiatowska, B., *Acta Phys. Polon. A* **71,** 91 (1987).

412. Baran, E. J., and Cabello, C. I., *Z. Naturforsch. A* **38,** 563 (1983).

413. Collin, R. J., Griffith, W. P., and Pawson, D., *J. Mol. Struct.* **19,** 531 (1973).

414. Bałuka, M., Hanuza, J., and Jeżowska-Trzebiatowska, B., *Bull. Acad. Polon. Sci., Ser. Chim.* **20,** 271 (1972).

415. George, G. N., Cleland, W. E., Enemark, J. H., Smith, B. E., Kipke, C. A., Roberts, S. A., and Cramer, S. P., *J. Am. Chem. Soc.* **112,** 2541 (1990).

416. Colton, R., and Tomkins, I. B., *Aust. J. Chem.* **21,** 1981 (1968).

417. Davison, A., Jones, A. G., and Abrams, M. J., *Inorg. Chem.* **20,** 4300 (1981).

418. Du Preez, J. G. H., Gerber, T. I. A., and Jacobs, R., *J. Coord. Chem.* **26,** 259 (1992).

419. Duatti, A., Marchi, A., Rossi, R., Magon, L., Deutsch, E., Bertolasi, V., and Bellucci, F., *Inorg. Chem.* **27,** 4208 (1988).

420. Davison, A., DePamphilis, B. V., Jones, A. G., Franklin, K. J., and Lock, C. J. L., *Inorg. Chim. Acta* **128,** 161 (1987).

421. Rochon, F. D., Melanson, R., and Kong, P.-C., *Acta Cryst. C* **48,** 785 (1992).

422. Abrams, M. J., Larsen, S. K., and Zubieta, J., *Inorg. Chem.* **30,** 2031 (1991).

423. Baldas, J., Colmanet, S. F., and Mackay, M. F., *J. Chem. Soc., Dalton Trans.,* 1725 (1988).

424. Hamor, T. A., Hussain, W., Jones, C. J., McCleverty, J. A., and Rothin, A. S., *Inorg. Chim. Acta* **146,** 181 (1988).

425. Smith, J. E., Byrne, E. F., Cotton, F. A., and Sekutowski, J. C., *J. Am. Chem. Soc.* **100,** 5571 (1978).

426. DePamphilis, B. V., Jones, A. G., Davis, M. A., and Davison, A., *J. Am. Chem. Soc.* **100,** 5570 (1978).

427. Colmanet, S. F., and Mackay, M. F., *Inorg. Chim. Acta* **147,** 173 (1988).

428. Colmanet, S. F., and Mackay, M. F., *Aust. J. Chem.* **41,** 151 (1988).

429. Bandoli, G., Nicolini, M., Mazzi, U., Spies, H., and Munze, R., *Transition Met. Chem.* **9,** 127 (1984).

430. Colmanet, S. F., and Mackay, M. F., *Aust. J. Chem.* **40,** 1301 (1987).

431. Jones, A. G., DePamphilis, B. V., and Davison, A., *Inorg. Chem.* **20,** 1617 (1981).

432. Bandoli, G., Mazzi, U., Abram, U., Spies, H., and Münze, R., *Polyhedron* **6,** 1547 (1987).

433. Huber, G., Anderegg, G., and May K., *Polyhedron* **6,** 1707 (1987).

434. Sykes, A. G., *in* "Comprehensive Coordination Chemistry" (G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Eds.), Vol. 3, p. 1250. Pergamon Press, Oxford, 1987.

435. Hashimoto, K., Yamada, Y., Omori, T., and Yoshihara, K., *J. Radioanal. Nucl. Chem., Lett.* **135,** 187 (1989).

436. Grases, F., Amat, E., Genestar, C., and Palou, J., *J. Radioanal. Nucl. Chem., Articles* **116,** 459 (1987).

437. Spies, H., and Johannsen, B., *React. Kinet. Catal. Lett.* **10,** 153 (1979).

438. Spies, H., *React. Kinet. Catal. Lett.* **10,** 131 (1979).

439. Spies, H., and Johannsen, B., *Inorg. Chim. Acta* **33,** L113 (1979).

440. Byrne, E. F., and Smith, J. E., *Inorg. Chem.* **18,** 1832 (1979).

441. Davison, A., Orvig, C., Trop, H. S., Sohn, M., DePamphilis, B. V., and Jones, A. G., *Inorg. Chem.* **19,** 1988 (1980).

442. Jones, A. G., Orvig, C., Trop, H. S., Davison, A., and Davis, M. A., *J. Nucl. Med.* **21,** 279 (1980).

443. Spies, H., and Johannsen, B., *Inorg. Chim. Acta* **48,** 255 (1981).

444. Du Preez, J. G. H., and Gerber, T. I. A., *Inorg. Chim. Acta* **110,** 59 (1985).

445. Abrams, M. J., Brenner, D., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **77,** L127 (1983).

446. Blower, P. J., Singh, J., and Clarke, S. E. M., *J. Nucl. Med.* **32,** 845 (1991).

447. Spies, H., and Scheller, D., *Inorg. Chim. Acta* **116,** 1 (1986).

448. Baldas, J., Bonnyman, J., and Ivanov, Z., *J. Nucl. Med.* **30,** 1240 (1989).

449. Pietzsch, H. J., Spies, H., Hoffmann, S., and Stach, J., *Inorg. Chim. Acta* **161,** 15 (1989).

450. Pietzsch, H.-J., Spies, H., and Hoffmann, S., *Inorg. Chim. Acta* **165,** 163 (1989); **168,** 7 (1990).

451. Morelock, M. M., Cormier, T. A., and Tolman, G. L., *Inorg. Chem.* **27,** 3137 (1988).

452. Abram, U., and Spies, H., *Z. Chem.* **24,** 74 (1984).

453. Fair, C. K., Troutner, D. E., Schlemper, E. O., Murmann, R. K., and Hoppe, M. L., *Acta Cryst. C* **40,** 1544 (1984).

454. Jurisson, S., Schlemper, E. O., Troutner, D. E., Canning, L. R., Nowotnik, D. P., and Neirinckx, R. D., *Inorg. Chem.* **25,** 543 (1986).

455. Jurisson, S., Aston, K., Fair, C. K., Schlemper, E. O., Sharp, P. R., and Troutner, D. E., *Inorg. Chem.* **26,** 3576 (1987).

456. Gerber, T. I. A., Kemp, H. J., du Preez, J. G. H., Bandoli, G., and Dolmella, A., *Inorg. Chim. Acta* **202,** 191 (1992).

457. Lawrence, A. J., Thornback, J. R., Zanelli, G. D., and Lawson, A., *Inorg. Chim. Acta* **141,** 165 (1988).

458. Deutsch, E. A., Elder, R. C., and Packard, A., *et al.*, cited in *Coord. Chem. Rev.* **44,** 191 (1982).

459. Jurisson, S., Lindoy, L. F., Dancey, K. P., McPartlin, M., Tasker, P. A., Uppal, D. K., and Deutsch, E., *Inorg. Chem.* **23,** 227 (1984).

460. Mazzi, U., Refosco, F., Tisato, F., Bandoli, G., and Nicolini, M., *J. Chem. Soc., Dalton Trans.,* 1623 (1986).

461. Abrams, M. J., Shaik, S. N., and Zubieta, J., *Inorg. Chim. Acta* **186,** 87 (1991).

462. Morgan, G. F., Abram, U., Evrard, G., Durant, F., Deblaton, M., Clemens, P., Van den Broeck, P., and Thornback, J. R., *J. Chem. Soc., Chem. Comm.,* 1772 (1990).

463. Morgan, G. F., Deblaton, M., Hussein, W., Thornback, J. R., Evrard, G., Durant, F., Stach, J., Abram, U., and Abram, S., *Inorg. Chim. Acta* **190,** 257 (1991).

464. Refosco, F., Tisato, F., Mazzi, U., Bandoli, G., and Nicolini, M., *J. Chem. Soc., Dalton Trans.,* 611 (1988).

465. Liu, S., Rettig, S. J., and Orvig, C., *Inorg. Chem.* **30,** 4915 (1991).

466. Duatti, A., Marchi, A., Magon, L., Deutsch, E., Bertolasi, V., and Gilli, G., *Inorg. Chem.* **26,** 2182 (1987).

467. Du Preez, J. G. H., Gerber, T. I. A., and Gibson, M. L., *J. Coord. Chem.* **22,** 159 (1990).

468. Du Preez, J. G. H., Gerber, T. I. A., and Kemp, H. J., *J. Coord. Chem.* **26,** 177 (1992).

469. Du Preez, J. G. H., Gerber, T. I. A., Fourie, P. J., and Van Wyk, A. J., *J. Coord. Chem.* **13,** 173 (1984).

470. Refosco, F., Tisato, F., Bandoli, G., Bolzati, C., Dolmella, A., Moresco, A., and Nicolini, M., *J. Chem. Soc., Dalton Trans.,* 605 (1993).

471. Lever, S. Z., Baidoo, K. E., and Mahmood, A., *Inorg. Chim. Acta* **176,** 183 (1990).

472. Mahmood, A., Halpin, W. A., Baidoo, K. E., Sweigart, D. A., and Lever, S. Z., *Acta Cryst. C* **47,** 254 (1991).

473. Kung, H. F., Guo, Y.-Z., Yu, C.-C., Billings, J., Subramanyam, V., and Calabrese, J. C., *J. Med. Chem.* **32,** 433 (1989).

474. John, C. S., Kung, M.-P., Billings, J., and Kung, H. F., *Nucl. Med. Biol.* **18,** 551 (1991).

475. DiZio, J. P., Anderson, C. J., Davison, J. A., Ehrhardt, G. J., Carlson, K. E., Welch, M. J., and Katzenellenbogen, J. A., *J. Nucl. Med.* **33,** 558 (1992).

476. Ohmomo, Y., Francesconi, L., Kung, M.-P., and Kung, H. F., *J. Med. Chem.* **35,** 157 (1992).

477. Francesconi, L. C., Graczyk, G., Wehrli, S., Shaik, S. N., McClinton, D., Liu, S., Zubieta, J., and Kung, H. F., *Inorg. Chem.* **32,** 3114 (1993).

478. Edwards, D. S., Cheesman, E. H., Watson, M. W., Maheu, L. J., Nguyen, S. A., Dimitre, L., Nason, T., Watson, A. D., and Walovitch, R., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 433. Cortina International, Verona/Raven Press, New York, 1990.

479. Faggiani, R., Lock, C. J. L., Epps, L. A., Kramer, A. V., and Brune, D., *Acta Cryst. C* **44,** 777 (1988).

480. Faggiani, R., Lock, C. J. L., Epps, L. A., Kramer, A. V., and Brune, H. D., *Acta Cryst. C* **46,** 2324 (1990).

481. Marchi, A., Marvelli, L., Rossi, R., Magon, L., Bertolasi, V., Ferretti, V., and Gilli, P., *J. Chem. Soc., Dalton Trans.,* 1485 (1992).

482. Stassinopoulou, C. I., Mastrostamatis, S., Papadopoulos, M., Vavouraki, H., Terzis, A., Hountas, A., and Chiotellis, E., *Inorg. Chim. Acta* **189,** 219 (1991).

483. Davison, A., Jones, A. G., Orvig, C., and Sohn, M., *Inorg. Chem.* **20,** 1629 (1981).

484. Jones, A. G., Davison, A., LaTegola, M. R., Brodack, J. W., Orvig, C., Sohn, M., Toothaker, A. K., Lock, C. J. L., Franklin, K. J., Costello, C. E., Carr, S. A., Biemann, K., and Kaplan, M. L., *J. Nucl. Med.* **23,** 801 (1982).

485. Chen, B., Heeg, M. J., and Deutsch, E., *Inorg. Chem.* **31,** 4683 (1992).

486. Brenner, D., Davison, A., Lister-James, J., and Jones, A. G., *Inorg. Chem.* **23,** 3793 (1984).

487. Rao, T. N., Adhikesavalu, D., Camerman, A., and Fritzberg, A. R., *J. Am. Chem. Soc.* **112,** 5798 (1990).

488. Bryson, N., Lister-James, J., Jones, A. G., Davis, W. M., and Davison, A., *Inorg. Chem.* **29,** 2948 (1990).

489. Canney, D. J., Billings, J., Francesconi, L. C., Guo, Y.-Z., Haggerty, B. S., Rheingold, A. L., and Kung, H. F., *J. Med. Chem.* **36,** 1032 (1993).

490. Chen, Y.-C. J., and Janda, K. D., *J. Am. Chem. Soc.* **114,** 1488 (1992).

491. Rao, T. N., Brixner, D. I., Srinivasan, A., Kasina, S., Vanderheyden, J.-L., Wester, D. W., and Fritzberg, A. R., *Appl. Radiat. Isot.* **42,** 525 (1991).

492. Bryson, N. J., Brenner, D., Lister-James, J., Jones, A. G., Dewan, J. C., and Davison, A., *Inorg. Chem.* **28,** 3825 (1989).

493. Bryson, N., Dewan, J. C., Lister-James, J., Jones, A. G., and Davison, A., *Inorg. Chem.* **27,** 2154 (1988).

494. Franklin, K. J., Howard-Lock, H. E., and Lock, C. J. L., *Inorg. Chem.* **21,** 1941 (1982).

495. Johnson D. E., Fritzberg, A. R., Hawkins, B. L., Kasina, S., and Eshima, D., *Inorg. Chem.* **23,** 4204 (1984).

496. Bandoli, G., and Gerber, T. I. A., *Inorg. Chim. Acta* **126,** 205 (1987).

497. Abram, U., Muenze, R., Hartung, J., Beyer, L., Kirmse, R., Koehler, K., Stach, J., Behm, H., and Beurskens, P. T., *Inorg. Chem.* **28,** 834 (1989).

498. Du Preez, J. G. H., Gerber, T. I., and Knoesen, O., *Inorg. Chim. Acta* **133,** 3 (1987).

499. Du Preez, J. G. H., Gerber, T. I. A., and Knoesen, O., *Inorg. Chim. Acta* **132,** 241 (1987).

500. Du Preez, J. G. H., Gerber, T. I. A., and Gibson, M. L., *J. Coord. Chem.* **22,** 321 (1991).

501. Nosco, D. L., Tofe, A. J., Dunn, T. J., Lyle, L. R., Wolfangel, R. G., Bushman, M. J., Grummon, G. D., Helling, D. E., Marmion, M. E., Miller, K. M., Pipes, D. W., Strubel, T. W., and Wester, D. W., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 381. Cortina International, Verona/Raven Press, New York, 1990.

502. Hansen, R., Cini, R., Taylor, A., and Marzilli, L. G., *Inorg. Chem.* **31,** 2801 (1992).

503. Fackler, P. H., Kastner, M. E., and Clarke, M. J., *Inorg. Chem.* **23,** 3968 (1984).

504. Du Preez, J. G. H., Gerber, T. I. A., Gibson, M. L., and Geyser, R., *J. Coord. Chem.* **22,** 249 (1990).

505. Pearlstein, R. M., Lock, C. J. L., Faggiani, R., Costello, C. E., Zeng, C.-H., Jones, A. G., and Davison, A., *Inorg. Chem.* **27,** 2409 (1988).

506. Thomas, R. W., Estes, G. W., Elder, R. C., and Deutsch, E., *J. Am. Chem. Soc.* **101,** 4581 (1979).

507. Wilcox, B. E., Heeg, M. J., and Deutsch, E., *Inorg. Chem.* **23,** 2962 (1984).

508. Omori, T., Yamada, Y., Iino, S., and Yoshihara, K., *J. Radioanal. Nucl. Chem., Lett.* **119,** 223 (1987).

509. Refosco, F., Mazzi, U., Deutsch, E., Kirchhoff, J. R., Heineman, W. R., and Seeber, R., *Inorg. Chem.* **27,** 4121 (1988).

510. Bandoli, G., Mazzi, U., Clemente, D. A., and Roncari, E., *J. Chem. Soc., Dalton Trans.,* 2455 (1982).

511. Tisato, F., Refosco, F., Moresco, A., Bandoli, G., Mazzi, U., and Nicolini, M., *J. Chem. Soc., Dalton Trans.*, 2225 (1990).

512. Bandoli, G., Mazzi, U., Wilcox, B. E., Jurisson, S., and Deutsch, E., *Inorg. Chim. Acta* **95,** 217 (1984).

513. Wilcox, B. E., Cooper, J. N., Elder, R. C., and Deutsch, E., *Inorg. Chim. Acta* **142,** 55 (1988).

514. Tisato, F., Refosco, F., Mazzi, U., Bandoli, G., and Nicolini, M., *J. Chem. Soc., Dalton Trans.*, 1693 (1987).

515. Bandoli, G., Mazzi, U., Pietzsch, H.-J., and Spies, H., *Acta Cryst. C* **48,** 1422 (1992).

516. Abram, U., Abram, S., Hiller, W., Morgan, G. F., Thornback, J. R., Deblaton, M., and Stach, J., *Z. Naturforsch. B* **46,** 453 (1991).

517. Pietzsch, H.-J., Spies, H., Leibnitz, P., Reck, G., Beger, J., and Jacobi, R., *Polyhedron* **12,** 187 (1993).

518. Johannsen, B., Noll, B., Leibnitz, P., Reck, G., Noll, S., and Spies, H., *Inorg. Chim. Acta* **210,** 209 (1993).

519. Du Preez, J. G. H., Gerber, T. I. A., and Knoesen, O., *Inorg. Chim. Acta* **130,** 9 (1987).

520. Du Preez, J. G. H., Gerber, T. I. A., and Knoesen, O., *J. Coord. Chem.* **16,** 285 (1987).

521. Pietzsch, H.-J., Spies, H., Hoffmann, S., and Scheller, D., *Appl. Radiat. Isot.* **41,** 185 (1990).

522. Nicholson, T., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **168,** 227 (1990).

523. Nicholson, T., Storm, S. L., Davis, W. M., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **196,** 27 (1992).

524. Holm, R. H., *Chem. Rev.* **87,** 1401 (1987).

525. Zuckman, S. A., Freeman, G. M., Troutner, D. E., Volkert, W. A., Holmes, R. A., Van Derveer, D. G., and Barefield, E. K., *Inorg. Chem.* **20,** 2386 (1981).

526. Kastner, M. E., Fackler, P. H., Clarke, M. J., and Deutsch, E., *Inorg. Chem.* **23,** 4683 (1984).

527. Truffer, S., Ianoz, E., Lerch, P., and Kosinski, M., *Inorg. Chim. Acta* **149,** 217 (1988).

528. Kuzina, A. F., Oblova, A. A., and Spitsyn, V. I., *Russ. J. Inorg. Chem. (Engl. Transl.)* **17,** 1377 (1972).

529. Kastner, M. E., Lindsay, M. J., and Clarke, M. J., *Inorg. Chem.* **21,** 2037 (1982).

530. Fackler, P. H., Lindsay, M. J., Clarke, M. J., and Kastner, M. E., *Inorg. Chim. Acta* **109,** 39 (1985).

531. Ianoz, E., Mantegazzi, D., Lerch, P., Nicolò, F., and Chapuis, G., *Inorg. Chim. Acta* **156,** 235 (1989).

532. Mantegazzi, D., Ianoz, E., Lerch, P., Nicolò, F., and Chapuis, G., *Inorg. Chim. Acta* **176,** 99 (1990).

533. Lin, Z., and Hall, M. B., *Coord. Chem. Rev.* **123,** 149 (1993).

534. Lu, J., and Clarke, M. J., *Inorg. Chem.* **28,** 2315 (1989).

535. Helm, L., Deutsch, K., Deutsch, E. A., and Merbach, A. E., *Helv. Chim. Acta* **75,** 210 (1992).

536. Kelly, J. D., Forster, A. M., Higley, B., Archer, C. M., Booker, F. S., Canning, L. R., Chui, K. W., Edwards, B., Gill, H. K., McPartlin, M., Nagle, K. R., Latham, I. A., Pickett, R. D., Storey, A. E., and Webbon, P. M., *J. Nucl. Med.* **34,** 222 (1993).

537. Spitsyn, V. I., Glinkina, M. I., and Kuzina, A. F., *Dokl. Akad. Nauk SSSR* **200,** 1372 [Engl. 875] (1971).

538. Du Preez, J. G. H., Gerber, T. I. A., Fourie, P. J., and Van Wyk, A. J., *Inorg. Chim. Acta* **82,** 201 (1984).

539. Trop, H. S., cited in *Int. J. Appl. Radiat. Isot.* **33,** 875 (1982).

540. Tisato, F., Mazzi, U., Bandoli, G., Cros, G., Darbieu, M.-H., Coulais, Y., and Guiraud, R., *J. Chem. Soc., Dalton Trans.*, 1301 (1991).

541. Pillai, M. R. A., John, C. S., Lo, J. M., Schlemper, E. O., and Troutner, D. E., *Inorg. Chem.* **29,** 1850 (1990).

542. Tisato, F., Refosco, F., Mazzi, U., Bandoli, G., and Dolmella, A., *Inorg. Chim. Acta* **164,** 127 (1989).

543. Bandoli, G., Nicolini, M., Mazzi, U., and Refosco, F., *J. Chem. Soc., Dalton Trans.*, 2505 (1984).

544. Lin, Z., and Hall, M. B., *Inorg. Chem.* **30,** 3817 (1991).

545. Davison, A., DePamphilis, B. V., Faggiani, R., Jones, A. G., Lock, C. J. L., and Orvig, C., *Can. J. Chem.* **63,** 319 (1985).

546. DePamphilis, B. V., Jones, A. G., and Davison, A., *Inorg. Chem.* **22,** 2292 (1983).

547. Du Preez, J. G. H., Gerber, T. I. A., and Gibson, M. L., *J. Coord. Chem.* **22,** 33 (1990).

548. Abrams, M. J., Costello, C. E., Shaik, S. N., and Zubieta, J., *Inorg. Chim. Acta* **180,** 9 (1991).

549. Duatti, A., Tisato, F., Refosco, F., Mazzi, U., and Nicolini, M., *Inorg. Chem.* **28,** 4564 (1989).

550. Baldas, J., Bonnyman, J., Pojer, P. M., Williams, G. A., and Mackay, M. F., *J. Chem. Soc., Dalton Trans.*, 1798 (1981).

551. Kaden, L., Lorenz, B., Schmidt, K., Sprinz, H., and Wahren, M., *Isotopenpraxis* **17,** 174 (1981).

552. Baldas, J., Bonnyman, J., and Williams, G. A., *Inorg. Chem.* **25,** 150 (1986).

553. Abram, U., Kirmse, R., Stach, J., and Lorenz, B., *Z. Chem.* **25,** 153 (1985).

554. Kirmse, R., Stach, J., and Abram, U., *Polyhedron* **4,** 1403 (1985).

555. Baldas, J., Boas, J. F., Colmanet, S. F., and Mackay, M. F., *Inorg. Chim. Acta* **170,** 233 (1990).

556. Leipoldt, J. G., Basson, S. S., Roodt, A., and Purcell, W., *Polyhedron* **11,** 2277 (1992).

557. Baldas, J., Colmanet, S. F., and Williams, G. A., unpublished results.

558. Baldas, J., and Ivanov, Z., unpublished results.

559. Baldas, J., Bonnyman, J., and Williams, G. A., *J. Chem. Soc., Dalton Trans.*, 833 (1984).

560. Williams, G. A., and Baldas, J., *J. Nucl. Med. Allied Sci.* **33,** 327 (1989).

561. Abram, U., Spies, H., Abram, S., Kirmse, R., and Stach, J., *Z. Chem.* **26,** 140 (1986).

562. Baldas, J., Heath, G. N., Raptis, R. G., and Williams, G. A., unpublished results.

563. Abram, U., Spies, H., Görner, W., Kirmse, R., and Stach, J., *Inorg. Chim. Acta* **109,** L9 (1985).

564. Rossi, R., Marchi, A., Magon, L., Casellato, U., and Graziani, R., *J. Chem. Soc., Dalton Trans.*, 2923 (1990).

565. Baldas, J., Boas, J. F., Colmanet, S. F., and Williams, G. A., *J. Chem. Soc., Dalton Trans.*, 2845 (1992).

566. Williams, G. A., and Baldas, J., *Aust. J. Chem.* **42,** 875 (1989).

567. Abram, U., Abram, S., Stach, J., Dietzsch, W., and Hiller, W., *Z. Naturforsch. B* **46,** 1183 (1991).

568. Baldas, J., and Bonnyman, J., *Inorg. Chim. Acta* **141,** 153 (1988).

569. Stach, J., Dietzsch, W., and Abram, U., *Z. Chem.* **29,** 295 (1989).

570. Baldas, J., and Bonnyman, J., *in* "Technetium and Rhenium in Chemistry and Nuclear Medicine 3" (M. Nicolini, G. Bandoli, and U. Mazzi, Eds.), p. 429. Cortina International, Verona/Raven Books, New York, 1990.

571. Pasqualini, R., and Duatti, A., *J. Chem. Soc., Chem. Comm.*, 1354 (1992).

572. Marchi, A., Garuti, P., Duatti, A., Magon, L., Rossi, R., Ferretti, V., and Bertolasi, V., *Inorg. Chem.* **29,** 2091 (1990).
573. Marchi, A., Rossi, R., Magon, L., Duatti, A., Casellato, U., Graziani, R., Vidal, M., and Riche, F., *J. Chem. Soc., Dalton Trans.,* 1935 (1990).
574. Duatti, A., Marchi, A., Bertolasi, V., and Ferretti, V., *J. Am. Chem. Soc.* **113,** 9680 (1991).
575. Bertolasi, V., Ferretti, V., Gilli, P., Marchi, A., and Marvelli, L., *Acta Cryst. C* **47,** 2535 (1991).
576. Archer, C. M., Dilworth, J. R., Griffiths, D. V., McPartlin, M., and Kelly, J. D., *J. Chem. Soc., Dalton Trans.,* 183 (1992).
577. Dilworth, J. R., Griffiths, D. V., Hughes, J. M., Morton, S., Hiller, W., Archer, C. M., Kelly, J. D., and Walton, G., *Inorg. Chim. Acta* **192,** 59 (1992).
578. Clarke, M. J., and Lu, J., *Inorg. Chem.* **31,** 2476 (1992).
579. Abram, U., Abram, S., Spies, H., Kirmse, R., Stach, J., and Köhler, K., *Z. Anorg. Allg. Chem.* **544,** 167 (1987).
580. Rummel, S., Hermann, M., and Schmidt, K., *Z. Chem.* **25,** 152 (1985).
581. de Vries, N., Costello, C. E., Jones, A. G., and Davison, A., *Inorg. Chem.* **29,** 1348 (1990).
582. Abram, U., Lorenz, B., Kaden, L., and Scheller, D., *Polyhedron* **7,** 285 (1988).
583. Abram, U., Mäding, P., Kirmse, R., and Köhler, K., *Z. Chem.* **29,** 183 (1989).
584. Duatti, A., Marchi, A., and Pasqualini, R., *J. Chem. Soc., Dalton Trans.,* 3729 (1990).
585. Abrams, M. J., Larsen, S. K., Shaikh, S. N., and Zubieta, J., *Inorg. Chim. Acta* **185,** 7 (1991).
586. Baldas, J., Boas, J. F., Colmanet, S. F., and Williams, G. A., *J. Chem. Soc., Dalton Trans.,* 2441 (1991).
587. Batsanov, A. S., Struchkov, Yu. T., Lorenz, B., and Olk, B., *Z. Anorg. Allg. Chem.* **564,** 129 (1988).
588. Dilworth, J. R., Archer, C. M., Latham, I. A., Kelly, J. D., Griffiths, D. V., York, D. C., Mahoney, P. M., and Higley, B., *Nucl. Med. Biol.* **18,** 547 (1991).
589. Marchi, A., Marvelli, L., Rossi, R., Magon, L., Uccelli, L., Bertolasi, V., Ferretti, V., and Zanobini, F., *J. Chem. Soc., Dalton Trans.,* 1281 (1993).
590. Abram, U., Münze, R., Jäger, E.-G., Stach, J., and Kirmse, R., *Inorg. Chim. Acta* **162,** 171 (1989).
591. Abram, U., Abram, S., Münze, R., Jäger, E.-G., Stach, J., Kirmse, R., Admiraal, G., and Beurskens, P. T., *Inorg. Chim. Acta* **182,** 233 (1991).
592. Marchi, A., Duatti, A., Rossi, R., Magon, L., Pasqualini, R., Bertolasi, V., Ferretti, V., and Gilli, G., *J. Chem. Soc., Dalton Trans.,* 1743 (1988).
593. Rossi, R., Marchi, A., Aggio, S., Magon, L., Duatti, A., Casellato, U., and Graziani, R., *J. Chem. Soc., Dalton Trans.,* 477 (1990).
594. Uhlemann, E., Spies, H., Pietzsch, H.-J., and Herzschuh, R., *Z. Naturforsch. B* **47,** 1441 (1992).
595. Abram, U., Hartung, J., Beyer, L., Stach, J., and Kirmse, R., *Z. Chem.* **30,** 180 (1990).
596. Nicholson, T., Davison, A., and Jones, A. G., *Inorg. Chim. Acta* **187,** 51 (1991).
597. Abrams, M. J., Shaikh, S. N., and Zubieta, J., *Inorg. Chim. Acta* **171,** 133 (1990).
598. Abrams, M. J., Larsen, S. K., and Zubieta, J., *Inorg. Chim. Acta* **173,** 133 (1990).
599. Nicholson, T., Mahmood, A., Morgan, G., Jones, A. G., and Davison, A., *Inorg. Chim. Acta* **179,** 53 (1991).
600. Cook, J., Davis, W. M., Davison, A., and Jones, A. G., *Inorg. Chem.* **30,** 1773 (1991).
601. Spies, H., Pietzsch, H.-J., and Hoffmann, I., *Inorg. Chim. Acta* **161,** 17 (1989).

602. Baldas, J., Boas, J. F., Bonnyman, J., Colmanet, S. F., and Williams, G. A., *J. Chem. Soc., Chem. Comm.*, 1163 (1990).
603. Selig, H., Chernik, C. L., and Malm, J. G., *J. Inorg. Nucl. Chem.* **19,** 377 (1961).
604. Deutsch, E., Heineman, W. R., Hurst, R., Sullivan, J. C., Mulac, W. A., and Gordon, S., *J. Chem. Soc., Chem. Comm.*, 1038 (1978).
605. Libson, K., Sullivan, J. C., Mulac, W. A., Gordon, S., and Deutsch, E., *Inorg. Chem.* **28,** 375 (1989).
606. Lawrance, G. A., and Sangster, D. F., *Polyhedron* **4,** 1095 (1985).
607. Kryuchkov, S. V., Pikaev, A. K., Kuzina, A. F., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* **247,** 1187 [Engl. 690] (1979).
608. Astheimer, L., Hauck, J., Schenk, H. J., and Schwochau, K., *J. Chem. Phys.* **63,** 1988 (1975).
609. Astheimer, L., and Schwochau, K., *J. Inorg. Nucl. Chem.* **38,** 1131 (1976).
610. Edwards, A. J., Jones, G. R., and Steventon, B. R., *J. Chem. Soc., Chem. Comm.*, 462 (1967).
611. Edwards, A. J., Jones, G. R., and Sills, R. J. C., *J. Chem. Soc. A*, 2521 (1970).
612. Kirmse, R., Stach, J., and Abram, U., *Inorg. Chem.* **24,** 2196 (1985).
613. Abram, U., Abram, S., Stach, J., and Kirmse, R., *J. Radioanal. Nucl. Chem., Articles* **100,** 325 (1986).
614. Baldas, J., Boas, J. F., Bonnyman, J., and Williams, G. A., *J. Chem. Soc., Dalton Trans.*, 2395 (1984).
615. Baldas, J., Colmanet, S. F., and Williams, G. A., *Inorg. Chim. Acta* **179,** 189 (1991).
616. Abram, U., Münze, R., Kirmse, R., Köhler, K., Dietzsch, W., and Golič, L., *Inorg. Chim. Acta* **169,** 49 (1990).
617. Lorenz, B., *Isotopenpraxis* **26,** 452 (1990).
618. Baldas, J., Bonnyman, J., and Williams, G. A., *Aust. J. Chem.* **38,** 215 (1985).
619. Baldas, J., Boas, J. F., Colmanet, S. F., Rae, A. D., and Williams, G. A., *Proc. R. Soc. London A* **442,** 437 (1993).
620. Baldas, J., Boas, J. F., and Bonnyman, J., *J. Chem. Soc., Dalton Trans.*, 1721 (1987).
621. Kohler, K., Kirmse, R., and Abram, U., *Z. Chem.* **26,** 339 (1986).
622. Kirmse, R., Köhler, K., Abram, U., Böttcher, R., Golič, L., and de Boer, E., *Chem. Phys.* **143,** 75 (1990).
623. Köhler, K., Kirmse, R., Böttcher, R., Abram, U., Gribnau, M. C. M., Keijzers, C. P., and de Boer, E., *Chem. Phys.* **143,** 83 (1990).
624. Köhler, K., Kirmse, R., Böttcher, R., and Abram, U., *Chem. Phys.* **160,** 281 (1991).
625. Figgis, B. N., Reynolds, P. A., and Cable, J. W., *J. Chem. Phys.* **98,** 7743 (1993).
626. Kirmse, R., Stach, J., and Abram, U., *Inorg. Chim. Acta* **117,** 117 (1986).
627. Köhler, K., Kirmse, R., and Abram, U., *Z. Anorg. Allg. Chem.* **600,** 83 (1991).
628. Baldas, J., Boas, J. F., and Bonnyman, J., *Aust. J. Chem.* **42,** 639 (1989).
629. Abram, U., Köhler, K., Kirmse, R., Kalinichenko, N. B., and Marov, I. N., *Inorg. Chim. Acta* **176,** 139 (1990).
630. Baldas, J., Boas, J. F., Ivanov, Z., and James, B. D., *Inorg. Chim. Acta* **204,** 199 (1993).
631. Pietzsch, H.-J., Abram, U., Kirmse, R., and Köhler, K., *Z. Chem.* **27,** 265 (1987).
632. Baldas, J., Colmanet, S. F., Ivanov, Z., Williams, G. A., and James, B. D., unpublished.
633. Jørgensen, C. K., *Prog. Inorg. Chem.* **12,** 101 (1970).
634. Lever, A. B. P., *J. Chem. Ed.* **51,** 612 (1974).
635. Baldas, J., and Bonnyman, J., *Int. J. Appl. Radiat. Isot.* **36,** 133 (1985); 919 (1985).

636. Alagui, A., Apparu, M., du Moulinet d'Hardemare, A., Riche, F., and Vidal, M., *Appl. Radiat. Isot.* **40,** 813 (1989).

637. Abram, U., and Wollert, R., *Radiochim. Acta* **63,** 149 (1993).

638. Baldas, J., Colmanet, S. F., and Williams, G. A., *J. Chem. Soc., Chem. Comm.,* 954 (1991).

639. Baldas, J., Colmanet, S. F., Craig, D. C., Rae, A. D., and Williams, G. A., unpublished results.

640. Baldas, J., Boas, J. F., Bonnyman, J., Colmanet, S. F., and Williams, G. A., *Inorg. Chim. Acta* **179,** 151 (1991).

641. Stiefel, E. I., *Prog. Inorg. Chem.* **22,** 1 (1977).

642. Williams, G. A., and Martin, L. J., personal communication.

643. Baldas, J., Boas, J. F., Colmanet, S. F., Ivanov, Z., and Williams, G. A., *Radiochim. Acta,* **63,** 111 (1993).

644. Ricard, L., Martin, C., Wiest, R., and Weiss, R., *Inorg. Chem.* 14, 2300 (1975).

645. Baldas, J., and Boas, J. F., *J. Chem. Soc., Dalton Trans.,* 2585 (1988).

646. Burrell, A. K., and Bryan, J. C., *Angew. Chem. Int. Ed. Engl.* **32,** 94 (1993).

647. Burrell, A. K., and Bryan, J. C., *Organometallics* **12,** 2426 (1993).

648. Kawashima, M., Koyama, M., and Fujinaga, T., *J. Inorg. Nucl. Chem.* **38,** 801 (1976).

649. Kirmse, R., Stach, J., and Spies, H., *Inorg. Chim. Acta* **45,** L251 (1980).

650. Baldas, J., Boas, J., Bonnyman, J., Mackay, M. F., and Williams, G. A., *Aust. J. Chem.* **35,** 2413 (1982).

651. Baldas, J., Boas, J. F., Bonnyman, J., Pilbrow, J. R., and Williams, G. A., *J. Am. Chem. Soc.* **107,** 1886 (1985).

652. deLearie, L. A., Haltiwanger, R. C., and Pierpont, C. G., *J. Am. Chem. Soc.* **111,** 4324 (1989).

653. Krebs, B., *Z. Anorg. Allg. Chem.* **380,** 146 (1971).

654. Boyd, G. E., *J. Chem. Ed.* **36,** 3 (1959).

655. Faggiani, R., Lock, C. J. L., and Pocé, J., *Acta Cryst. B* **36,** 231 (1980).

656. German, K. E., Grigor'ev, M. S., Kuzina, A. F., and Spitsyn, V. I., *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **32,** 667 (1987).

657. Rochon, F. D., Kong, P. C., and Melanson, R., *Acta Cryst. C* **46,** 8 (1990).

658. Keller, C., and Kanellakopulos, B., *Radiochim. Acta* 1, 107 (1963).

659. Krebs, B., and Hasse, K.-D., *Acta Cryst. B* **32,** 1334 (1976).

660. Chakravorti, M. C., *Coord. Chem. Rev.* **106,** 205 (1990).

661. Truffer-Caron, S., Ianoz, E., and Lerch, P., *Inorg. Chim. Acta* **149,** 119 (1988).

662. Kemp, T. J., Thyer, A. M., and Wilson, P. D., *J. Chem. Soc., Dalton Trans.,* 2601 (1993); 2607 (1993).

663. Müller, A., Krebs, B., and Diemann, E., *Z. Anorg. Allg. Chem.* **353,** 259 (1967).

664. Kanellakopulos, B., Raptis, K., Nuber, B., and Ziegler, M. L., *Z. Naturforsch. B* **46,** 15 (1991).

665. Nugent, W. A., *Inorg. Chem.* **22,** 965 (1983).

666. Bryan, J. C., Burrell, A. K., Miller, M. M., Smith, W. H., Burns, C. J., and Sattelberger, A. P., *Polyhedron* **12,** 1769 (1993).

667. Selig, H., and Malm, J. G., *J. Inorg. Nucl. Chem.* **25,** 349 (1963).

668. Binenboyn, J., El-Gad, U., and Selig, H., *Inorg. Chem.* **13,** 319 (1974).

669. Guest, A., Howard-Lock, H. E., and Lock, C. J. L., *J. Mol. Spectrosc.* **43,** 273 (1972).

670. Baran, E. J., *Spectrosc. Lett.* **8,** 599 (1975).

671. Franklin, K. J., Lock, C. J. L., Sayer, B. G., and Schrobilgen, G. J., *J. Am. Chem. Soc.* **104,** 5303 (1982).

672. Mercier, H. P. A., and Schrobilgen, G. J., *Inorg. Chem.* **32,** 145 (1993).
673. Aronson, F. L., Hwang, L. L.-Y., Ronca, N., Solomon, N. A., and Steigman, J., *Inorg. Chem.* **24,** 541 (1985).
674. Pearlstein, R. M., and Davison, A., *Polyhedron* **7,** 1981 (1988).
675. Thomas, J. A., and Davison, A., *Inorg. Chem.* **31,** 1976 (1992).
676. Banbery, H. J., Hussain, W., Evans, I. G., Hamor, T. A., Jones, C. J., McCleverty, J. A., Schulte, H.-J., Engles, B., and Kläui, W., *Polyhedron* **9,** 2549 (1990).
677. Thomas, J. A., and Davison, A., *Inorg. Chim. Acta* **190,** 231 (1991).
678. Baldas, J., Colmanet, S. F., and Mackay, M. F., *J. Chem. Soc., Chem. Comm.,* 1890 (1989).
679. Baldas, J., and Colmanet, S. F., *Inorg. Chim. Acta* **176,** 1 (1990).
680. Baldas, J., Colmanet, S. F., and Williams, G. A., *J. Chem. Soc., Dalton Trans.,* 1631 (1991).
681. Abrams, M. J., Chen, Q., Shaikh, S. N., and Zubieta, J., *Inorg. Chim. Acta* **176,** 11 (1990).
682. Burrell, A. K., and Bryan, J. C., *Organometallics* **11,** 3501 (1992).
683. Ginsberg, A. P., *Inorg. Chem.* **3,** 567 (1964).
684. Abrahams, S. C., Ginsberg, A. P., and Knox, K., *Inorg. Chem.* **3,** 558 (1964).
685. Kaden, L., Lorenz, B., and Wahren, M., *Isotopenpraxis* **18,** 400 (1982).