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Structural survey of technetium complexes

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ABSTRACT

The review, with 294 references and 41 figures, reports on the main structural features of 240 Tc complexes whose X-ray crystal structure has been determined during the period 1986–1992. It comprises seven major sections: oxo-; nitrido-; diazenido-, hydrazido- and imido-; Schiff base-; chalcogenide-; pnictide-; nitrosyl- and thionitrosyl-technetium complexes. The survey concludes with two comprehensive tables summarizing some properties of Tc complexes *vs.* oxidation state.

1. INTRODUCTION

In the last two decades the inter-relationship between chemistry and nuclear medicine has been playing a fundamental role in developing the knowledge of element number 43, discovered in 1937 by Perrier and Segrè [1]. Among technetium nuclides, long-lived ^{99}Tc ($t_{1/2}=2.12\times10^5$ years; $\beta^-=292$ keV), is currently handled by inorganic chemists, while the short-lived isomer ^{99m}Tc ($t_{1/2}=6.02$ h; $\gamma=140$ keV) is the radio-tracer most commonly used in nuclear medicine. At present, various ^{99m}Tc agents are used to image the heart, brain, kidneys, etc. [2–10], and they cover more than three-quarters of the routine nuclear medicine procedures [11]. The first injection of $[^{99m}TcO_4]^-$ in humans was in 1961 [12], immediately following the development of the ^{99}Mo/^{99m}Tc generator [13,14]. The continuous effort to obtain a basic understanding of technetium chemistry has produced a wide spectrum of Tc complexes [15–18], as demonstrated by the increasing number of chemical studies and X-ray structures which have appeared in *Chemical Abstracts* between 1980 and 1991 (Fig. 1).

Recently, development in ligand design has led to a new generation of Tc radiopharmaceuticals, which contain the so-called “double-faced” or “bifunctional” chelate. Such a ligand consists of a biologically active pendant function, properly linked to a system highly specific for the technetium metal. Most of the present studies (and presumably future work) include the incorporation of biologically active molecules into well-known ligand backbones to promote the synthesis of new specific radioactive receptor site agents, able to image functions and substrate metabolism.

2. COMMENTS

The present review covers structural studies on technetium compounds, and includes all reported molecular structures appearing in *Chemical Abstracts* between 1986 and August 1992. Most of them are collected in the Cambridge Structural Database (CSD) [19], but the survey also reports the Tc-crystal structures communi-

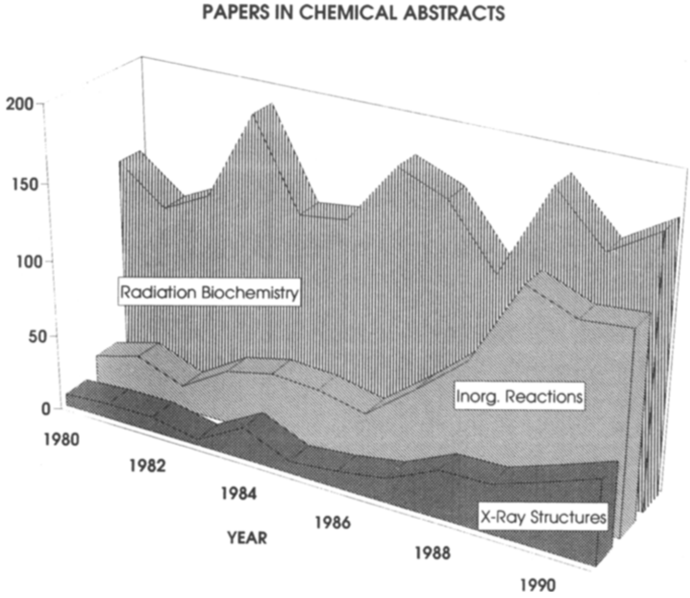


Fig. 1. Distribution of technetium entries in *Chemical Abstracts* between 1980 and 1991.

cated at three recent symposia dedicated to this subject; in particular, the IXth Radiopharmaceutical Chemistry Symposium (Paris, 1992) and the IInd and IIIrd Symposia on Technetium and Rhenium in Chemistry and Nuclear Medicine (Padova, 1985 and 1989), which are not published elsewhere. In addition, the structures appearing up to May 1993 are reported in the Addendum at the end of the review. This structural survey follows two previous reviews published in the field by Bandoli *et al.* [17] in 1982 and by Melnik *et al.* [18] in 1987. The three studies are believed to comprise all technetium molecular structures ever reported: to date, 340 crystal structures have been referred to, 260 of which are collected in this paper. Other excellent reviews, to which we refer, discuss the coordination chemistry and the structure–activity relationship, which form the basis for nuclear medicine applications of Tc radiopharmaceuticals under clinical use and of the most promising diagnostics under development [2,6,8–10,20].

X-Ray structures are grouped into ten thematic sections following, as far as possible, objective schematic rules, such as the presence in the molecule of:

i. distinctive cores (*e.g.* Tc-oxo, Tc-nitrido and related multiple Tc–nitrogen bonds, Tc-nitrosyl and Tc-thionitrosyl);

ii. homogeneous class of ligands (*e.g.* Schiff-base);

iii. homogeneous set of coordinating atoms (*e.g.* only chalcogenide, N_nS_{4-n}, pnictide, halide donors, etc.)

In addition, the sections have been further divided into sections following the rules mentioned above, or containing families of similar complexes (*e.g.* BATO- and PnAO-like species).

A perspective molecular drawing (PLUTO program [21]) is presented for intriguing and characteristic compounds. Throughout the paper, the estimated standard deviations of individual bond distance and angle are reported, since they are indicative of the accuracy attained in the structure determination. The acronyms and abbreviations utilized in the text may differ from those reported in the original references.

We acknowledge those authors who, requested for unpublished crystal data and final fractional atomic coordinates, have made our work possible. Although we have tried to be as complete as possible, we should like to apologize in advance to the authors of any article we may have inadvertently omitted.

3. OXO-TECHNETIUM(V) COMPLEXES

Usually, Tc(V) compounds contain a core, *i.e.* a moiety constituted by one or more multiple-bonded oxygen or nitrogen atoms attached to a Tc center. The most widely studied core, which is characteristic of the 5+ oxidation state, is the $[Tc{=}O]^{3+}$ moiety.

In this section, 43 X-ray crystal structures are cited. Those containing Schiff-base ligands are not included, since they will be the subject of a specific section (6.1).

Tc complexes containing the mono-oxo core are diamagnetic, being technetium in a spin-paired d^2 configuration. The p electrons of the oxo-oxygen strongly interact with the p-symmetric d_{xz}, d_{yz} orbitals of the metal. This π interaction, along with the strong σ interaction of the ligands for both five- and six-coordinate mono-oxo complexes, leads to an energy level diagram in which the two paired electrons are placed in a non-bonding d_{xy} orbital [16]. The result is a strong multiple $\sigma+\pi$ bonding of the oxo group.

The most common preparation method for Tc-oxo compounds starts from a pre-reduced precursor $[n\text{-}Bu_4N][Tc^{V}OX_4]$ ($X = Cl,Br$), but direct preparation from $[NH_4][Tc^{VII}O_4]$ is also possible using an internal (the ligand itself) or external reductant.

3.1. *Only chalcogenide donor atoms*

Twelve complexes are included in this section: they are all anionic, except $[TcO(tibt)_3(py)]$, and five-coordinate in a square-pyramidal geometry, except for the six-coordinate $[TcO(ox)_2(oxH)]^{2-}$.

Three crystal structures, $[TcO(cat)2]^-$ (Fig. 2) [22], $[TcO(cat\text{-}Cl_4)_2]^-$ [23] and $[TcO(cat\text{-}NO_2)_2]^-$ [24], contain the catechol ligand and its derivatives, while in the unexpected six-coordinate dianionic complex $[TcO(ox)_2(oxH)]^{2-}$ (Fig. 3) [25] two oxalates act as dinegative bidentate ligands, the third as a mononegative and

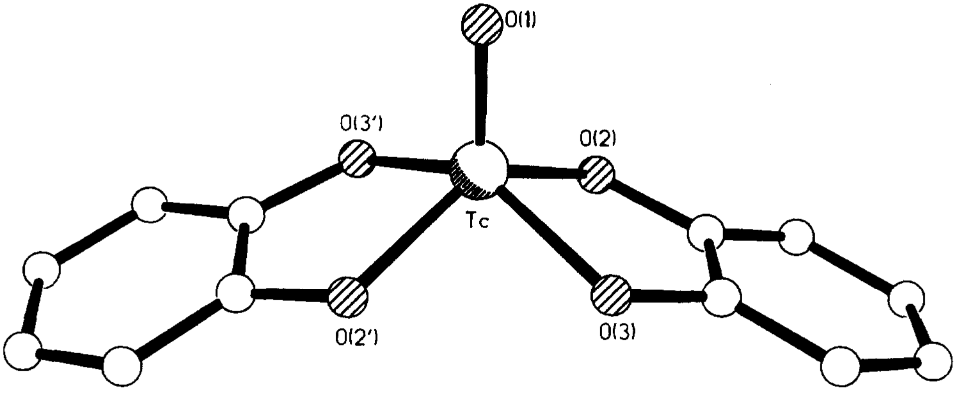


Fig. 2. $[TcO(cat)_2]^-$.

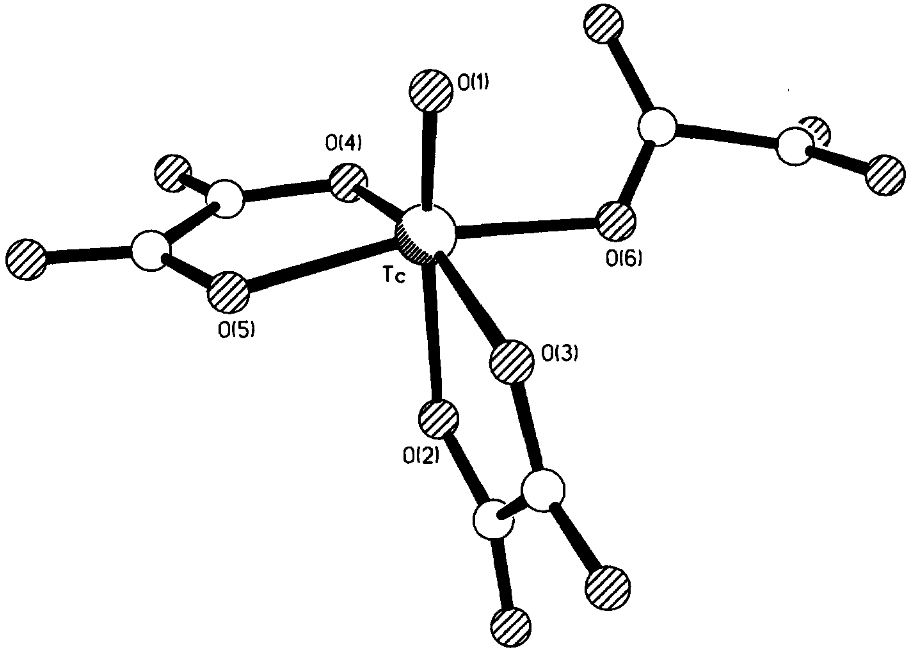


Fig. 3. $[TcO(ox)_2(oxH)]^{2-}$

unidentate ligand. When two oxygen atoms of the oxalate are replaced by two sulfurs, the coordination about $[Tc{=}O]^{3+}$ again turns out to be a square-pyramidal arrangement, as in $[TcO(dto)_2]^-$ [26], or in the similar complexes $[TcO(bdt)_2]^-$ [27] and $[TcO(mnt)_2]^-$ [28], in which the Tc=O and Tc–S bond distances are consistent with those observed in previously reported $[TcO(edt)_2]^-$ and $[TcO(SCH_2\text{-}COS)_2]^-$ complexes [29,30].

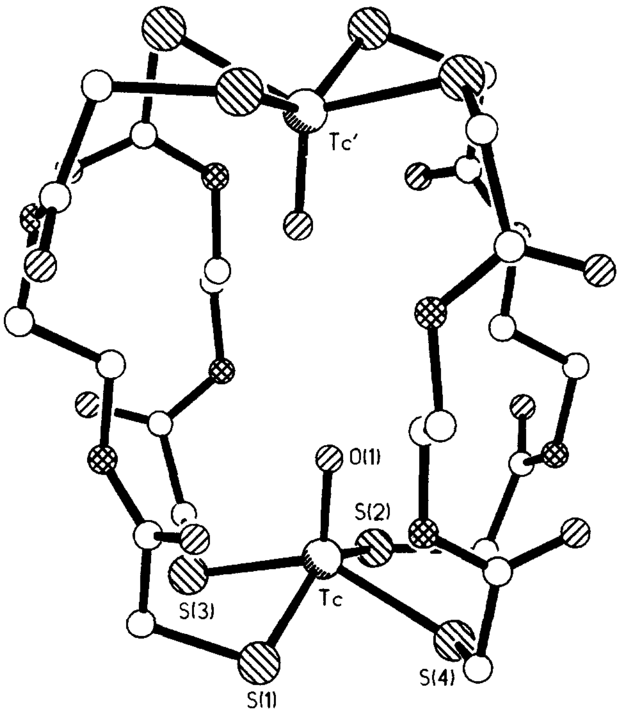


Fig. 4. $[Tc_2O_2(emaH_2)_4]^{2-}$.

In the unique species containing a $TcOSe_4$ inner sphere, $[TcO(mns)_2]^-$ [31], the four Tc–Se bond distances are in close agreement with each other (mean, 2.471 Å) and they are longer by 0.15 Å than the mean Tc–S value of analogous five-coordinate Tc-oxo complexes, as expected on the basis of the covalent radii of Se and S (1.17 and 1.04 Å, respectively).

Three structures contain monothiols:

i. the anion $[TcO(trimbt)_4]^-$ [32] displays four coordinate sulfurs,

ii. the neutral five-coordinate $[TcO(tibt)_3(py)]$ [33] in addition contains a pyridine ligand,

iii. $[Tc_2O_2(emaH_2)_4]^{2-}$ (Fig. 4) [34] consists of a centrosymmetric dianion with two square-pyramidal $[TcOS_4]$ units bridged four-fold by the $[emaH_2]^{2-}$ monodentate dithiolato ligand.

The Tc-oxo groups are oriented into the center of the cage created by the bridging ligands, giving what is referred to as a "lantern" structure.

In the complex $[TcO(Me_2dtc)(Me_4tu)_2]^{2+}$ (Fig. 5) [35], the only cationic complex of the section, the Tc–Stu bond distances are normal, while the Tc–S_{dtc} (average, 2.342 Å) are slightly shorter than the values (average, 2.398 Å) observed in the neutral Tc(V) compound $[TcN(Et_2dtc)_2]$ [36].

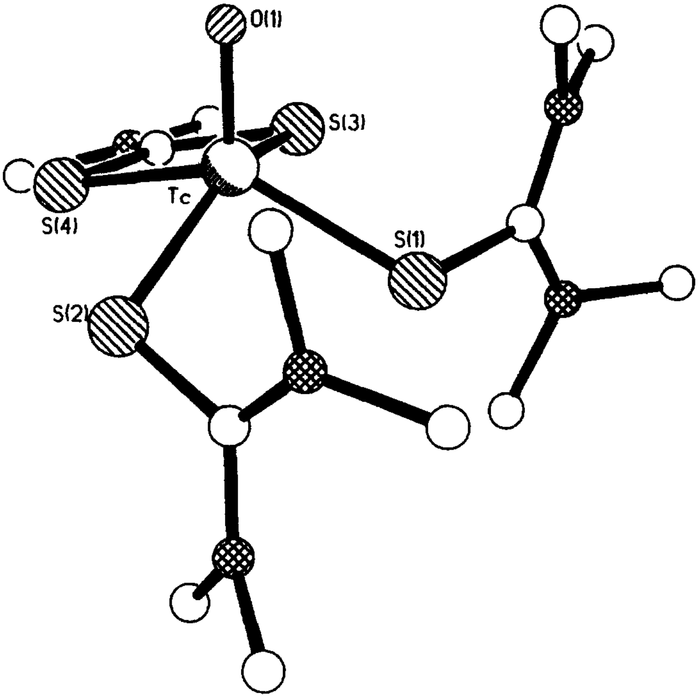


Fig. 5. $[TcO(Me_2dtc)(Me_4tu)_2]^{2+}$.

3.2. Nitrogen and sulfur donor atoms

In this section, 22 X-ray crystal structures of Tc(V)-oxo complexes are reviewed. All are five-coordinate in a square-pyramidal geometry, the only exception being the complex $[TcO_2(14\text{-ane-}N_2S_2)]^+$, which is dioxo-six-coordinate. The complexes contain ligands usually referred to as bis-aminothiole (BAT) or diamino-dithiole (DADT or DADS); they are generally prepared by reacting $[NH_4][TcO_4]$ and the appropriate ligand in basic medium (NaOH) using sodium dithionite as reductant, or by ligand-exchange reactions from $[TcOCl_4]^-$ in the presence of NaOH, which promotes the deprotonation of the thiolic groups. The coordination occurs through the ionized thiole groups and through the nitrogens. Depending on the degree of deprotonation of the amino nitrogen(s), charged or neutral complexes are obtained. The compounds exhibit a Tc=O bond distance in the range 1.65–1.69 Å.

A number of species differ only by the presence of biologically active functional groups in the ligand backbone, and, for those compounds containing tetradentate acyclic ligands, *syn* and/or *anti* epimers are expected when the coordination framework is derivatized. Some of these complexes have been successfully evaluated at tracer level (Tc-99m) as potential radiopharmaceuticals; the neutral ones as brain agents, the cationic ones as myocardial perfusion agents and the anionic ones for renal function imaging [8,9].

Essentially three groups of complexes can be distinguished within this section. The first includes five cationic complexes [37–40], which bear a classic N_2S_2-diamino dithiole donor set; three of them are *N*-alkyl substituted. Although both nitrogens are sp^3-hybridized, Tc–N as well as Tc–S distances show values which are non-equivalent within the same molecule, owing to the distortion from the ideal square-pyramidal configuration. The Tc–N values range from 2.107(1) to 2.186(8) Å, the upper value being that in the complex $[TcO([N\text{-}Me]_2daodt)]^+$ [38] and the lower one in $[TcO(Et_4daodt)]^+$ [39]. Analogously, the Tc–S distances range from 2.224(3) Å (in *syn*-$[TcO(PIP)]^+$ [40] to 2.273(1) Å (in $[TcO(Et_4daodt)]+$.

In the eight neutral complexes, neutrality is achieved by deprotonation of one of the amine nitrogens which is consistently sp^2 hybridized. This results in Tc–N distances considerably different from each other within the same molecule. The $Tc\text{–}N_{sp^2}$ bond distances range from 1.909(5) Å relative to *syn*-$[TcO([N\text{-}Me]Me_4daodt)]$ (Fig. 6) [41] to 1.937(8) Å for $[TcO(Me_6daodt)]$ [42]. These values are comparable to those usually observed for $Tc\text{-}N_{amido}$ bonds. Within the group, the $Tc\text{–}N_{sp3}$ bond distances range from 2.127(4) Å for *syn*-[TcO(BPA-BAT)] [43] to 2.224(2) Å relative to *syn*-$[TcO([N\text{-}Et]Me_4daodt)]$ [44], while Tc–S bond distances range from 2.265(1) Å for *syn*-$[TcO([N\text{-}Et]Me_4daodt)]$ to 2.314(2) Å for *anti*-$[TcO([N\text{-}Me]Me_4daodt)]$ [41].

The X-ray structure of the complex [TcO(L,L-ECD)] (Fig. 7) was briefly reported in 1989 [45]. At tracer level the complex [^{99m}TcO(L,L-ECD)] (Neurolite®) [46] readily crosses the blood–brain barrier in a pattern consistent with regional cerebral perfusion, and it is retained in the brain for hours. The mechanism of retention has been identified as a metabolic trapping in the brain due to the hydrolysis

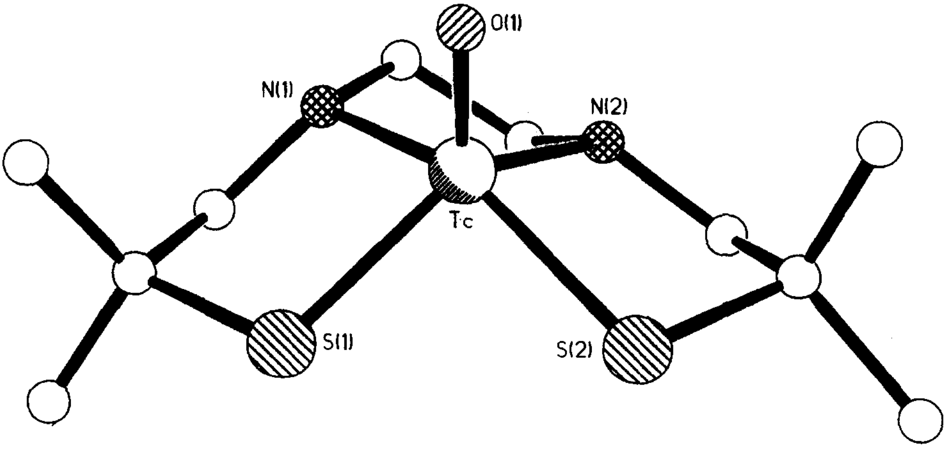


Fig. 6. *syn*-$[TcO([N\text{-}Me]Me_4daodt)]$.

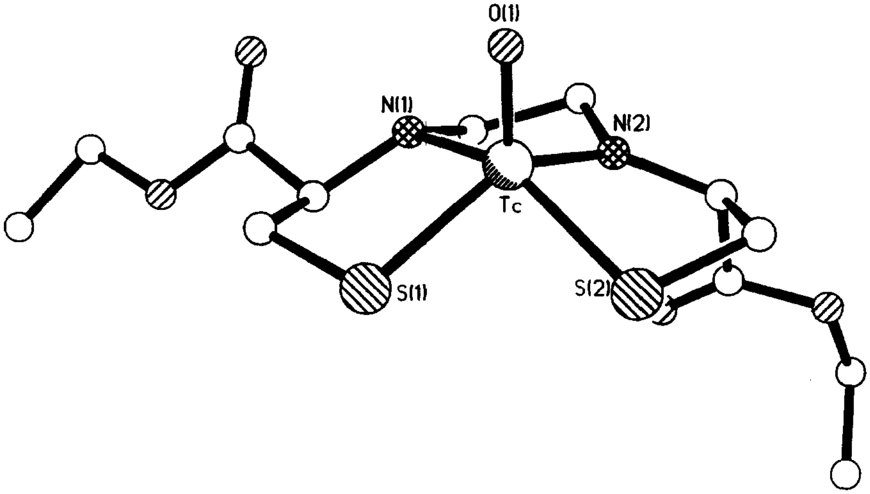


Fig. 7. [TcO(L,L-ECD)].

of one ester group of the ligand backbone. Consequently, the initially neutral complex assumes anionic character and the increased polarity is responsible for trapping in the brain cells. The two ester groups are one above (*syn* to the Tc=O unit) and one below the plane (*anti* to the Tc=O) and there is a partial interaction of the carbonyl oxygen of the *syn* COOEt group with the hydrogen at N(1).

In the two BAT derivatives [47] the ligand contains a three-membered carbon chain in between the nitrogens, including a phenyl ring. The complexes differ from each other by the degree of protonation at the amine nitrogens. In the neutral [TcO(U-BAT)], the nitrogen closer to the phenyl ring is deprotonated (Tc–N, 1.972 Å), while the distance between Tc and the protonated one is 2.184 Å. The bond distances in the oxidized form [TcO(OU-BAT)] indicate extended conjugation of the N–Tc–N chelating bonds, and Tc–N distances (2.066 and 2.011 Å) fall in between single- and double-bond values.

Only the dioxo-$[TcO_2(14\text{-ane-}N_2S_2)]^+$ (Fig. 8) [48] complex possesses a Tc=O bond distance which is about 0.1 Å longer than that in the acyclic N_2S_2 mono-oxo derivatives.

The third group includes neutral and anionic complexes which contain N_2S_2-bis-amido bis-thiole or N_3S-tris-amido thiole ligands. The Tc=O bond distances fall in a rather narrow range (from 1.644(5) Å in *anti*-$[TcO(map)]^-$ [49] to 1.658(3) Å in *anti*-[TcO(ema-morph)] [50], while the $Tc–N_{amido}$ bond distances are broadened from 1.89 to 2.03 Å and in [TcO(PIC)] [51] the $Tc–N_{py}$ bond distance of 2.102(4) Å is slightly shorter than those observed in *trans*-$[TcO_2(4\text{-}t\text{-butpy})_4]^+$ (2.146(7) Å [52]) and closer to that in $[TcO(tibt)_3(py)]$ [33].

The "MAG_3" derivatives are directly derived from the above class of ligands. The complex $[^{99m}TcO(MAG_3)]^-$ has recently joined the commercially available Tc

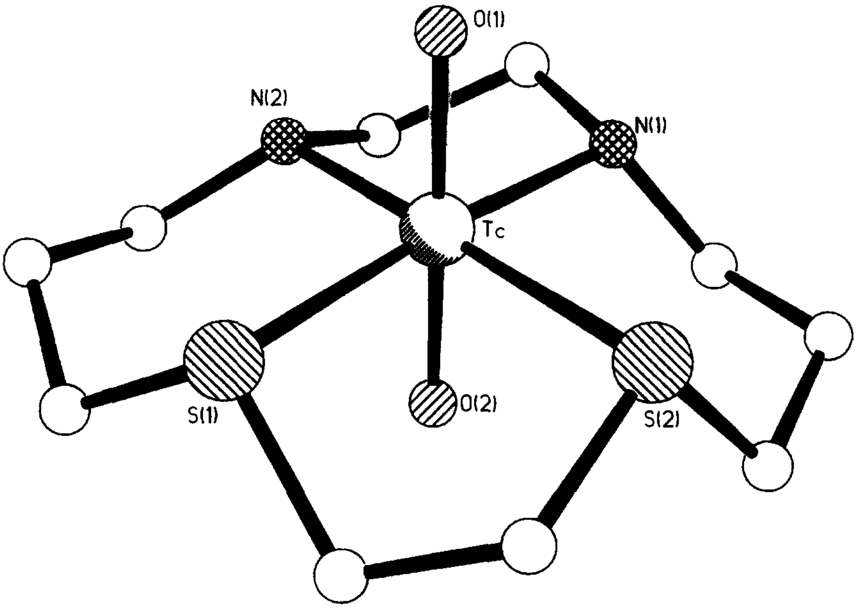


Fig. 8. $[TcO_2[14\text{-ane-}N_2S_2)]^+$.

radiopharmaceuticals. TechneScan MAG_3® is handled by the kidneys in a manner similar to that of [I-131]OIH [53,54], by active secretion into the urine at tubular sites of the nephron, in addition to the passive filtration of the glomerules. These biological properties seem to derive from the particular stereochemistry of the uncoordinated carboxylic group. The crystal structure of $[TcO(MAG_3]^-$ (Fig. 9) has been reported [55]; it shows the Tc atom in the usual square-pyramidal environment with the carboxylic group *syn*-oriented with respect to the Tc=O linkage. The similar complex $[TcO(MAG_3\text{-}OMe)]^-$ [55] is generated as impurity when using the ligand MAG_3H_4 prepared by the original method [53]. The epimers *syn* and *anti* have been characterized, and the relevant data, available only for the *syn* epimer, are: Tc=O, 1.655(7) Å; Tc–N(1), 1.993(6) Å; Tc–N(2), 1.968(5) Å; Tc–N(3), 2.030(6) Å and Tc–S, 2.287(3) Å.

Finally, the complexes $[TcO(abt)_2]^-$ [56] and $[TcO(Et_2tcb)_2]^+$ [57] contain two NS-bidentate ligands. The ligand abt is dianionic and *trans*-coordinate in the basal plane of the square pyramid, while Et_2tcb is monoanionic (the amino group mono-deprotonated) and *cis*- coordinated. The Tc=O bond distance (1.73(2) Å) in $[TcO(abt)_2]^-$ is exceptionally long for a mono-oxo complex.

3.3. Various donor atoms

The crystal structure of the $[TcOCl_4]^-$ anion [58], one of the ideal Tc(V) starting materials for the synthesis of most Tc(V)-oxo complexes via ligand-exchange

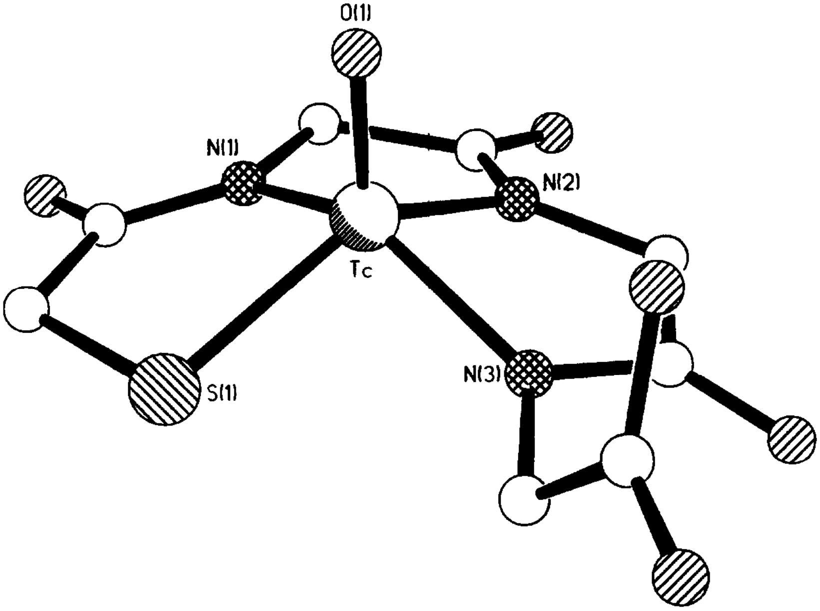


Fig. 9. $[TcO(MAG_3)]^-$

reactions, possesses ideal C_{4v} symmetry with the technetium atom in a square-pyramidal environment, in contrast with an earlier structural determination which showed only approximate C_{2v} symmetry [59]. A slight variation is introduced in the $[TcOBr_4(OH_2)]^-$ complex [60], where the coordination sphere is expanded to six in a distorted octahedral environment. Both five- and six-coordinate tetrahalotechnetate complexes show Tc=O bond distances (1.593(8) and 1.618(9) Å, respectively) at the short end of the range exhibited by analogous mono-oxo Tc(V) complexes. A similar short Tc=O bond length (1.612(8) Å) is shown in the dianionic distorted octahedral $[TcO(CN)_4(NCS)]^{2-}$ [61] complex. The SCN^- ligand is *trans*-coordinated to the oxo moiety via the nitrogen atom, in agreement with the hard and soft acid/base theory, the Tc(V) center being clearly a "hard" acid.

A rare example of a nitrogen coordination *trans* to the Tc=O linkage is exhibited by the mixed complex [TcOCl(eg)(phen)] (Fig. 10) [62], where the phen ligand spans *cis* and a *trans* to the Tc=O position, with the remaining equatorial sites occupied by the diolate and chloride ligands in a highly distorted octahedral coordination sphere. The diolate chelate exerts an unusual marked *trans* influence (long Tc–Cl distance of 2.418(2) Å), which, combined with short lengths for the C–C bond (1.491(1) Å) and for the Tc–O linkages (mean, 1.914 Å), suggests partial multiple bonding between the technetium and the diolate. Remarkably, the three reported oxo-complexes, having an imine nitrogen coordinated *trans* to the yl group [63,64], present a ν(Tc=O) stretching in the narrow range (962–956 cm^{-1}).

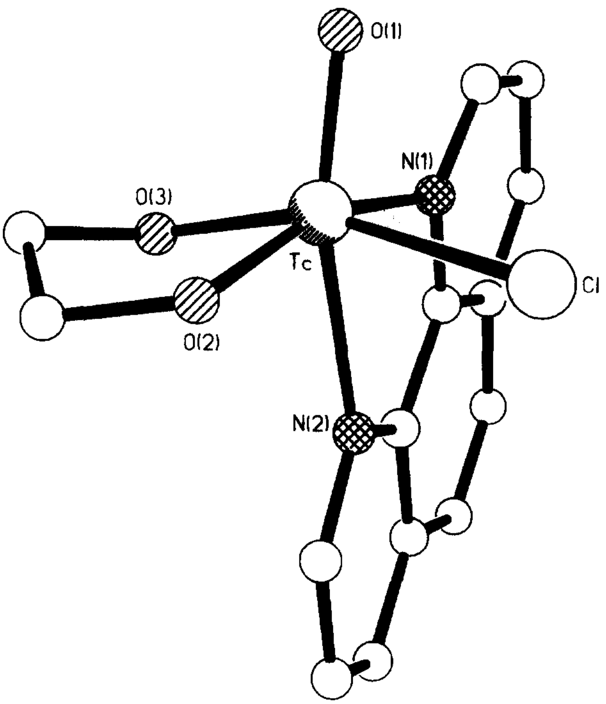


Fig. 10. [TcOCl(eg)(phen)].

The unique example of a square-pyramidal Tc(V)-oxo crystal structure containing the N_2O_2-donor set in the basal plane, is the anionic complex $[TcO(epa)]^-$ [65]. The presence of two electron-withdrawing groups in the bis-acetamide backbone contributes to quadruple-deprotonating the ligand and makes the resulting complex the hydroxyl analog of the mercaptoacetamido-propanoato epimers $[TcO(map)]^-$ [49]. In contrast, tetradentate N_2O_2 ligands, prepared by reducing the Schiff-base derived from salH and appropriate symmetric alkyl diamines, react with pertechnetate, in the presence of tin tartrate, to give the neutral six-coordinate binuclear compounds μ-O$[TcO(OPh_2pn)]_2$, μ-O$[TcO(OPh_2bu)]_2$ and μ-O$[TcO(OPh_2Me_2pn)]_2$ [66]. All three complexes show an oxygen-bridged $[Tc_2O_3]^{4+}$ core. The comparison of relevant bond lengths of μ-O$[TcO(OPh_2pn)]_2$ with those exhibited by the μ-O$[TcO(sal_2pn)]_2$ complex [67], containing the parent tetradentate Schiff-base ligand, shows only significant differences in the Tc–N lengths; these are slightly longer in the amino derivative.

A mixed donor atom set (SNNO) coordinates on the equatorial plane orthogonal to the $[Tc{=}O]^{3+}$ moiety in the anionic $[TcO(MAG_2)]^-$ complex [68]. The ligand is quadruple-deprotonated upon coordination, and its backbone represents an unprotected and reduced version of the widely studied SN_3-mercaptoacetyl triglycine analog (MAG_3).

The summary on Tc(V)-oxo cores is completed by the *trans* dioxo moiety shown in the six-coordinate polymeric complex $\{Li[TcO_2(tet)](CF_3SO_3)_2\}_n$ [69]. As reported in the early 1980s, for analogous $[TcO_2(cyclam)]^+$ [70] and $[TcO_2(en)_2]^+$ [71] complexes, both diamines and cyclic or acyclic tetraamines coordinate to the metal as neutral ligand, affording cationic and hydrophilic species. Both of these physico-chemical properties make this class of complexes interesting in view of radiopharmaceutical design, since they are quickly excreted through the urinary tract.

4. NITRIDO-TECHNETIUM COMPLEXES

Tc-nitrido complexes contain the Tc≡N multiple-bond unit. The nitrido group is among the strongest π-electron donors, and when it acts as a terminal ligand, the [Tc≡N·] moiety has a formal bond order corresponding to a triple bond. In particular, the three bond lines represent one σ and two π bonds, the latter arising from the overlap of occupied p orbitals of the nitrogen with two unoccupied technetium 4d orbitals of appropriate symmetry. Such a condition is well-satisfied when the Tc atom is in high oxidation states; indeed, up to now, only Tc(V), Tc(VI) and Tc(VII) nitrido complexes are known. When the metal is in the oxidation state 5+, the core $[Tc{\equiv}N\cdot]^{2+}$ is isoelectronic with $[Tc{=}O]^{3+}$. The stronger π donor ability of Tc≡N with respect to Tc=O is reflected by:

i. the shorter bond length for Tc≡N than Tc=O,

ii. the stronger *trans* labilizing effect operated by the [Tc≡N] core which, consequently, gives rise to five-coordinate Tc-nitrido complexes rather than six-coordinate ones, as in the case of Tc-oxo complexes,

iii. the longer $Tc{-}L_{eq}$ bond distances for nitrido complexes, when oxidation state and ligands are the same;

iv. the terminal nitrido ligand exerts a smaller steric effect, producing N≡Tc–L angles generally narrower than O=Tc–L.

In this section, we review 26 crystal structures: the number is still rather small when compared with that of Tc-oxo complexes, but the interest in Tc-nitrido chemistry has rapidly expanded recently, owing to the new synthetic method of producing the "Tc≡N" species at the tracer level [72].

4.1. *Only chalcogenide donor atoms*

Mononuclear complexes are dianionic and generally adopt the square-pyramidal geometry, with the nitrido ligand in the apical position. In particular, $[TcN(dto)_2]^{2-}$ [73,74] has been characterized in two different crystal systems (triclinic and monoclinic) with $[AsPh_4]^+$ as counter-ion. The compounds $[TcN(mnt)_2]^{2-}$ [75] and $[TcN(mns)_2]^{2-}$ [76] show identical Tc≡N bond distance (1.61(1) Å), while the Tc–Se distances (average, 2.520 Å) are 0.13 Å longer than the Tc–S ones (average, 2.390 Å). This difference is in agreement with that found in the

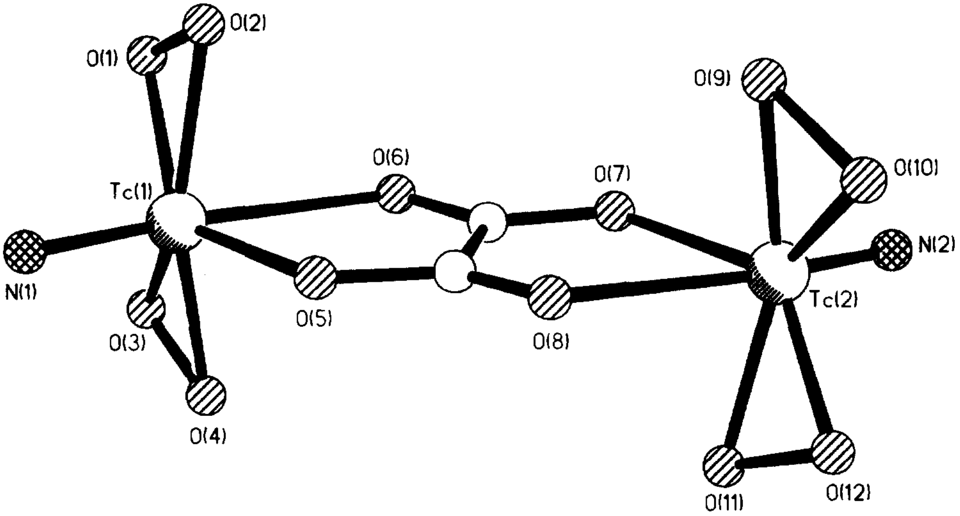


Fig. 11. $\{(\mu\text{-ox})[TcN(O_2)_2]_2\}^{2-}$.

analogous Tc-oxo complexes. In $[TcN(S_2CO)_2]^{2-}$ [77], owing to the steric constrains imposed by the geometry of the ligands, the base of the pyramid is rectangular (with internal S···S bites of 2.87 Å and external S···S contacts of 3.55 Å), while in the neutral dimeric complex $(\mu\text{-O})_2[Tc^{VI}N(Et_2dtc)]_2$ [78], the short Tc···Tc separation, along with the acute Tc–O–Tc angles (81.8(1) and 82.1(1)°), indicates a direct metal–metal interaction.

The complex $[TcN(O_2)_2Cl]^-$ [79] is the first example of a transition metal nitrido peroxo complex and the unique example of a stable peroxo complex of a metal in the 7+ oxidation state: the dimeric species $\{(\mu\text{-ox})[TcN(O_2)_2]_2\}^{2-}$ (Fig. 11) [80] is directly synthesized from the monomer. In the mononuclear complex, the coordination about the Tc atom is best described as a distorted pentagonal pyramid with the peroxo ligands sideways-bonded (mean O–O distance of 1.43 Å) with "bite" angles of 42.6(5) and 43.9(6)°. The dimer consists of two $[TcN(O_2)_2]$ units bridged by a quadridentate sideways-bonded oxalato. The geometry about Tc is a distorted pentagonal bipyramid, with the ligands in the equatorial positions. The Tc–O distances relative to the oxygen *trans* to the nitrido moiety are 0.3 Å longer than those of other oxalate oxygens owing to the strong *trans* labilizing effect exerted by the nitrido group.

In the cyclic tetranuclear $[Tc_4N_4O_2(ox)_6]^{4-}$ complex [81] each Tc(VI) atom is coordinated by five oxygens and one nitrogen to give a distorted octahedron. In each half of the anion, a quadridentate oxalate ligand forms a bridge between two octahedra, each of which is also linked to an adjacent octahedron by a bridging oxo ligand. In each polyhedron, two oxygen atoms of a bidentate oxalate ligand and a nitrido atom complete the octahedral coordination.

4.2. Nitrogen donor atoms

Four out of five of the following X-ray crystal structures are of cationic complexes which contain di- or tetra-amines and tetra-azamacrocycles coordinated on the equatorial plane of a pseudo-octahedral geometry, and a negative or neutral ligand weakly bonded *trans* to the nitrido moiety. As for the oxo-complexes, in general it appears that, when the ligands are neutral and poor π-donors, like amines or cyclam, octahedral Tc(V) complexes are formed, while with better π-donors, like phosphines, arsine, Schiff-bases or negatively charged ligands (dichalcogenide, dithiocarbamate), five-coordination is preferred.

In particular, the $[TcNCl(en)_2]^+$ and $[TcNCl(tad)]^+$ [82] complexes contain chelating amines which, upon coordination to the $[TcN]^{2+}$ core, do not deprotonate. The resulting octahedral complexes possess a chloride *trans* to the nitrido moiety. Both the large steric requirement and the *trans* influence of the N^{3-} keep the chloride to the longest Tc–Cl distances ever observed for technetium complexes (2.732(1) Å in [TcNCl(en)2]$^+$ and 2.663(2) Å in [TcNCl(tad)]+).

The complexes $[TcN(tactdd)(OH_2)]$ [83] and $[TcN(tactdo)(OH_2)]^+$ [84] have been obtained by using mono-and di-tetraazamacrocyclic ligands containing electron-withdrawing groups in the backbone. The increased acidity exhibited by the amide proton(s), with respect to the amine ones, allows their deprotonation, partially contributing to saturating the positive charge of the $[Tc{\equiv}N]^{2+}$ core. Thus, a water molecule binds to the apical position *trans* to the N^{3-} ligand, affording neutral or cationic pseudo-octahedral complexes, depending on the number of the amide groups in the ligand framework. In both complexes the Tc≡N bond distance is 1.615(4) Å, and the $Tc–OH_2$ distances are exceptionally long as a consequence of the *trans* weakening operated by $[Tc{\equiv}N]^{2+}$.

A good example of ligand degradation promoted by a technetium nitrido species is shown in the complex $[TcN(en)_2(aeca)]^{2+}$ [85]. The complex $[TcNCl_2(PPh_3)_2]$ reacts with excess of dien in a benzene/EtOH mixture under aerobic conditions and the resulting $[TcN(en)_2(aeca)]^{2+}$ (Fig. 12) complex reveals the coordinated aeca ligand frozen in a peculiar "transient state" originated by an uncommon weakening of a carbon–nitrogen bond. The net charge of the complex is 2+, and thus it constitutes the first example of a dicationic complex containing the Tc≡N multiple bond.

4.3. Various donor atoms

Twelve X-ray crystal structures, most of them contain halide (Cl, Br) and phosphine ligands in a distorted octahedral geometry, are reviewed. The complexes $[TcNCl_4]^-$ [86], $[TcNBr_4(OH_2)]^-$ and $[TcNCl_5]^{2-}$ [87], with the metal in the 6+ oxidation state, are all anionic. Both $[TcNCl_5]^{2-}$ and $[TcNBr_4(OH_2)]^-$ exhibit short Tc≡N distances (1.60(1) Å) and long $Tc–L_{trans}$ lengths (Tc–Cl, 2.740(5) Å; $Tc–OH_2$, 2.443(7) Å). The structure of the complex $[TcNCl_4][Cs(18\text{-crown-}6)]$ [86]

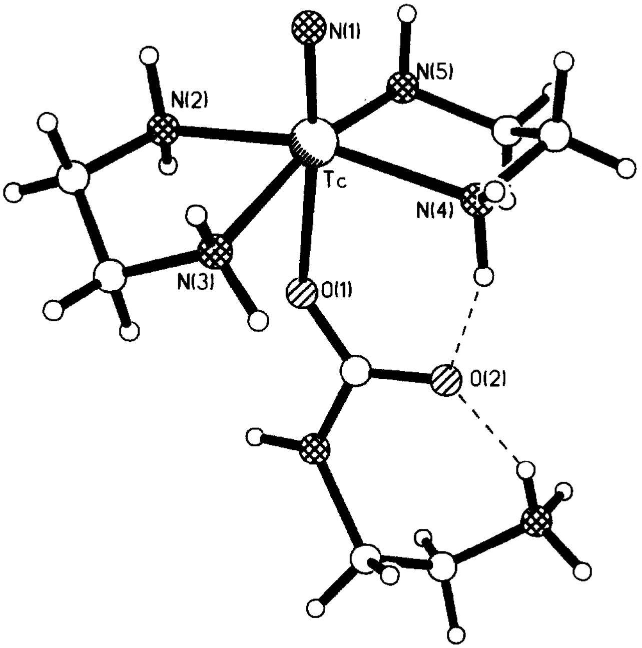


Fig. 12. $[TcN(en)_2(aeca)]^{2+}$

is interesting only in that it contains two types of polymeric $[TcNCl_4]^-$ anions and the unprecedented "infinite sandwich" alkali metal cation/crown ether complexation. In the tetragonal unit cell there are two distinct pairs of anti-parallel chains of $\cdots Tc{\equiv}N\cdots Tc{\equiv}N\cdots$.

The dianionic complex $[TcN(CN)_4(OH_2)]^{2-}$ [88] shows the Tc(V) atom coordinated by four cyano groups in the equatorial plane with a nitrido group and a water molecule at the apices of a distorted octahedron.

In the complexes $[TcNCl_2E_2]$ ($E = PPh_3$ [89] or $AsPh_3$ [90]), only two bulky π-ligands are bonded on the equatorial plane and the coordination geometry is square pyramidal. Both phosphino and arsino complexes have identical Tc≡N bond distances (1.601(6) Å), as well as Tc–Cl (2.374(2) Å), while, as expected from periodicity, the average Tc–P distance of 2.463 Å is shorter than the average Tc–As distance (2.544 Å). By using a less encumbering phosphine, such as PMe_2Ph, an octahedral geometry can be obtained, as shown by $[TcNCl_2(PMe_2Ph)_3]$ [91].

The octahedral complex $[TcNCl(dmpe)_2]^+$ [92] contains two di-phosphines coordinated on the equatorial plane with Tc–P bond distances in the range 2.443–2.453 Å. These values are slightly longer than the mean Tc^{III}–P bond length of 2.436 Å found in the "dichloro" analogs [93]. In the octahedral complexes $[TcNBr(bpy)_2]^+$ [94] and $[TcNCl(phen)_2]^+$ [95], a poly-pyridine ligand spans a site on the equatorial plane and the site *trans* to the $[Tc{\equiv}N]^{2+}$ core, the coordination sphere being completed by a halide and a further polypyridine ligand. The complex $[TcNBr(bpy)_2]^+$ crystallizes utilizing the novel tetrahedral $[TcBr_4]^{2-}$ counteranion.

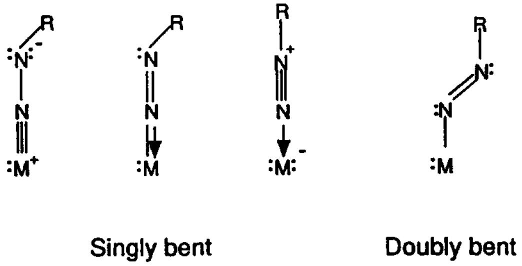
In the neutral complex $[TcNBr_2(bmepa)]$ [96] the polydentate ligand contains two pyridines joined by a three-atom chain with the tertiary amino nitrogen as the central atom. The geometry is octahedral, with the two pyridine residues coordinate on the equatorial plane and the amino group forced to bond *trans* to the $[Tc{\equiv}N]^{2+}$ core in a *fac* environment.

5. ORGANO-DIAZENIDO, -HYDRAZIDO AND -IMIDO TECHNETIUM COMPLEXES

Among a variety of nitrogenous donor ligands forming Tc complexes, the organo-diazenido, -hydrazido, and -imido ligands have been the most recently studied. The first crystal structure was reported only in 1989. In this section, we consider eight structures, but three more X-ray crystal determinations have been merely communicated [97].

Technetium complexes that incorporate the organo-diazenido, -hydrazido and -imido ligands contain multiple metal–nitrogen bonds. Such strong TcN bonds, in combination with appropriate ancillary ligands devoted to controlling biological targeting, may open up new perspectives in the development of Tc-based radiopharmaceuticals.

Organo-diazenido ligands, abbreviated as RN_2^+/RN_2^-, can adopt, upon coordination to a transition metal, one of the geometries shown in the scheme below [98]:



Generally, in these complexes the assessment of the effective oxidation state is not an easy task, since the formal oxidation state, attributed by the structural data according to the ligand geometry, is often not confirmed by magnetic measurements. However, for organo-hydrazido derivatives a rationalization can be made, considering that, for each bidentate ligand incorporated into a given Tc complex, the oxidation state of the Tc precursor is reduced by two electrons and the organohydrazine ligand oxidized to organo-diazene. Furthermore, if the ligand contains a weakly bonded chelating moiety or a good leaving group, N–N bond cleavage can occur, to yield a Tc≡N moiety in a native complex with enhanced stability. Hereafter, the complexes are classified according to the ligand configuration adopted upon coordination.

The prevalent bonding mode in Tc-diazenido complexes is described as a singly-bent geometry, the metric parameters to consider for this attribution being Tc–N$_\alpha$–N$_\beta$ and N$_\alpha$–N$_\beta$–C angles along with the N$_\alpha$–N$_\beta$ and Tc–N distances.

[$TcCl(NNC_6H_4Br)_2(PPh_3)_2$] was the first Tc-diazenido complex reported [99]: it shows (Fig. 13) a trigonal-bipyramidal configuration with the PPh_3 ligands occupying the apical positions. Tc–N distances are almost equal (1.796(6) and 1.783(7) Å), the short values suggesting significant metal-to-ligand back-bonding. The Tc–N$_\alpha$–N$_\beta$ linkages are roughly linear (170°) and, along with bond length values, reflect multiple bonding throughout the unit. The geometry of the ligand is that of "singly bent" organo-diazenido, which serves formally as a monocationic two-electron donating ligand, so that the formal oxidation state of Tc is 1−. However, the ^{99}Tc NMR spectra of the complex show a signal close to the region assigned for Tc(V) complexes [99].

In [$Tc(NNC_6H_4Cl)(Me_2dtc)_2(PPh_3)$] [100] the diazenido ligand adopts the singly-bent" geometry with a Tc–N–N angle of 178.6(4)°, and thus behaves as monocationic two-electron donor with the Tc center formally 1+. As a result of the *trans* influence operated by the Tc=N– unit, the *trans* Tc–S distance of 2.537(1) Å is much longer when compared to the others (2.452(2), 2.477(2) and 2.412(2) Å).

The complex [$Tc(HNNC(Ph)S)_2(S_2CPh)$] [101] is the first example of a

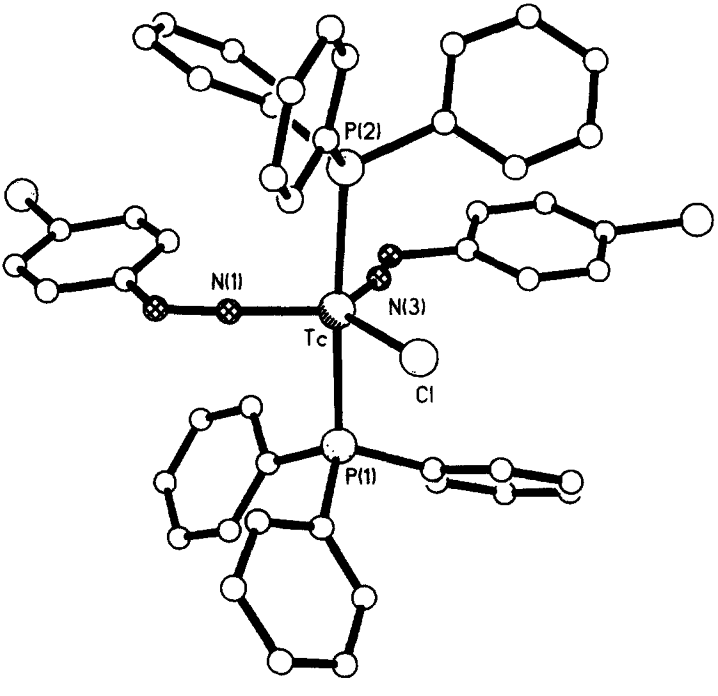


Fig. 13. [$TcCl(NNC_6H_4Br)_2(PPh_3)_2$].

Tc-diazene compound. Upon coordination, two thiobenzoylhydrazine ligands are oxidized to diazene, yielding four electrons, which reduce the $[Tc^VOCl_4]^-$ precursor to Tc(I). Neutrality is achieved by coordination of a deprotonated molecule of dithiobenzoic acid, which is present as a persistent contaminant from the synthesis of the organo-hydrazine ligand. The Tc center exhibits a distorted trigonal prismatic geometry through ligation of the S donors of the bidentate thiobenzoate group and the N and S donors of the chelating diazene ligands.

In the mononuclear Tc-hydrazido complexes $[TcO(PhNNCON_2HPh)(tibt)_2]$ [102] and $[TcCl_2(hph)(PPh_3)_2]$ (Fig. 14) [103] the hydrazido-ligands act as bidentate, thus forming a cycle about the Tc center. The coordination geometry of $[TcO(PhNNCON_2HPh)(tibt)_2]$ is intermediate between square-pyramidal and trigonal bipyramidal, according to the criteria of Muetterties and Guggenberg [104]. The organo-hydrazide ligand coordinates via the carbonyl group in the site pseudo-*trans* to the oxo group with the O–Tc–O bond angle of 127.5(1)°. The presence of the Tc=O unit, with its strong π-character, weakens the Tc–N distance (2.139(2) Å), which results in a value consistent with a single bond. The exocyclic N–N unit was unambiguously found to contain the N–H proton, and the exocyclic bond angles reflect sp^2 hybridization and establish the ligand's cationic nature. Since the complex results formally in Tc(III), it represents the unique formal example of a Tc(III)-oxo compound.

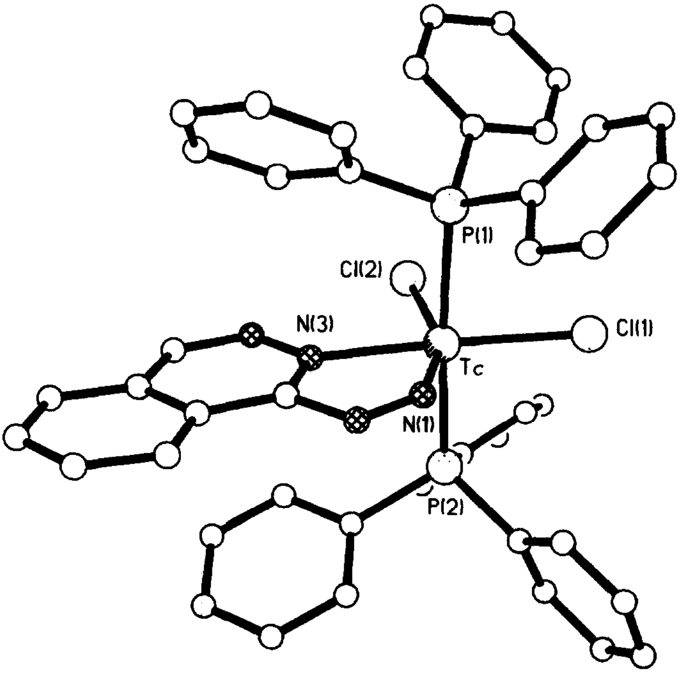


Fig. 14. $[TcCl_2(hph)(PPh_3)_2]$.

In the octahedral complex $[TcCl_2(hph)(PPh_3)_2]$, owing to the anionic nature of the ligand and charge delocalization, all bonds of the organo-hydrazide chelate are significantly contracted, with respect to the complex $[TcO(PhNNCON_2HPh)(tibt)_2]$. In particular, the Tc–N(1) bond length is dramatically shortened (1.77(1) *vs.* 2.139(2) Å), in agreement with significant multiple-bonding of the hydrazido unit in the complex.

The complex $[TcN(NNPh_2)(tibt)_2]_2$ [105], wherein an N–N cleavage leads to the formation of TcN, consists of binuclear Tc(VII) entities, each one residing in a distorted square pyramid with the basal plane defined by the sulfur donors of the bridging thiolate ligands, the sulfur of the terminal thiolate and the N_α of the hydrazido(2-) ligand. The apical position is occupied, as usual, by the nitrido ligand. The Tc–N–N angle of 142(1)° deviates considerably from 180°, and therefore it is consistent with a hydrazido(2-) description of the ligand. The Tc=N– mean distance of 1.88 Å is significantly longer (about 0.1 Å) than the corresponding ones in $[TcCl(NNC_6H_4Br)_2(PPh_3)_2]$ and $[TcCl_2(hph)(PPh_3)_2]$.

In the anionic complex $[Tc_2(NNPh_2)_2(cat\text{-}Cl_4)_4]^-$ [106], since the average oxidation state of the Tc centers is 5.5+, it appears that the ligand serves both as oxidant and ligating group; nevertheless, NMR spectroscopy reveals the complex to be paramagnetic. The structure consists of discrete binuclear units with distorted octahedral geometries about the metals, each Tc binds two terminal bidentate catecholate ligands and the N_α donors of the two bridging hydrazido(2-) groups. The catecholate ligands are disposed so that each one places an oxygen donor *trans* to a bridging hydrazido nitrogen in the $Tc_2N_2O_4$ plane, and a second oxygen donor in an axial position *trans* to an oxygen of the second catecholate group. The Tc···Tc bond length of 2.612(2) Å indicates a significant metal–metal interaction, and the complex may be formally considered an example of mixed-valence Tc(V)/Tc(VI) species containing symmetrically bridging η^1-hydrazido(2-) ligands.

$[TcCl_3(NPh)(PPh_3)_2]$ (Fig. 15) [107] is synthesized from $[TcO_4]-$, PPh_3 and 1-acetyl-2-phenylhydrazine in MeOH with the addition of HCl, or directly from $[TcOCl_4]^-$ without using HCl. The Tc–N length (1.704(4) Å) is in perfect agreement with the value found in the complex $[TcCl_3(Ntol)(PPh_3)_2]$ [108]. The Tc–N–C bond angle of 171.8(4)° confirms the linear coordination mode of the triply bonded phenylimido unit. The imido ligand acts as a four-electron donor giving the Tc complex an overall 18-electron valence configuration.

6. SCHIFF-BASE TECHNETIUM COMPLEXES

Primary amines add readily and reversibly to the carbonyl groups of most aldehydes and ketones, then undergo spontaneous dehydration, particularly in the presence of an acid or base catalyst, to give substituted imines, usually referred to as Schiff bases. This class of ligands is characterized by the presence of a multiple C=N bond with the imine nitrogen sp^2-hybridized [109].

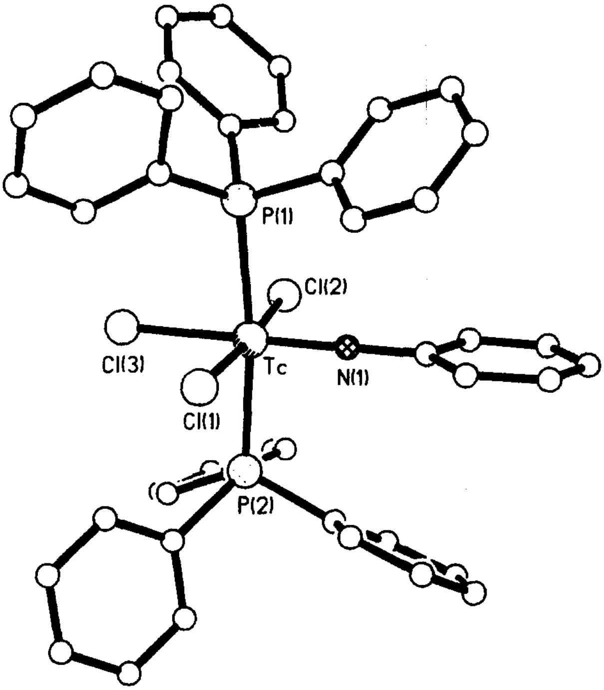


Fig. 15. $[TcCl_3(NPh)(PPh_3)_2]$.

Nine crystal structures of Schiff-base technetium complexes were published before 1986 [17,18], but the interest in this area has rapidly expanded in the late 1980s, encouraged by the impact in the radiopharmaceutical field of some ^{99m}Tc-derivatives.

6.1. Oxo(V) species

The 13 compounds surveyed here, 11 of which are neutral, exhibit both five-coordination (square-pyramidal configuration with the oxo group at the apex and the Schiff-base donors in the basal plane) and six-coordination (distorted octahedral geometry with the axial sites occupied by the oxo group and a nucleophilic agent). Within this class, therefore, the question seems to be whether five- or six-coordination occurs. The concomitant *trans*-labilizing effect of the Tc=O linkage, and the need of such a core to delocalize its heavy electron density, play an opposite role in determining the resulting coordination sphere. The presence of a ligand coordinated in the sixth position *trans* to the oxo group is obviously related to the nature of the *cis*-substituents; in particular, the presence of "soft" donor (*e.g.* halide or thiolate) and/or acceptor ligands (*e.g.* Schiff-base imine nitrogen) in the equatorial plane induces the formation of a square-pyramidal environment by partially neutralizing the charge of the Tc(V) center, while the presence of "hard" donors (*e.g.* oxygen) supports six-coordination. Frequently, the Tc=O group accommodates in the *trans* position a further oxygen-donor ligand, probably by virtue of the optimal energy fit between the $d_z{}^2$ orbital of the metal and the p_z orbital of the oxygen donor.

The substitution reactions onto $[TcOX_4]^-$ (X=Cl,Br) species of the hbtH ligand are helpful in understanding the reaction mechanism with NO-bidentate Schiff bases. The first step produces the anionic species $[TcOCl_3(hbt)]^-$ [110], which shows the ligand spanning an equatorial and axial position *trans* to the oxo moiety. Reaction of the charged complex with an excess of ligand affords the bis-substituted $[TcOCl(hbt)_2]$ complex [111], which retains a phenolato group *trans* to the Tc=O linkage. Curiously, the hbtH ligand can act as a monoanionic NO-bidentate chelate in its oxidized form, as outlined above, or as a dianionic NOS-tridentate one in the reduced Schiff-base form.

Upon coordination, NOS-tridentate Schiff bases give neutral square-pyramidal species. The ligand is completely coordinated on the basal plane along with a halide, while the apical position is occupied by the oxo group. Two crystal structures have been determined: [TcOCl(SMe-Ondtcz)] [112] and [TcOCl(SPhsal)] [113]. The unique technetium complex containing a tridentate ONN-Schiff-base, $[TcOCl_2(quinaph)]$ [64], has a distorted octahedral geometry with two *trans* chloride atoms and the N_2O-ligand atom set meridionally coordinated, with the central imino nitrogen *trans* to the oxo group. It represents one of the rare examples of the pseudo-linear $[O{=}Tc{-}N]^{3+}$ moiety.

Symmetric XNNX (X=O,S) tetradentate Schiff-base ligands react with the $[TcOCl_4]^-$ precursor, affording six-coordinate Tc(V)-oxo complexes, whose cores and overall charge depend upon the nature of the donor atoms and, mainly, on the synthesis procedures employed. In any case, the Schiff-base donors are coordinated on the equatorial plane of a distorted octahedron with the apices saturated by the oxo group and a monodentate nucleophile (*i.e.* water in the cationic species $[TcO(sacac_2en)(OH_2)]^+$ [114] and an oxygen joining two identical residues in the dimer μ-$O[TcO(sal_2pnOH)]_2$ [115]). In spite of the distortion exhibited by the octahedron of the dimeric species, the Tc–O–Tc angle is nearly linear (173(1)°). In contrast, asymmetric and acyclic ONNX (X=N,S) tetradentate ligands, referred to as MRPn chelates (from *M*edgenix *R*adio*P*harmaceuticals), produce five-coordinate species. The charge of the $[Tc{=}O]^{3+}$ core is neutralized by triple deprotonation of the ligand backbones to give [TcO(MRP20)] (Fig. 16) [116,117] and [TcO(MRP40)] [118]. These neutral lipophilic complexes cross the blood–brain barrier (BBB) and, among them, the metastable $[^{99m}TcO(MRP20)]$ species (Neuroscint®) are confirmed by chromatographic studies to have the same structure exhibited by the long-lived Tc complex. The tracer-level agent is currently undergoing clinical evaluation for mapping regional cerebral blood flow [8,119,120].

Mixed tridentate, bidentate or pentadentate Schiff-base ligands, containing only nitrogen and oxygen donor atoms, react with appropriate Tc(V) precursors,

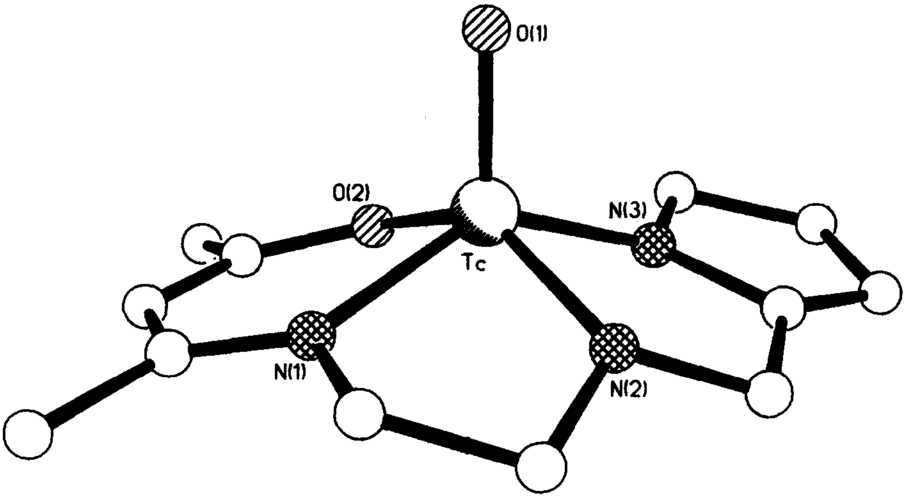


Fig. 16. [TcO(MRP20)].

always giving six-coordinate neutral species. [TcO(OPhsal)(quin)] [121] and [TcO(glusal)(sal)] [122] complexes present the ONO-tridentate ligand coordinated on the equatorial plane and the bidentate one sharing the equatorial plane and the sixth position *trans* to the oxo moiety.

By reaction of potentially pentadentate ONNNO-Schiff-base ligands with $[TcOCl_4]^-$, neutral and stable [TcO(sal$_2$tren)] (Fig. 17) [123] and [TcO(apa)] [124] complexes are obtained. They have a highly distorted octahedral geometry comprising a $[Tc{=}O]^{3+}$ core and a triply deprotonated pentadentate ligand wrapped around the metal. The distance between the deprotonated amine nitrogen and the metal (1.880(2) Å for the "apa" derivative and 1.894(8) Å for the "sal$_2$tren" one) is significantly shorter than a normal single Tc–N bond length, suggesting a partial double-bond character. As a consequence, all technetium–oxygen bonds are lengthened. In fact, the Tc=O mean distance of 1.68 Å for both complexes is at the long end of the range observed for mono-oxo Tc(V) species: also single Tc–O lengths, in the range 2.12–2.15 Å, are significantly longer for a covalent metal–oxygen bond, indicating a sort of conflict between the multiple Tc=O and Tc=N linkages for being the driving core in the molecule.

In this class of complexes, the Tc–N$_{imino}$ distances comprise a large range: from 2.01 Å in [TcO(glusal)(sal)] [122] to 2.20(2) Å in [TcOCl(hbt)$_2$] [111].

6.2. *PnAO-like species*

Amine oximes (AO) represent a class of nitrogen-donor imines formally derived from hydroxylamine. By joining with an alkyl chain the terminal amine group of two AO chelates, tetradentate amine-oximes were prepared in the 1950s [125–127].

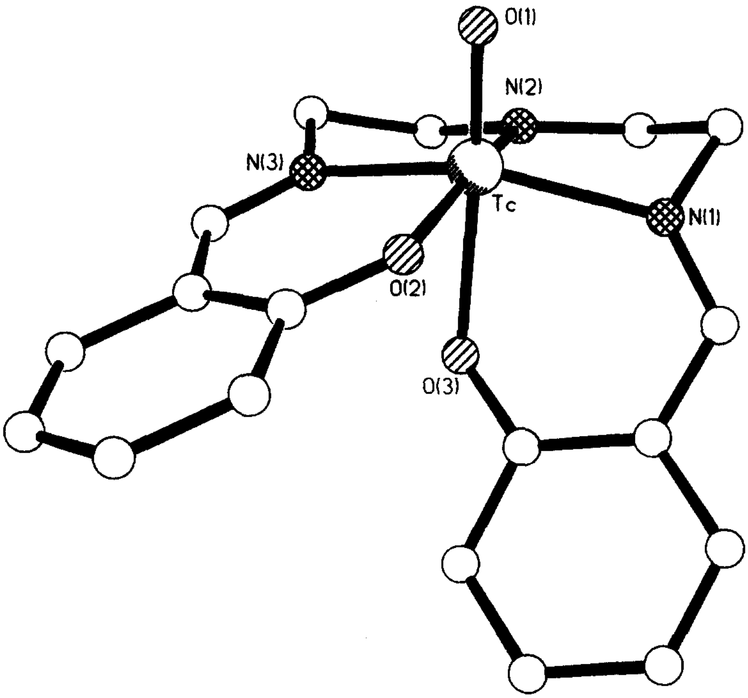


Fig. 17. [TcO(sal$_2$tren)].

Reaction of pertechnetate with such ligands in the presence of a suitable reducing agent (usually Sn(II)) gives neutral and lipophilic technetium(V) complexes [128,129]. Five of the six crystal structures show them to be mono-oxo five-coordinate technetium(V) species with the oxo group situated at the apex of a square pyramid and the technetium lying an average of 0.68 Å (for PnAO derivatives) and 0.77 Å (for EnAO) above the plane defined by the four nitrogen atoms of the tetradentate amine-oxime. In each case the tetradentate ligand loses three protons on coordination to the Tc(V) center, resulting in an overall charge of zero for the complex, multiple bonding between the amide nitrogens and the technetium, and intramolecular hydrogen bonding between the oxime oxygens.

Increasing the length of the hydrocarbon backbone of the amine oxime ligand from propylene (Pn) to pentyl (Pent) causes remarkable changes in the coordination geometry of the complexes. The complexes are still neutral, but contain six-coordinate *trans*-dioxo technetium(V) species. They have a somewhat distorted octahedral geometry, and show an unusual eight-membered chelate ring. To saturate the positive charge of the $[TcO_2]^+$ core, the Pent(AO)$_2$ ligand loses only an oxime proton on coordination and retains the two amine nitrogen protons. Steric interactions of the pentyl backbone in the $\{TcO_2[Pent(AO)_2]\}$ [129] complex constrain the distance between the amine nitrogen to be much longer (3.68 Å) than the average distance of

2.72 Å in TcO[Pn(AO)$_2$] and 2.49 Å in {TcO[En(AO)$_2$]} [129] and make conditions very unfavourable for such nitrogens to be close enough to each other, and to the technetium atom, to deprotonate. Within the Pn(AO)$_2$ class, the substitution of one (or more) hydrogen atom(s) for methyl group(s) in the backbone gives rise to optically active mixtures (D, L and *meso* forms) either of ligands and Tc complexes. The X-ray structures of both D,L-{TcO[Me$_2$Pn(AO-Me)$_2$]} (Fig. 18) and *meso*-{TcO[Me$_2$Pn(AO-Me)$_2$]} are reported [128]. Tetramethyl and pentamethyl Pn(AO)$_2$ ligands give the *meso*-{TcO[Pn(AO-Me)$_2$]} and TcO[Pn(AO)(AO-Me)] complexes, respectively [128]. The hexamethyl Pn(AO) chelates, frequently referred to as HM-PAO, which correspond to the Me$_2$Pn(AO-Me)$_2$ backbone discussed above, have proven to be the most useful medically and, in particular, the D,L-[^{99m}TcO(HM-PAO)] species (Ceretec®) is widely used as cerebral perfusion agent [130,131].

6.3. Nitrido(V) species

Neutral, five-coordinate nitrido Tc(V) complexes can be obtained either by reduction–substitution reactions from labile [Tc^{VI}NX$_4$]$^-$ (X=Cl,Br) or ligand-exchange reactions from [TcNCl$_2$(PPh$_3$)$_2$], using suitable bi- or tri-dentate Schiff-base chelates. All the complexes show a more or less distorted square-pyramidal

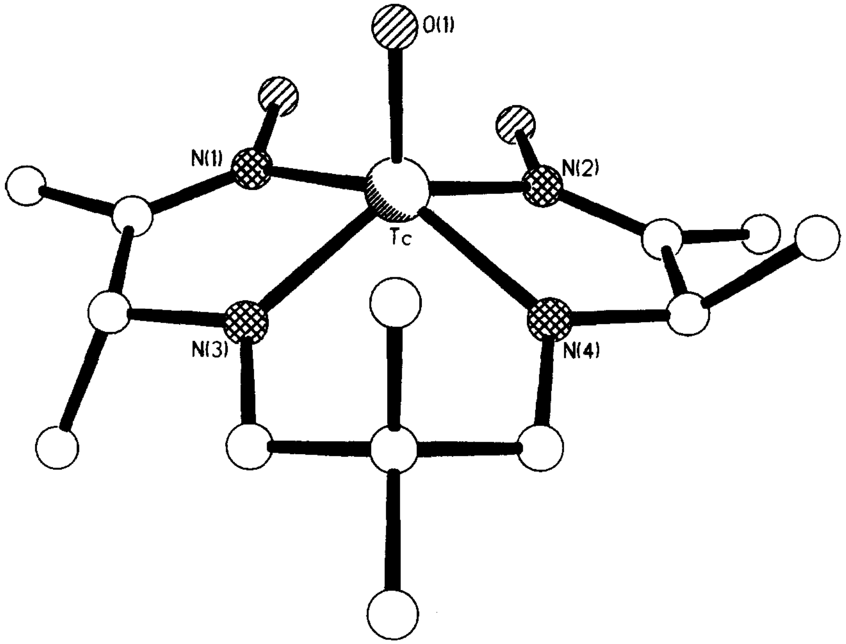


Fig. 18. D,L-{TcO[Me$_2$Pn(AO-Me)$_2$]}.

geometry with an apical multiple-bonded nitrogen atom and the basal sites filled with the Schiff-base donors. Two bidentate NS-Schiff-base ligands are arranged with the like donor atoms diametrically opposed as in the [TcN(tquin)$_2$] [132] and [TcN(SMe-Me$_2$dtcz)$_2$] [133] complexes. Remarkably, MequinH, an oxygen-analog of tquinH, reacts with [TcOX$_4$]$^-$ (X = Cl,Br), affording a distorted octahedral bis-substituted mono-oxo Tc(V) complex, namely [TcOCl(Mequin)$_2$] [134]. In this case the coordination sphere around the metal is expanded to six, with a quinolinolate oxygen *trans* to the oxo group. Such behavior is quite common; another example is offered by the SNNS-tetradentate sacac$_2$enH$_2$ ligand, which, upon coordination, defines a nearly perfect pyramidal base framework in the nitrido derivative [TcN(sacac$_2$en)] [135], while the ligand determines a distorted octahedral array in the oxo species [TcO(sacac$_2$en)(OH$_2$)]$^+$ [114], where a weakly bonded water molecule is coordinated *trans* to the oxo moiety.

Tridentate Schiff-base ligands coordinate as doubly negative-charged chelates on the equatorial plane normal to the nitrido moiety, the fourth basal site being occupied by PPh$_3$, which is retained after ligand-exchange reactions, from the [TcNCl$_2$(PPh$_3$)$_2$] starting material. The geometry exhibited by the two representative structures [TcN(ecbap)(PPh$_3$)] [136] and [TcN(SMe-OPhdtcz)(PPh$_3$)] [133] is the usual distorted square pyramid with the metal displaced from the basal plane toward the apical nitrido nitrogen by 0.66 Å in the former complex and by 0.57 Å in the latter.

A quite strange reaction takes place when [TcNCl$_4$]$^-$ reacts with a monothiol in the presence of the supposed "non-coordinating" base TMG. The five-coordinate, neutral *trans*-[TcN(tmbt)$_2$(TMG)$_2$] complex [137] represents the first crystallographically characterized transition-metal compound containing TMG. The compound exhibits square-pyramidal geometry with the nitrido group in the apical position and thiolate and TMG ligands alternating around the base. The Tc–N$_{\mathrm{imino}}$ lengths range from 2.067(4) in [TcN(ecbap)(PPh$_3$)] [136] to 2.161(2) Å in [TcN(SMe-Me$_2$dtcz)$_2$] [133], while the Tc≡N distances are restricted to a narrow range: from 1.608(5) in [TcN(ecbap)(PPh$_3$)] [136] to 1.623(4) Å in [TcN(tquin)$_2$] [132].

During the investigation on the reactivity of Tc(V) species towards pseudoallyl ligands, the monosubstituted thiazetidine five-coordinate complex TcNCl[PhN=C(OEt)S](PPh$_3$) [138] was obtained.

6.4. *BATO-like species*

In addition, dioxime ligands can be described as Schiff-base chelates, formally derived from condensation reactions of suitable carbonyl-containing precursors and hydroxylamine [139]. The resulting symmetric bidentate ligand contains two imino nitrogen donors, each bearing an hydroxyl group.

Reduction of pertechnetate by SnCl$_2$ in the presence of vicinal dioximes leads to the isolation of the tin-capped complexes [Tc(dioxime)$_3$(μ-OH)SnCl$_3$] (dioxime = DMG,CDO) via oxidation of the reaction mixture with air or peroxide [140]. The crystal structure of the binuclear derivative [Tc(DMG)$_3$(μ-OH)SnCl$_3$] has been reported since 1976 [141], but the interest in a related class of compounds only became considerable ten years later because of their potential use as radiopharmaceuticals. The tin-capped [Tc(dioxime)$_3$(μ-OH)SnCl$_3$] complexes can be easily converted into a new class of uncapped tris-dioxime species [TcCl(dioxime)$_3$] by treatment with HCl [142]. Both the "tin-capped" and "uncapped" tris(dioxime) complexes can be further converted into a class of boron-capped technetium dioxime compounds [TcCl(oxime)$_3$BR] (R = alkyl,OH) by reaction with boronic acids or with boric acid at low pH values [143]. Monocapped *B*oronic Acid *A*dducts of *T*echnetium tris(di*o*xime) complexes (BATO) can also be prepared by template synthesis, starting from pertechnetate and stannous ion, or from [TcOCl$_4$]$^-$ and [TcX$_6$]$^{2-}$ (X = Cl,Br). In these neutral, seven-coordinate Tc(III) compounds the metal is bound to six nitrogen atoms of the three vicinal dioximes and to a monodentate anion (halide or hydroxide). One oxygen of each of the three dioximes is joined to a common boron cap, while the oxygens of the uncapped end are intramolecularly hydrogen-bonded to two bridging protons. The six ligating nitrogen atoms form a monocapped distorted trigonal prism; the average Tc–N distance at the capped end (2.05 Å) is about 0.1 Å smaller than the average Tc–N distance at the uncapped end.

Four classic BATO complexes have been structurally characterized: [TcCl(DMG)$_3$BMe] [142], [TcBr(DMG)$_3$B-*n*-bu] [143], [TcBr(CDO)$_3$BMe] (Fig. 19) [143] and [TcBr(CDO)$_3$B-*n*-bu] [143]. The parent uncapped complex [TcCl(DMG)$_3$] [142] reveals that the donor set and coordination geometry about the Tc atom are similar to that seen in the classic BATO complexes. Quite surprisingly, by reacting the pre-reduced technetium compound [Tc^{III}Cl$_3$(MeCN)(PPh$_3$)$_2$] with dioximes and ethylboronic acid, beside the usual BATO complexes, an unusual BATO-like imine-oxime complex is also obtained. The X-ray analysis of [TcCl(DMG)$_2$(BDI)BEt] [144] shows its structure is very similar to that of the previously analyzed [TcCl(dioxime)$_3$BR], except that one of the uncapped oxime ligands on the molecule is reduced to an imine oxime, and consequently the hydrogen bonding occurs only between the remaining pair of uncapped oximes. By varying the nature of the dioximes, boronic acid and the monodentate axial ligand, a large number of BATOs were synthesized and the use of two of them as radiopharmaceuticals has been established [145–147]. One complex, [^{99m}TcCl(CDO)$_3$BMe] (Cardiotec®) [148], has been approved by the FDA for myocardial perfusion imaging.

6.5. *Low-valent species*

Reaction of Tc(V)-oxo Schiff-base complexes with an excess of monotertiary phosphine, under mild conditions, yields a new class of neutral Tc(III) Schiff-base species. The phosphine acts both as reductant (by extracting the oxo group from

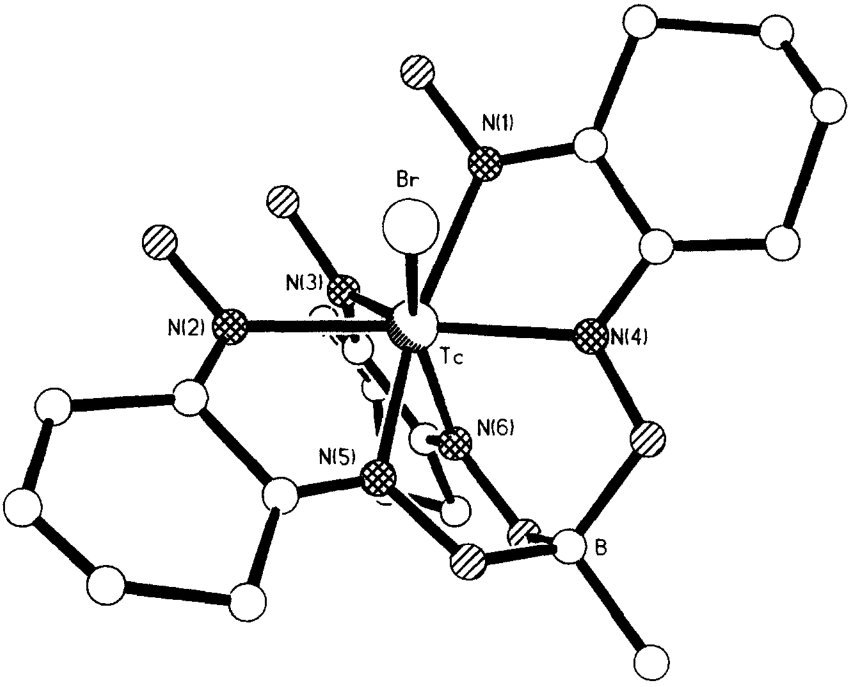


Fig. 19. [$TcBr(CDO)_3BMe$].

the substrate) and coordinating agent, giving complexes of approximately octahedral geometry. The facile cleavage of the Tc–oxo bond is accompanied, where necessary, by an intramolecular rearrangement of the Schiff-base donors in order to face the incoming phosphorus to an imine nitrogen atom. The resulting *trans* Tc–P, Tc–N and Tc–O bond lengths in [$TcCl(Phsal)_2(PMe_2Ph)$] [149] and [$Tc(OPhsal)(quin)(PEt_2Ph)$] [150] have almost identical values. By using the consolidated reduction–substitution reaction, a rare example of a binuclear Tc(III) complex is reported: μ-O[$TcO(OPhsal)(PMe_2Ph)_2$]$_2$ [151], which shows an oxo-bridge with a nearly linear Tc–O–Tc angle (176.1°).

The geometry of the complex [$TcCl_2(SMe\text{-}OPhdtcz)(PPh_3)_2$] [112], can be described as distorted octahedral with a *trans*-P, *cis*-Cl configuration, the coordination sphere being completed by the monoanionic Schiff base, which ligates through the neutral imine nitrogen and the thiolate sulfur atom.

Most of the reported Schiff-base technetium complexes contain the metal in the 5+ and 3+ oxidation states, the latter being stabilized by introducing phosphine ligands in the coordination sphere or by expanding such a sphere from six to seven, as in BATO derivatives. In spite of this general behavior, a few other examples, covering lower technetium oxidation states, are reported. The displacement of one carbon monoxide and a chloride ligand from [$Tc^{I}Cl(PPh_3)_2(CO)_3$], by the bidentate

Schiff-base salthzH, produces the mixed complex [Tc(salthz)$(PPh_3)_2(CO)_2$] [152], neutrality being achieved by deprotonation of the phenolic group of the Schiff-base chelate. The resulting compound shows a distorted octahedral geometry with a *trans*-P, *cis*-CO configuration, as in the Tc[PhN=C(OEt)S]$(PPh_3)_2(CO)_2$ [138] complex.

The potentially hepta-dentate, "umbrella-type" Schiff-base ligand tren-py$_3$ reacts with [$TcCl_3$(MeCN)$(PPh_3)_2$] in MeOH solution to give a pseudo seven-coordinate capped octahedral dicationic Tc(II) complex: [Tc(tren-py$_3$)]$^{2+}$ (Fig. 20) [153], in which the metal is totally encapsulated by seven nitrogen donors. A brief report on a rare Tc(IV) complex containing a six-coordinate N_3O_3-Schiff-base ligand, namely Tc[(4-OMesal)$_3$TAME]$^+$, has been reported [55]. In addition, in this octahedral complex the metal is totally surrounded by the ligand, which is obtained by the condensation of tris(aminomethyl)ethane (TAME) with 4-methoxysalicylaldehyde.

7. TECHNETIUM COMPLEXES WITH ONLY CHALCOGENIDE DONORS

All the X-ray crystal structures reported in this section contain mainly oxygen and/or sulfur donor atoms in the coordination sphere. Most of the compounds

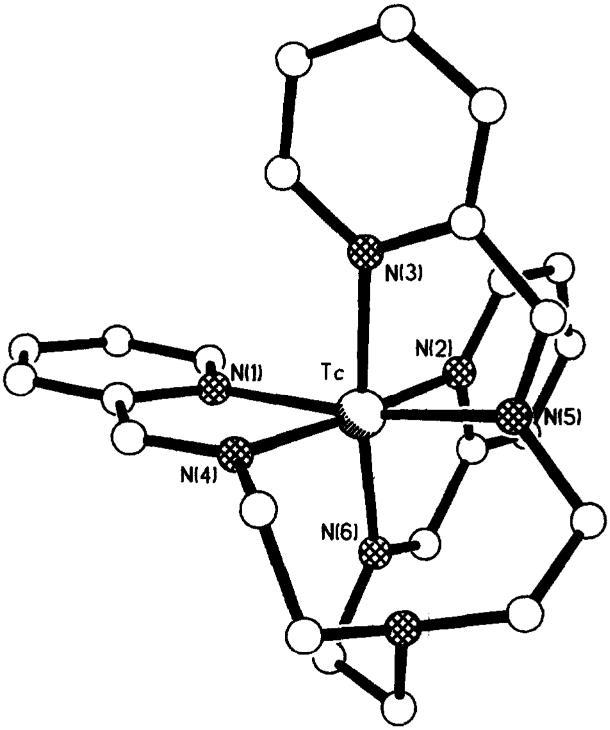


Fig. 20. [Tc(tren-py$_3$)]$^{2+}$.

exhibit the metal in the 3+ or 4+ oxidation state; however, two examples of Tc(V) and Tc(VI) complexes, along with a number of pertechnetate salts, are reported.

7.1. Monodentate ligands

Four complexes containing the [$Tc^{III}(tmbt)_3$] moiety possess an identical configuration: the tmbt ligands sit in the equatorial plane of a trigonal bipyramid and two π-accepting co-ligands occupy the axial positions. In all these 14-electron complexes, two of the aryl thiolate rings are consistently on the same side of the plane defined by the sulfur atoms, while the third is on the opposite side (two-up, one-down orientation), as shown by the complex [$Tc(tmbt)_3(MeCN)_2$] (Fig. 21) [154]. Quite surprisingly, the MeCN ligand is found in the more sterically hindered side of the molecule in [$Tc(tmbt)_3(CO)(MeCN)$] [154]. Conversely, the pyridine ligand in the complex [$Tc(tmbt)_3(CO)(py)$] [154] and the S-bonded DMSO molecule in [$Tc(tmbt)_3(MeCN)(DMSO)$] [155] sit in the less sterically hindered side of the molecule.

The two homoleptic Tc-thiourea compounds [$Tc(Metu)_6]^{3+}$ and [$Tc(Me_2tu)_6]^{3+}$ [156] show distorted octahedral geometries. In [$Tc(Metu)_6]^{3+}$, all *cis* S–Tc–S bond angles differ considerably from the ideal 90° (range 82.2–97.8°), and the shortening of two Tc–S bonds is attributed to a tetragonal distortion.

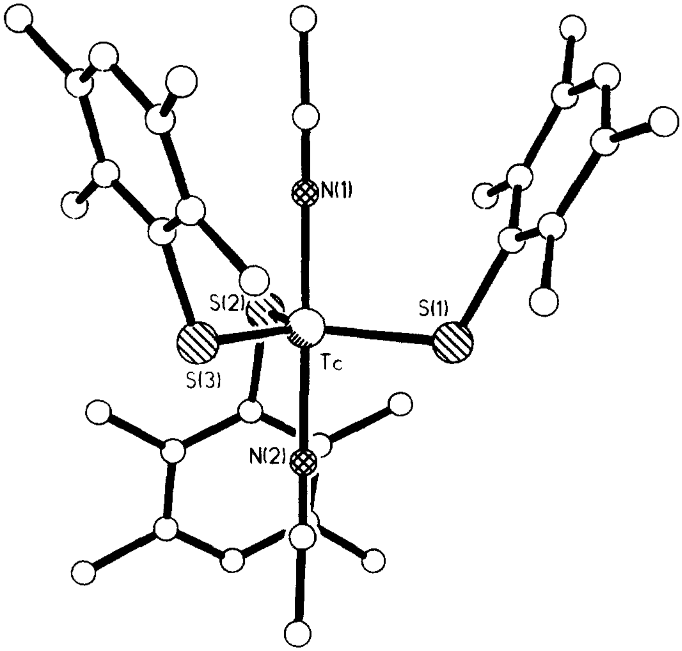


Fig. 21. [$Tc(tmbt)_3(MeCN)_2$].

The unusual polymeric pertechnetate derivative $[Me_2SnOTcO_3]_n$ has recently been reported [157]. The structure consists of a heteronuclear polymeric entity, where tetrahedral $[TcO_4]$ units bridge, through two oxygens, and two quasi-trigonal-bipyramidal $SnMe_3$ units. The overall molecule appears as a zigzag chain of the type $(Tc–O–Sn–O–)_n$. The Tc=O terminal bond distances (average, 1.65 Å) are comparable with those found in $K[TcO_4]$ [158], while the Tc–O bridging distances (1.71(1) Å) are longer, but equal to each other.

Finally, for completeness, a number of $[TcO_4]^-$ crystal structures have been reported, which differ merely in the counter-ion used [158,159].

7.2. Polydentate ligands

Most of the complexes in this section contain ligands already mentioned in Section 3.1, where they coordinated to the $[Tc{=}O]^{3+}$ core. These ligands, usually bidentate, react with $[TcX_6]^{2-}$ (X=F,Cl,Br) or $[TcO_4]^-$, to produce homoleptic neutral or polyanionic six-coordinate complexes with the Tc atom in oxidation states ranging from 3+ to 6+.

As is well-known, for six-coordinate complexes of the type $[M(L\text{-}L)_3]^{n-}$ there are two limiting coordination geometries: the trigonal-prismatic and the octahedral one. These geometries are characterized by the normalized bite (the ratio of intraligand distance to the metal distance) and the angle of twist ϑ (chelate twist angle) between the upper and lower triangular faces. In general, O$\cap$O bidentate ligands produce complexes with the octahedral configuration, while S$\cap$S ligands give trigonal-prismatic geometries.

The complex $[Tc(ox)_3]^{2-}$ [160] is in a distorted octahedral array; the triangular faces O(1),O(2′),O(3) and O(1′),O(2),O(3′) are almost parallel, while the individual twist angles for the three oxalato ligands are 47.9° and 50.2°.

The dimeric complex $\{(\mu\text{-}O)_2[Tc(ox)_2]_2\}^{4-}$ [161], contains an approximately four-membered ring $[Tc(\mu\text{-}O)_2Tc]$ unit, with a short Tc–Tc interaction (2.361(1) Å). Each Tc atom is bound to two oxalato anions, resulting in an octahedral coordination consistent with the lowest intramolecular repulsion between the ligands. The Tc–O–Tc angles of the bridging oxygens are somewhat wider than those in the corresponding Tc-EDTA system [162,163].

In the complex $[Tc^{IV}(THMT)_2]$ [164] the "tripodal" ligand presents the three alcoholic groups deprotonated, two of the ligands bind the Tc atom in an octahedral geometry with idealized D_{3d} symmetry. Assuming all the oxygens are deprotonated, the THMT ligand has formally a 2^- charge, with the resulting oxidation state of Tc being 4+.

In $[Tc(DBcat)_3]$ [165] the catecholate ion acts also as a reducing agent, and reduces the Tc(VII) to Tc(VI), yielding a neutral complex. The coordination geometry is roughly octahedral, but some distortion toward a prismatic structure is found in the value of the chelate twist angle (41.7°), while the complex [$Tc^{III}(acac)_3$] [166] shows typical octahedral coordination with no substantial distortion.

The ligand $bdtH_2$ produces two different compounds: the tris-bidentate complex [$Tc^V(bdt)_3$]$^-$ [160] and the dimer {(μ-bdt)$_2$[Tc(bdt)]$_2$} [167], both are coordinated by a trigonal-prismatic array of six sulfur atoms. The thiolate ligands radiate out from the Tc atom in a "paddle wheel" arrangement only in the monomeric species, where the Tc–S bond lengths (range, 2.322–2.369 Å) are similar to M–S distances found in other tris 1,2-dithiolato complexes [168]. As expected, the Tc–S distances of the terminal ligands in the dimer are significantly shorter (average, 2.295 Å) than those of the bridging ligands (average, 2.408 Å), while the Tc–Tc bond distance of 2.591(3) Å is considerably longer than those found in other compounds like [Tc_2Cl_8]$^{3-}$ (2.117(2) Å) [169] and [$Tc_2Cl_2(piv)_4$]$^{2+}$ (2.192 Å) [170].

In the analogous dimeric complex {(μ-edt)$_2$[Tc(e=dt)]$_2$} (Fig. 22) [171] two terminal dithiolene and two bridging dithiolate ligands coordinate in a trigonal prismatic array around the Tc centers. The different ligating mode of edt and e=dt moieties are confirmed by the difference in C(1)–C(2) and C(3)=C(4) distances (1.49(2) and 1.39(2) Å, respectively). In contrast, in the complex [$Tc(mnt)_3$]$^{2-}$ [172], six sulfur atoms bind the Tc center in a distorted octahedral geometry; analogously, the OS-bidentate ligand mtbmH reacts with [$Tc(tu)_6$]$^{3+}$ to produce the [$Tc(mtbm)_3$] complex [173], in which the Tc(III) atom is accommodated in an essentially octahe-

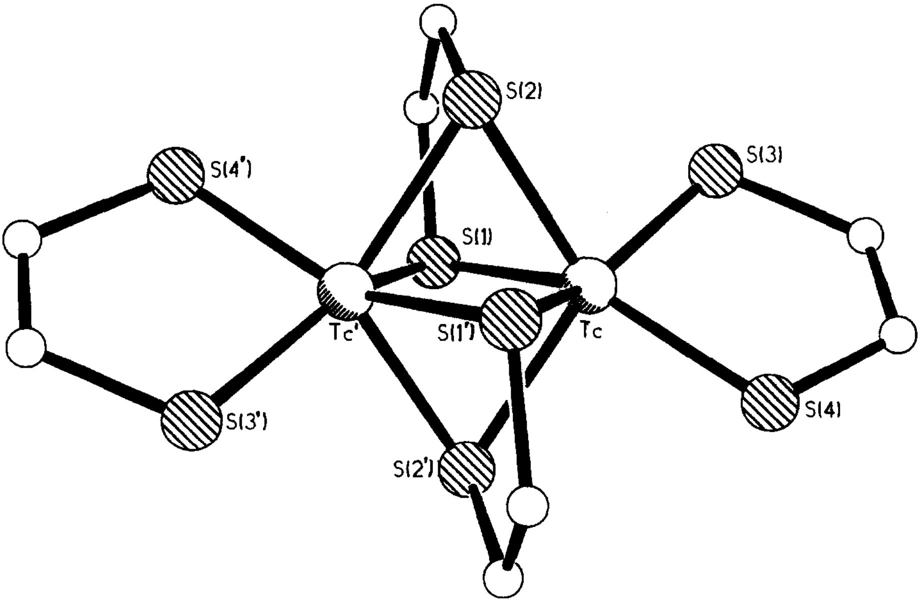


Fig. 22. {(μ-edt)$_2$[Tc(e=dt)]$_2$}.

dral environment. The monothio-β-diketone ligands are disposed in a *fac* configuration, in order that the sulfur faces the oxygen atom of another ligand.

The X-ray structure of [Tc(BX)$_3$(PPh$_3$)] (Fig. 23) [174] shows an unusual seven-coordinate capped octahedral geometry, with the Tc(III) and the phosphorus atoms each sitting on three-fold axes. The bond lengths from the Tc to the capped-face sulfur atoms are equivalent to those of the sulfurs in the uncapped face (2.462 Å), suggesting that the delocalization of the C=S bond is not influenced by a *trans* effect imposed by PPh$_3$ in the pseudo-*trans* position. However, the Tc–S bonds are significantly longer than those in trigonal-bipyramidal Tc(III) tris-thiolate complexes (2.245–2.265 Å) (Section 7.1).

Very recently, a mixed thioether-thiolato cationic Tc complex has been reported: *cis*-[Tc(bt)$_2$(TTOD)]$^+$ (Fig. 24) [175]. The Tc(III) atom is surrounded by six sulfurs in a distorted octahedral geometry. The cationic compound belongs to a new type of entirely sulfur-coordinated Tc(III) complexes involving a polythioether in the coordination sphere. The Tc–S$_{\text{thioether}}$ distances (2.419–2.464 Å) are longer than those involving the benzenethiolate groups (2.291(2) and 2.266(2) Å). While Tc(III) diphosphine-thiolato complexes (*vide infra*) show both *cis* and *trans* arrangements, depend-

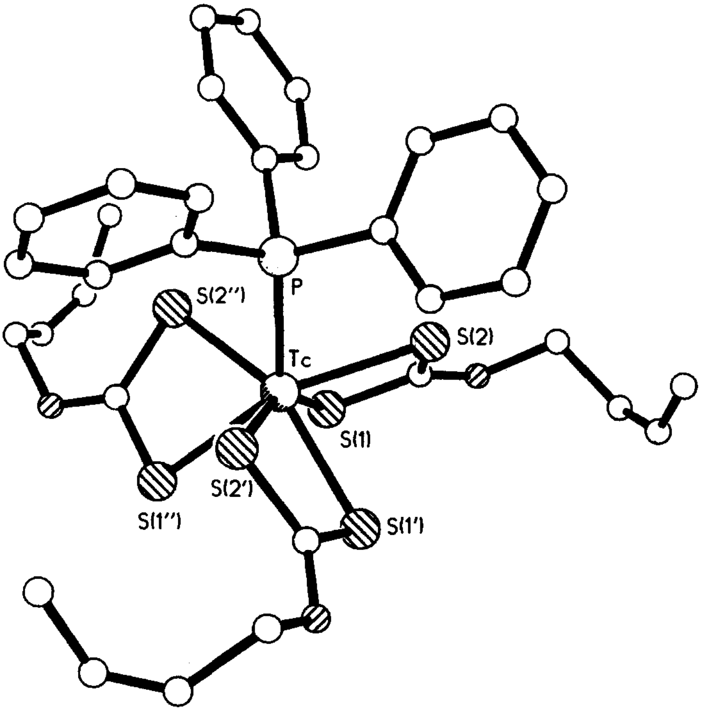


Fig. 23. [Tc(BX)$_3$(PPh$_3$)].

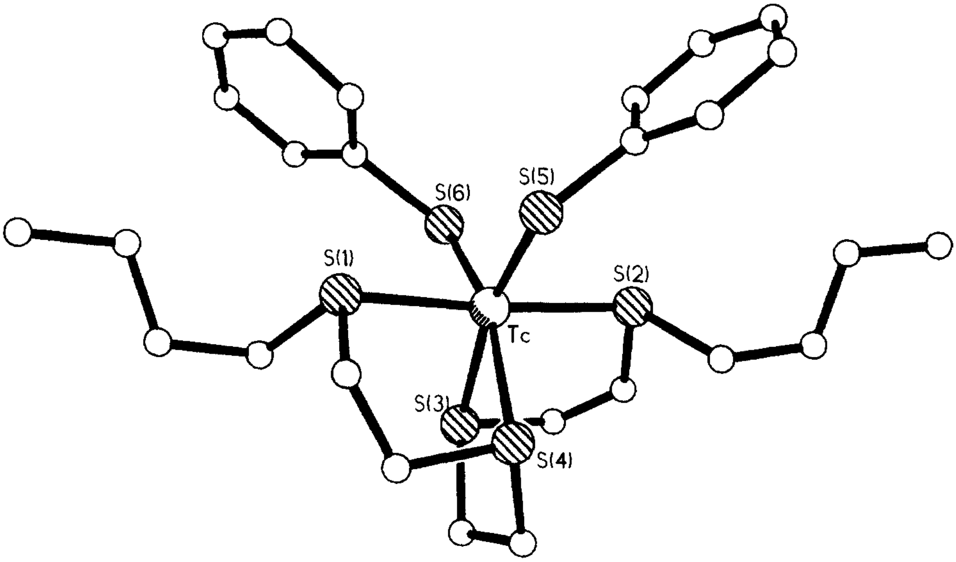


Fig. 24. *cis*-$[Tc(bt)_2(TTOD)]^+$.

ing on the thiolate ligand employed [176–178], only the *cis*-orientation of the bt ligands is found in this complex.

8. TECHNETIUM COMPLEXES WITH PNICTIDE* DONORS

8.1. D_2X_2-type species

The following section covers Tc complexes of general formula $[TcD_2X_2]^{+/0}$, where D represents a tertiary diphosphine or diarsine, and X a halide or thiolate group. In addition, X_2 can represent a bidentate chalcogenide donor ligand.

In these compounds the coordination sphere about technetium is always approximately octahedral, with the metal occupying a crystallographic two-fold axis in the *cis*-X complexes and a crystallographic inversion center in the *trans*-X ones.

Only the *trans*-X geometry has thus far been observed for $[TcD_2X_2]$ complexes when X = halide or thiocyanate [179–182]. Analogously, the recent crystal structure determinations of $[TcCl_2(dppe)_2]$ and $[TcCl_2(dppe)_2]^+$ [183] show the complexes being octahedral with a *trans*-Cl geometry. Oxidation of the Tc(II) complex to Tc(III) causes a shortening of the Tc–Cl bond by about 0.10 Å, consistent with the prevalent ionic nature of this interaction. Conversely, oxidation from Tc(II) to

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* Following the recent recommendation of the Commission on the Nomenclature of Inorganic Chemistry, the group 15 is referred to as "pentelide".

Tc(III) causes a lengthening of the Tc–P bond by about 0.07 Å, consistent with the prevalence in this interaction of π-backbonding from Tc to P.

The substitution of halide(s) with thiolate groups allows a new class of $[TcD_2(SR)_2]^{+/0}$ complexes to be synthesized via reduction–substitution reaction from $[TcO(OH)D_2]^{2+}$ in the presence of an excess of appropriate thiol. This acts both as reductant and coordinating ligand, giving: *trans*-$[Tc(mt)_2(dmpe)2]^+$, *trans*-$[Tc(mt)_2(depe)_2]^+$ [176] and *trans*-$[Tc(mt)_2(diars)_2]^+$ (Fig. 25) [184].

The incorporation of aryl groups in the –S–R thiolate ligand makes the resulting complexes more flexible, and Tc(II) and Tc(III) species with both *cis* and *trans* geometries become easily accessible. The neutral *trans*-$[Tc(bt)_2(diars)_2]$ [184] complex shows longer Tc–S (2.410(2) Å) distances (by 0.12 Å) and somewhat shorter (by only 0.03 Å) Tc–As lengths (mean of 2.471 Å) when compared to the oxidized Tc(III) form.

Analogous geometry is exhibited by the *trans*-$[Tc(bt\text{-}Cl)_2(dmpe)_2]$ [178] complex, which is, however, easily isomerized into the more stable *cis*-$[Tc(bt\text{-}Cl)_2(dmpe)_2]$ (Fig. 26) [179] form. For the *cis*/*trans* pair of $[Tc(bt\text{-}Cl)_2(dmpe)_2]$ complexes, the most striking structural change in the first coordination sphere is the discrepancy in Tc–P bond lengths. In the *cis* isomer there is a sulfur-induced structural *trans* effect; the Tc–P bonds (2.439(3) Å) *trans* to sulfur are 0.054 Å longer than those *trans* to phosphorus. Since the Tc^{II}–P bond is known to be dominated by π-back-bonding interactions, and the structural data seem to suggest that the electronic requirements of the sulfur atoms are satisfied at some expense to the *trans* Tc–P bond, the authors speculate that the arene-thiolate ligand may itself be a potent π-acceptor ligand which competes effectively with the *trans*-situated phosphine. Consistent results are shown by the *cis*-$[Tc(bt)_2(dmpe)_2]^+$ [185] com-

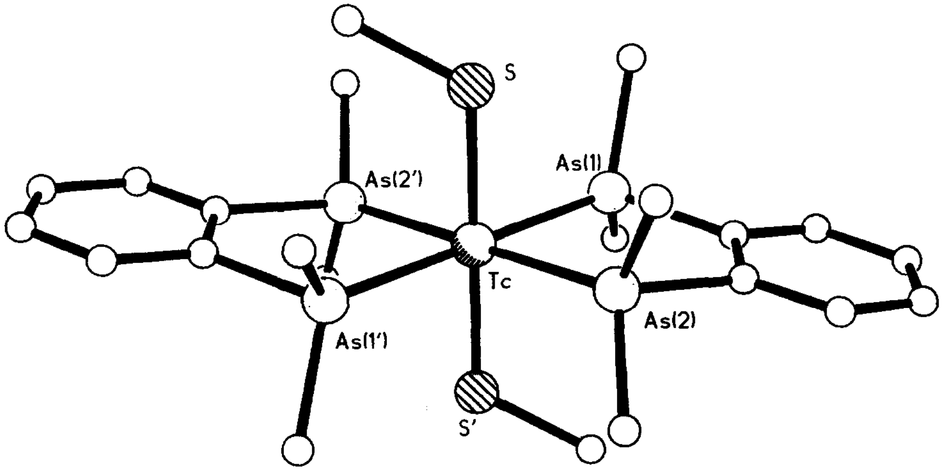

Fig. 25. *trans*-$[Tc(mt)_2(diars)_2]^+$.

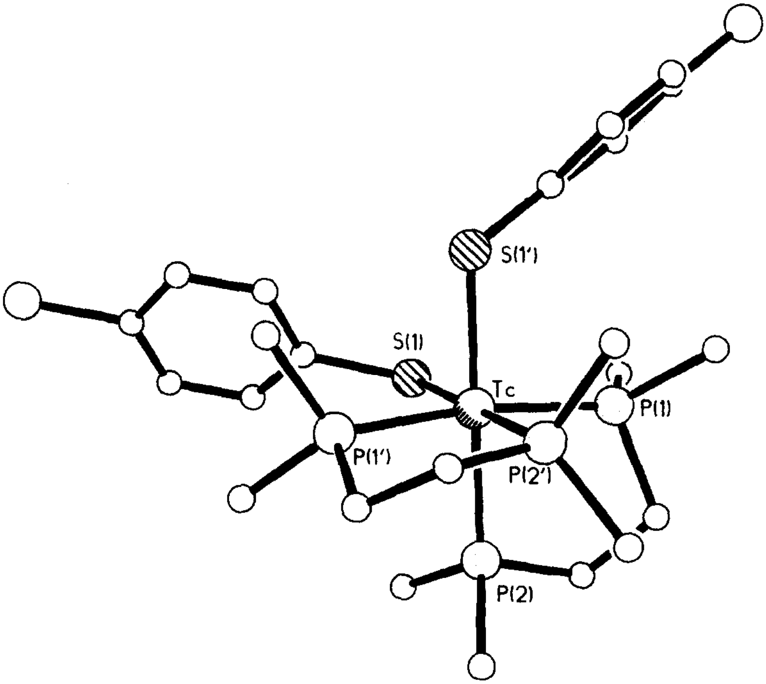

Fig. 26. *cis*-[Tc(bt-Cl)$_2$(dmpe)$_2$].

plex, where the Tc–P distances (mean of 2.49 Å) *trans* to the bt groups are 0.07 Å longer than those *trans* to phosphorus. The loss of one electron, combined with the lack of the *para*-chloro substituent in the bt frameworks, causes a remarkable shortening of the Tc–S bonds (2.29 *vs.* 2.42 Å) when traversing from *cis*-[Tc(bt)$_2$(dmpe)$_2$]$^+$ to *cis*-[Tc(bt-Cl)$_2$(dmpe)$_2$].

Three more complexes, [Tc(meph)(dmpe)$_2$]$^+$ [186], [Tc(ox)(dppe)$_2$] [187] and [Tc(Et$_2$dtc)(dppe)$_2$]$^+$ [35], are included in the section; they all contain a bis-diphosphine and a *cis*-chalcogenide bidentate ligand in a distorted octahedral geometry.

8.2. Functionalized phosphine species

In the recent past, polydentate functionalized phosphine ligands have been proposed for binding the technetium metal. This relatively new class of chelates matches the well-established reduction capability of P(III) toward pertechnetate, with the coordination ability offered by a properly positioned functional group. Since reduction of pertechnetate generally requires the use of a reductant in conjunction with a coordinating agent, the employment of a functionalized phosphine ligand may simplify the synthesis of low-valent Tc complexes.

The coordination sphere of the resulting complexes is strongly dependent on the nature and number of functional groups in the chelate and on steric constraints imposed by the geometry of the ligand itself upon coordination. Tetradentate "umbrella"-type ligand PS_3H_3, which provides technetium with a phosphine and three thiolate groups, gives, by reaction with pertechnetate in the presence of sodium dithionite and proper alkylisocyanide, trigonal bipyramidal Tc(III) species. The structure has the three thiolates in the equatorial plane and two π-accepting groups (the phosphorus of the PS_3 chelating ligand and an isocyanide) in the axial positions. With this "umbrella" system the six-coordinated $[Tc(PS_3)(CN\text{-i-pr})_2]$ (Fig. 27) [188] complex can also be isolated, when a large excess of isocyanide is used. It shows a very distorted octahedral geometry but, despite the second isonitrile, is labile. There is very little difference between the two Tc–C lengths (2.081(7) and 2.058(8) Å). In contrast, the Tc–S(1) distance is significantly longer (by 0.07 Å) than the others (mean, 2.319 Å) and the angle exhibited by the *trans*-coordinated sulfur atoms through the metal is remarkably out of linearity (147.9(1)°). Both facts induce the complex to arrange to the thermodynamically more stable trigonal-bipyramidal form by losing the equatorial isocyanide ligand, in order to maximize π-donation from sulfur to technetium and from technetium to the axial π-acceptor ligands [189].

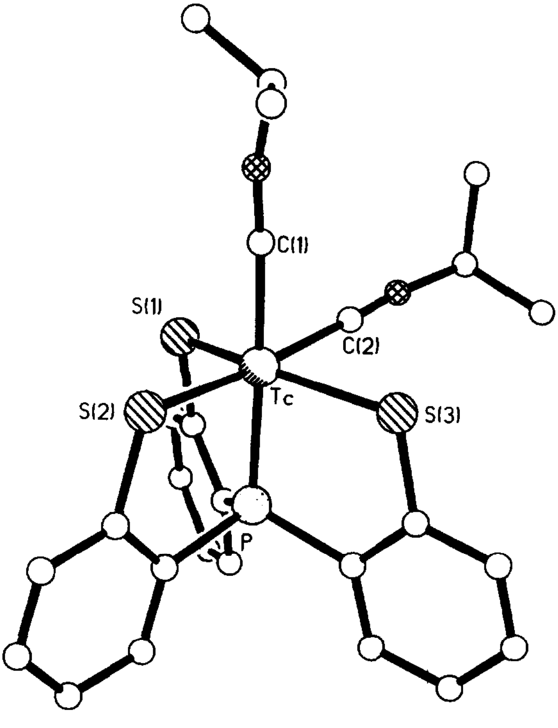

Fig. 27. $[Tc(PS_3)(CN\text{-i-pr})_2]$.

By treating $[TcOCl_4]^-$ with the bidentate ligand (2-diphenylphosphino)-benzaldehyde (PCHO), a complicated reduction–substitution reaction occurs. The metal assists a catalytic bimolecular reduction of two aldehyde groups and the formation of a carbon–carbon bond in a native POOP-tetradentate ligand. The resulting neutral and paramagnetic d^3 complex $[TcCl_2(P_2O_2)]$ (Fig. 28) [190] contains a pinacolate system. Other bidentate PX-functionalized phosphines (X = COOH,OH,SH,NH_2), give homoleptic tris-substituted and *mer*-Tc(III) octahedral complexes. The complex $[Tc(PNH)_2(PNH_2)]^+$ [191] is positively charged, while $[Tc(PS)_3]$ [192,193], $[Tc(PO)_3]$ [192] and $[Tc(PCOO)_3]$ (Fig. 29) [194] are neutral owing to the triple deprotonation of the functional groups. In the cationic complex the strong π-donor property of the amido group labilizes the two *trans*-coordinate nitrogen atoms, resulting in the lengthening of one Tc–N bond, along with the lengthening of the Tc–P bond of the same ligand. In acid media such nitrogen becomes protonated, giving a coordinative Tc–N bond length of 2.048(5) Å; a value significantly longer than those of the covalent $Tc–N_{amido}$ distances (1.948(5) and 1.979(5) Å). A similar π effect is responsible for the labilization of one of the three chelates in the $[Tc(PS)_3]$ complex [192,193]. The difference between the Tc–S bond distance of the labilized ligand (2.489(2) Å) and those of the other metal–sulfur

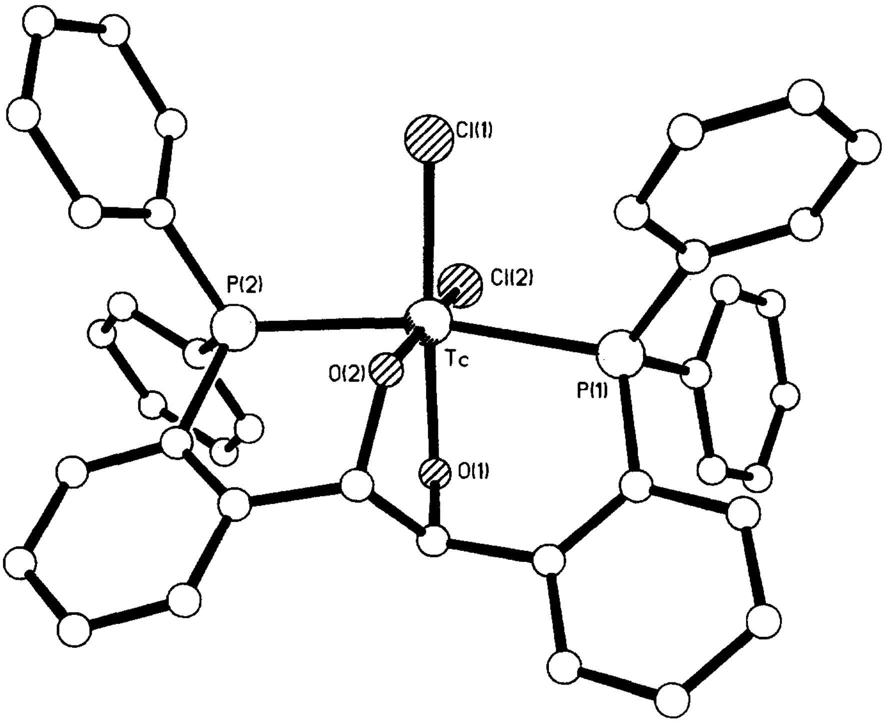

Fig. 28. $[TcCl_2(P_2O_2)]$.

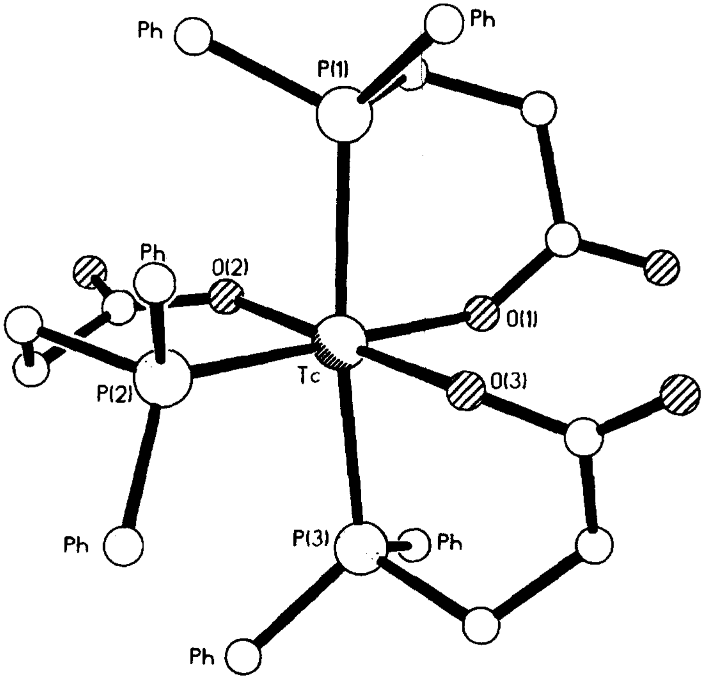

Fig. 29. [Tc(PCOO)$_3$].

bonds (2.258(1) and 2.279(1) Å) is remarkable, and is accompanied by a less dramatic deviation of the associated Tc–P distances (2.477(1) *vs.* 2.406(1) and 2.424(1) Å). Conversely, bidentate phosphines bearing oxygen functional groups produce tris-substituted species whose *trans* Tc–O distances are similar and reinforced.

Among the rare examples of Tc(V)-phosphino compounds, [TcO(PNH)$_2$(OMe)] (Fig. 30) [195] and [TcO(P$_2$N$_2$)(OMe)] [195] represent the only species so far structurally characterized which contain a mono-oxo unit. The former neutral complex, containing two phosphinoamido ligands coordinated mutually *cis* in the equatorial plane of a distorted octahedron, is a labile side-product obtained in the synthesis of the charged [Tc(PNH)$_2$(PNH$_2$)]$^+$. Both complexes exhibit rather long Tc=O bond lengths (1.70(1) and 1.69(1) for the "bis-bidentate" and "tetradentate", respectively).

8.3. *Mixed halide-phosphine species*

Technetium phosphine-halide complexes represent a class of well-known Tc compounds. They are usually obtained by reduction of pertechnetate in the presence of tertiary phosphine and hydrohalogenic acid. Several Tc complexes were synthe-

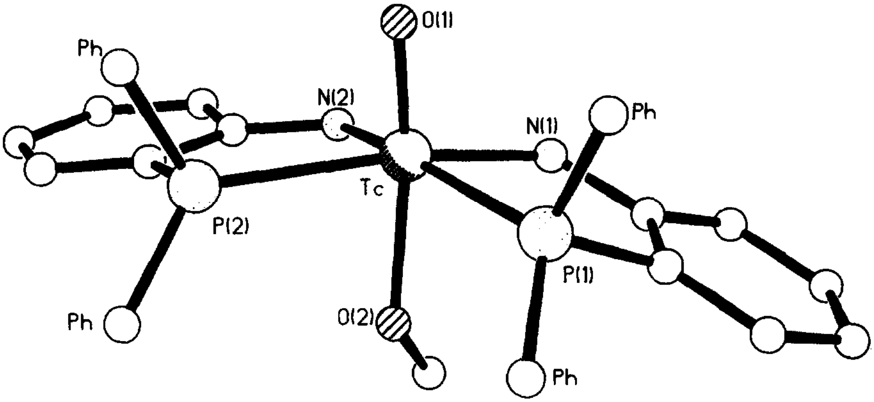

Fig. 30. $[TcO(PNH)_2(OMe)]$.

sized in the late 1970s, and they are among the first structurally characterized technetium compounds [196–198].

Recently new interest in this field has developed because of the utilization of phosphines as reducing agents towards pertechnetate and in order to find out possible trends in metal–phosphorus lengths through both horizontal and vertical series of homologous $[MCl_4(PR_3)_2]$ and $[MCl_3(PR_3)_3]$ compounds (M = transition metal; R = aryl and/or alkyl groups). Thus, three new neutral Tc(IV) complexes, $[TcCl_4(PEt_3)_2]$ [199], $[TcCl_4(PMe_2Ph)_2]$ [200] and $[TcCl_4(PMePh_2)_2]$ [199], have been characterized by means of structural analysis. They all adopt a *trans*-phosphine configuration, with the halides completing the basal plane in a nearly octahedral geometry. The anionic $[TcCl_5(PEt_3)]^-$ [199] and neutral *mer*-$[TcCl_3(PMe_3)_3]$ species [201] do not deserve comment, because of the structural consistency with the already characterized $[TcCl_5(PPh_3)]^-$ [202] and *mer*-$[TcCl_3(PMe_2Ph)_3]$ [198] complexes.

8.4. Low-valent with various donor species

The production of low-valent (oxidation states 1+, 2+, 3+) technetium-mixed complexes, containing at least a tertiary phosphine and a variety of mono- or polydentate chelates, has been limited in the past by the paucity of suitable pre-reduced technetium precursors. It seems that *mer*-$[TcCl_3(PPh_3)_2(MeCN)]$ [203] is much more reactive than either of the alternative Tc(III) complexes $[Tc(tu)_6]^{3+}$ [204] and $[TcCl_3(PMe_2Ph)_3]$ [198] or Tc(IV) species $[TcCl_4(PPh_3)_2]$ so far utilized. The lability of this newly synthesized Tc(III) compound is confirmed by its instability in solution, so that only a partial X-ray structural characterization has been performed on the homologous *mer*-$[TcCl_3(Ptol_3)_2(MeCN)]$ [205]. As expected on steric grounds, the phosphine ligands are disposed mutually *trans* and the chloride atoms are meridional in a nearly octahedral coordination geometry. The reaction of $[TcCl_3(PPh_3)_2(MeCN)]$ with CO gas yields *mer*-$[TcCl_3(PPh_3)_2(CO)]$ [203]; its Tc–P bonds are quite long (2.525(2) Å), together with short *trans* equatorial Tc–Cl distances (2.322(2) Å) and an unusually long Tc–C distance of 1.985(9) Å. A similar complex, namely *mer*-$[TcCl_3(PPh_3)_2(DMF)]$ [206], is directly synthesized from pertechnetate in the presence of PPh_3 and HCl in DMF solution. The complex, which co-crystallizes with two PPh_3 molecules in the lattice, represents the only example so far available of a Tc-DMF compound.

Again, the lack of suitable precursors has made the lowest oxidation states (from 2+ to 1−) of Tc chemistry not systematically explored. Known compounds, such as $[Tc_2(CO)_{10}]$, $[TcX(CO)_5]$ (X = halide) and $[Tc(CO)6]^+$, are not easily available, because of the concomitant problems due to radiation safety and high-pressure reactions. However, the presence among the currently employed technetium radiopharmaceuticals of the cationic hexakis-isonitrile species of general formula $[Tc(CNR)_6]^+$ (R = alkyl) [207,208] has opened the field to further investigation. Recently, the already known Tc(I) species $[TcCl(PPh_3)_2(CO)_3]$ [209] has been recognized as a suitable starting material for preparing low-valent Tc species. $[TcCl(PPh_3)_2(CO)_3]$ presents an almost undistorted octahedral core geometry with a meridional substituent pattern for the carbonyl ligands. The phosphines are located in *trans* positions to each other. Reactions of $[TcCl(PPh_3)_2(CO)_3]$ with the tridentate cyclic amine TAN or with $KHBpz_3$ easily displace one carbon monoxide, one PPh_3 and the chloride ligands to give water-stable $[Tc(HBpz_3)(PPh_3)(CO)_2]$ [209] and $[Tc(TAN)(PPh_3)(CO)_2]^+$ [209] complexes. Both compounds possess octahedral geometry with the three nitrogen atoms coordinating the facial positions of the polyhedron, while $[Tc(Phdtc)(PPh_3)_2(CO)_2]$ [210] contains a dithiocarbamate moiety to complete the octahedral coordination sphere of the *cis*-CO *trans*-P configuration.

An interesting example of seven-coordination is exhibited by the cationic Tc(III) phosphine-hydride complex $[TcH(\eta^2\text{-tu})(PMe_3)_4]^+$ (Fig. 31) [201]. This complex is peculiar in that it represents one of the rare examples of both Tc hydride and trimethylphosphine species, and contains an unusual N,S-bidentate thiourea coordination. The geometry about the metal cannot be fully described, since the Tc-bound hydride has not been located in the determination of the crystal structure. Ignoring the hydride ligand, well described through proton ^{31}P decoupled NMR investigation, the geometry around the technetium atom appears as a distorted octahedron. The largest vacancy in the coordination sphere lies *trans* to the η^2-N,S-thiourea ligand, between the *cis* equatorial phosphines, and the hydride could reside in this position.

Several mixed polypyridyl-technetium complexes have recently been synthesized following the already-known extensive chemistry of its third-row congener rhenium. They are prepared by polypyridyl-ligand substitution onto the *mer*-$[TcCl_3(PR_3)_3]$ or $[TcCl_4(PR_3)_2]$. Neutral *fac*-$[TcCl_3(PPh_3)(bpy)]$ [211] is

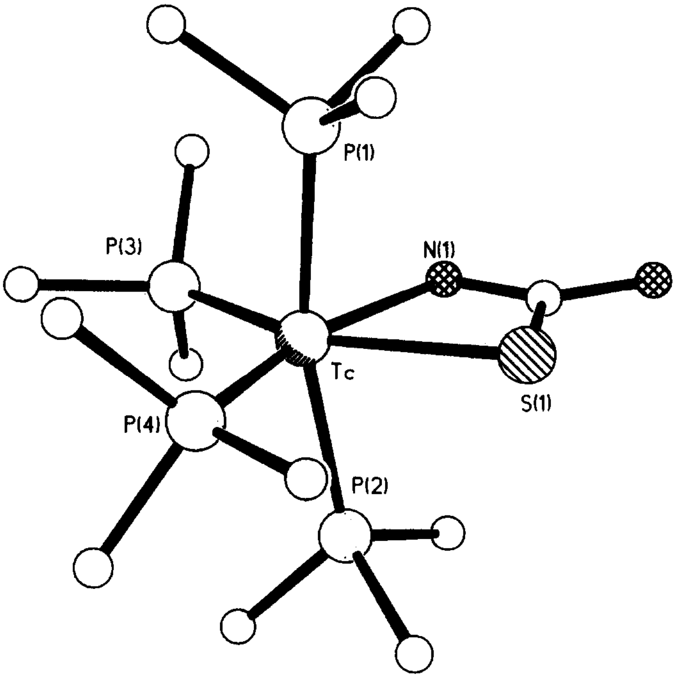

Fig. 31. $[TcH(\eta^2\text{-tu})(PMe_3)_4]^+$.

obtained in low yield from the latter, while an accurate crystal structure analysis of three analogous Tc(III) complexes, $[TcCl_2(PEtPh_2)_2(bpy)]^+$ [212], $[TcCl_2(PMe_2Ph)_2(bpy)]^+$ [212] and $[TcCl_2(PMe_2Ph)_2(phen)]^+$ [212] present the opportunity to evaluate finely the structural effects resulting from small changes in the ligands. All three complexes contain the metal residing in a slightly distorted octahedral environment, with two mutually *trans* phosphine ligands, while the two mutually *cis* chloride atoms are *trans* to the two nitrogens of the bidentate bpy or phen ligand. Reduction of cationic Tc(III) species to the neutral $[TcCl_2(PMe_2Ph)_2(bpy)]$ [213] complex is a base-induced reaction in EtOH solution. The comparison of structural data for the couple Tc(III/II) shows:

i. Tc–P distances in the reduced form are significantly shorter (average difference [III − II] = +0.07 Å), as well as the Tc–N ones (average difference [III − II] = +0.03 Å), than the corresponding distances in its oxidized analog;

ii. in contrast, the Tc–Cl distances in the Tc(II) complex are longer than those in the Tc(III) form (average difference [III − II] = −0.08 Å).

Such an inversion in the sign of the [III − II] difference occurs because the Tc–Cl linkage is dominated by electrostatic interactions, while the Tc–P and Tc–N linkages are dominated by π-back-bonding interactions. The effect of both shorter Tc–P and Tc–N bond lengths in the Tc(II) species creates more steric crowding between the phosphine and phen ligands than in the oxidized analogs, and this in turn results in the phosphine ligands being canted away from the phen ligand to a greater extent in the Tc(II) complex. The P–Tc–P angle in the Tc(II) form is 173.9(2)°, whereas in the Tc(III) it is 179.6(1)°. A similar effect is manifested in the $[TcBr(PMe_2Ph)_2(terpy)]^+$ complex [213], where the P–Tc–P angle is 173.6(2)°.

Three more polypyridyl-technetium complexes are structurally characterized. One of them, $[TcNBr(bpy)_2]^{2+}$ [94] has already been discussed in Section 4.3, while for $\{\mu\text{-}O[TcCl(bpy)_2]_2\}^{2+}$ [214] and $[Tc(bpy)_3]^{2+}$ (Λ isomer) [205] only a preliminary report has been made.

9. NITROSYL AND THIONITROSYL TECHNETIUM COMPLEXES

Although the preparation of the first technetium nitrosyl compound was reported in 1963 [215], and its identification performed in 1976 [216], only a few Tc nitrosyl compounds are known [217]. Recently, a convenient high-yield synthesis of the versatile starting material $[n\text{-}Bu_4N][Tc(NO)Cl_4]$ has been proposed [218], prompting renewed interest in "Tc(NO)" chemistry.

Even though the first structural report on a Tc-thionitrosyl complex was reported in 1984 [219], only recently have thionitrosyl complexes regained interest because of their easy synthesis by transfer of the S atom from S_2Cl_2 to the $[TcN]^{2+}$ core, with a contemporary four-electron reduction of the Tc center. Nitrosyl or thionitrosyl cores are usually linearly coordinated to the metal as NO^+ or NS^+ groups, and the N–O distances range from 1.14(2) Å for $[Tc(NO)Br_2(CN\text{-}t\text{-}bu)_3]$ [220] to 1.17(2) Å in $[Tc(NO)Cl_4(MeOH)]^-$ [221], the only exception being in the complex $[Tc(NO)Cl_3(acac)]^-$ [222], where the distance is 1.20(4) Å and the Tc–N–O angle (159(3)°) deviates dramatically from 180°.

The linear NO^+ ligand is a good π-acceptor, and deviation from linearity results in a decreased π-accepting ability. The involvement of π-contribution in the Tc–N bond causes the contraction of the Tc–N length, which in fact results in shorter complexes where Tc–N–O angles are close to 180°. Since sulfur is a better π-acceptor than oxygen, the thionitrosyl ligand is a better π-acceptor than nitrosyl. As a consequence, the deviation from linearity for the relevant moiety is less pronounced in thionitrosyl complexes. Lastly, the π-bonding affects the octahedral geometry, displacing the Tc atom toward the (thio)nitrosyl ligand above the mean plane of the equatorial ligands. In terms of *trans* effect the thionitrosyl, an effective π-acceptor, has a less marked influence than the nitrido and the oxo groups, which are strong π-donors; thus, there are examples of nitrosyl complexes where the $M\text{-}L_{trans}$ distances are shorter than the corresponding $M\text{-}L_{cis}$, even if their differences are small. This behavior is ascribed to the weak σ- and strong π-bonds formed between M and N in octahedral complexes; an interaction resulting in a nitrosyl ligand having a strong π *trans* influence and weak σ *trans* influence. As a consequence, ligands of predominantly character should be held more firmly in the *trans* position.

Conversely, it is suggested that M–NS bonds should be stronger than M–NO bonds, since the thionitrosyl ligand has better σ- and π-properties than the nitrosyl one. Therefore, it is reasonable to expect a greater tendency for lengthening of the Tc–L_{trans} bond in thionitrosyl complexes [223,224].

In the anionic complexes $[Tc(NO)Cl_4(MeOH)]^-$ [221] and $[Tc(NO)Cl_3(acac)]^-$ [222], the geometry about the Tc(II) atom is distorted octahedral, and both contain an oxygen atom *trans* to the $[Tc\text{-}NO]^{3+}$ core. The most significant difference between the two complexes is the Tc–N–O angle (176(1)° for the "tetrachloro" complex and 159(3)° for the "acac" one. The Tc–N distance is 1.69(1) Å for the "tetrachloro" derivative, the shortest of the complexes reported herein, and 1.74(3) Å for the "acac" derivative.

The neutral complex $[TcI(NO)Br_2(CN\text{-}t\text{-}bu)_3]$ [220] is slightly distorted from octahedral geometry, with the three isonitrile ligands meridionally ligated. The Tc–N–O bond angle (176(2)°) confirms the assignment of the nitrosyl ligand as NO^+, and the Tc–NO bond length (1.73(2) Å) compares well to the Tc–NO distance of 1.74(1) Å found in $[Tc(NO)(NH_3)(phen)_2]^{2+}$ (Fig. 32) [225], wherein, according to the effective π-back-donation to the phenanthroline ligands, the mean equatorial Tc–N_{phen} distance is 2.11(1) Å, which is 0.075 Å shorter than the Tc–NH_3 length.

The unique structurally characterized five-coordinate Tc(III) nitrosyl complex, $[Tc(NO)Cl(tmbt)_3]$ [226], presents a trigonal-bipyramidal geometry. Of the three

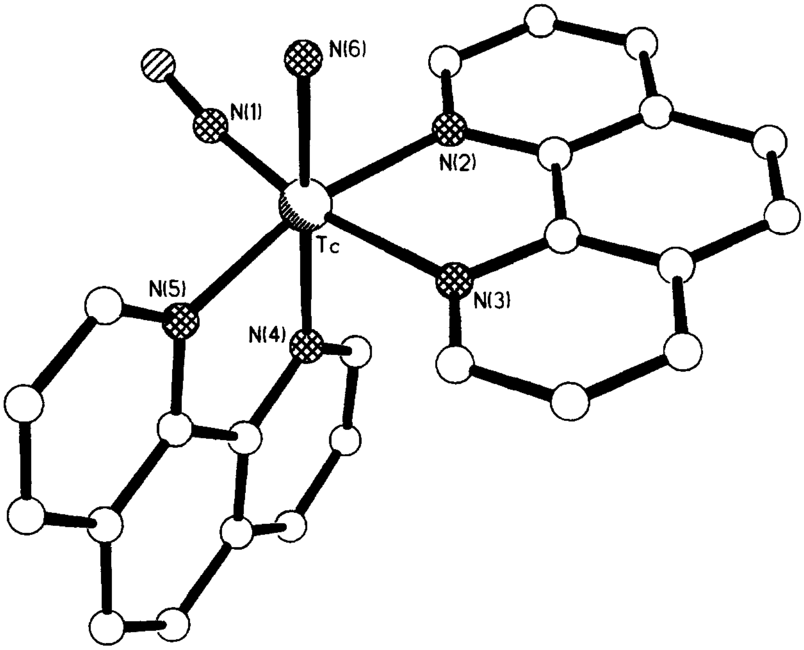

Fig. 32. $[Tc(NO)(NH_3)(phen)_2]^{2+}$.

aryl-thiolate groups, one is directed toward the chloride ligand and the remaining two are directed toward a linear nitrosyl unit.

By reacting [$TcNCl_2(PMe_2Ph)_3$] with an equimolar amount of S_2Cl_2 in CH_2Cl_2 at room temperature, [$Tc(NS)Cl_2(PMe_2Ph)_3$] [227] is obtained, while, by using an excess of S_2Cl_2 at reflux, [$Tc^I(NS)Cl_3(PMe_2Ph)(OPMe_2Ph)$] [228] is recovered. In the "dichloro" compound the three phosphines are meridionally coordinated about the Tc(I), all *cis* to the NS moiety, and in the "trichloro" one the chlorides replaces the phosphines. In both complexes the [Tc–NS]$^{3+}$ core is almost linear and the Tc–Cl bond *trans* to the NS group is shorter than the Tc–Cl bond *trans* to the phosphine. In [$Tc(NS)Cl_3(PMe_2Ph)(OPMe_2Ph)$] the phosphinoxide is coordinated via oxygen with a Tc–O length of 2.097(4) Å, a value slightly longer than those usually observed for other axial Tc–O bonds. In the octahedral [$Tc^I(NS)Cl(phen)_2$]$^+$ [225] the phen ligand, bonded with a nitrogen *trans* to the NS unit, shows the longest Tc–N bond (2.179(4) Å) and the angle Tc–N=S (170.0(4)°) deviates from linearity more than in any other thionitrosyl complex. The shortest Tc–NS distance of the series (1.73(1) Å) is exhibited by [$Tc(NS)Cl_2(4\text{-pic})_3$] [223], which presents the three picoline ligands coordinated in the equatorial plane of the octahedron.

In the seven-coordinate Tc(III) complex [$Tc(NS)Br_2(Et_2dtc)_2$] (Fig. 33) [224] the geometry about the Tc atom is a distorted pentagonal bipyramid with the four sulfur atoms of the ligands determining a mean plane from which Tc and Br(2) are out by 0.11 and 0.23 Å, respectively, toward the axial thionitrosyl group.

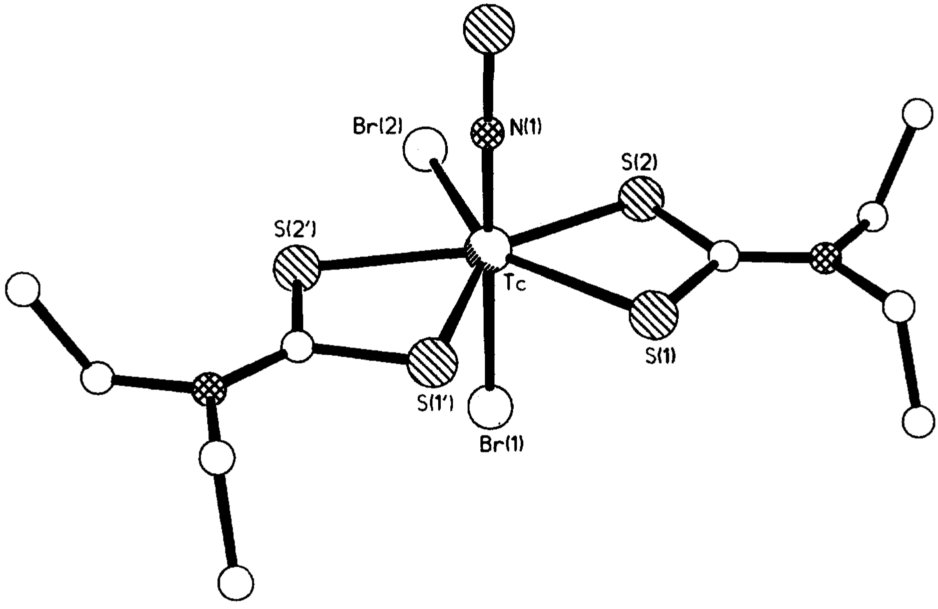

Fig. 33. [$Tc(NS)Br_2(Et_2dtc)_2$].

10. ORGANOMETALLIC TECHNETIUM COMPLEXES

Technetium organometallic chemistry has received a great impetus in the last few years. The low-valent Tc(0) species $[Tc_2(CO)_{10}]$ was the first structurally characterized Tc-organometallic complex, reported in 1965 [229]. The synthesis of the decacarbonyl complex requires both high temperature and high CO pressure, thus reducing the possible interest in the field. But the growing importance of Tc radiopharmaceuticals and the contemporary development of rhenium organometallic chemistry [230–235] have made such research attractive.

In the alkoxy Tc(I) complex of cubane-type geometry $Na[Tc_3(CO)_9(OMe)_4]$ (Fig. 34) [236] the vertices of the cubic inner core are occupied by four oxygens of the methanolate groups, three technetium and one sodium atoms. Each Tc atom is approximately octahedrally coordinated, bearing also three carbonyl groups in the outer side of the cubic vertices, while the remaining oxygen and sodium atoms are virtually tetrahedrally coordinated. $[Tc_3(CO)_9(OMe)_4]^-$ represents a convenient starting material, as well as $[Tc(CO)_5I]$ and $[Tc_2(CO)_{10}]$, for the synthesis of a class of tricarbonyl complexes of general formula $[Tc(CO)_3Cp]$. Four representatives, $[Tc(CO)_3(\eta^5\text{-}Me_5Cp')]$ [237], $[Tc(CO)_3(\eta^5\text{-}Me_4EtCp')]$ [237], $[Tc(CO)_3(\eta^5\text{-}Me_4pnNMe_3Cp')]^+$ [238] and $[Tc(CO)_3(Ind)]$ [237], have been structurally char-

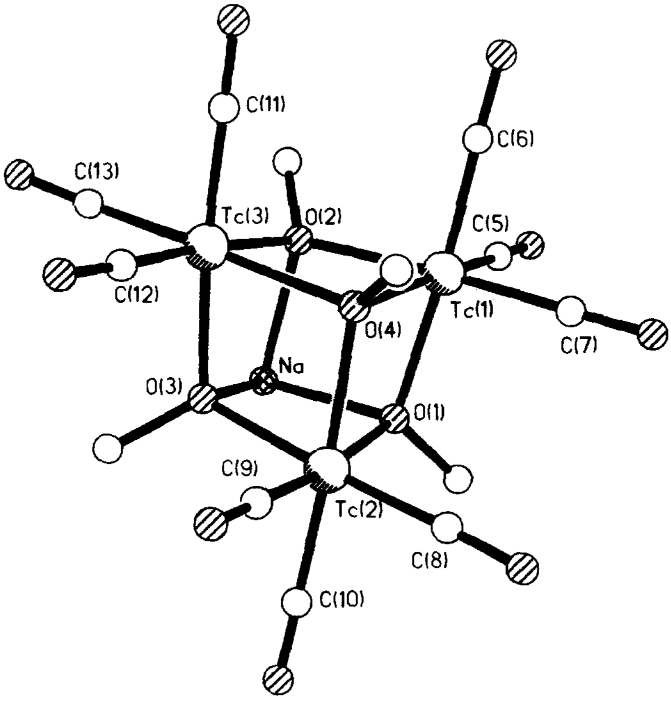

Fig. 34. $[Tc_3(CO)_9(OMe)_4]^-$.

acterized by varying the nature of the Cp side chain. All tricarbonyl complexes have formal coordination number four with the geometry about Tc being best described as a "piano stool", with a symmetrically bonded η^5-Cp ligand and three terminal CO groups. The Tc–C_{CO} distance is consistently close to 1.90 Å, with an almost linear Tc–C–O moiety (mean angle of 177°) and right angles for C_{CO}–Tc–C_{CO}. The Tc–C_{Cp} bond distances fall in the range 2.275–2.350 Å, while the distance between the technetium atom and the centroid of the ring averages 1.94 Å.

By irradiating $[Tc(CO)_3(\eta^5\text{-}Me_5Cp')]$ in cyclohexane with a low-pressure mercury lamp, the binuclear $\{(\mu\text{-}CO)_3[Tc(\eta^5\text{-}Me_5Cp')]_2\}$ complex [239] is obtained, along with other polynuclear species. The geometry of the dimeric complex resembles that of the parent compound, with three bridging CO groups joining the two metal centers (Tc···Tc distance of 2.413(3) Å), whose coordination is completed by two terminal η^5-Cp ligands.

Oxidation of the tricarbonyl complex $[Tc(CO)_3(\eta^5\text{-}Me_5Cp')]$ with 30% hydrogen peroxide in benzene at room temperature produces the polymeric $\{(\mu\text{-}O)3[Tc(\eta^5\text{-}Me_5Cp)]_2\}_n$ species [240]. The two Tc atoms are bridged by three μ-oxo ligands, and the coordination of the metals is completed by a η^5-Cp ring. These Cp rings are, however, concomitantly a component of neighboring units. The planes of the Cp rings and of the oxo-bridged ligands are crystallographically-imposed parallel to one another, giving a sort of "poly-decker" structure.

The treatment of Tc_2O_7 with tetramethyltin at 10 °C yields the methyltrioxotechnetium(VII) species, which, above 20 °C, leads to the formation of a large number of reduced products, among which is the paramagnetic sublimable Tc(VI) complex $[Tc_2O_2(\mu\text{-}O)_2Me_4]$ [241]. The coordination sphere about the Tc atoms is best described as distorted square-pyramidal with a Tc···Tc distance of 2.562(1) Å. This value supports the assumption of a single bond, irrespective of the paramagnetism of the complex. The oxo group occupies the apex of the pyramid, with the basal sites filled with two bridging oxygens and two terminal methyl groups.

$TcCl_4$ reacts with KCp in THF to give the diamagnetic, air-stable $[TcCl(\eta^5\text{-}Cp)_2]$ complex (Fig. 35) [242]. The structure shows a formal coordination number three with the two η^5-Cp rings flanking the Tc-Cl moiety. The short ring–metal distance (1.877(5) Å), as well as the Tc–Cl length of 2.450(3) Å, are indicative of high covalent bonds. Reaction of $[TcCl(\eta^5\text{-}Cp)_2]$ with further KCp gives the similar complex $[Tc(\eta^5\text{-}Cp)_2(\eta^1\text{-}Cp)]$ [243] a derivative with a formal replacement of the halide by a σ-bonded Cp. The complex shows a π-ring–metal distance of 1.781(2) and 1.883(1) Å, the third asymmetrically bonded Cp being responsible for this difference. The dihedral angle formed between the η^5-bonded Cp planes is 169.4(5)°, a value greater than that exhibited by the corresponding planes in the parent compound (143.7(6)°).

Finally, the photolysis of $[Tc_2(CO)_{10}]$ in the presence of butadiene at −20 °C in pentane gives a mixture of products, from which the only characterizable

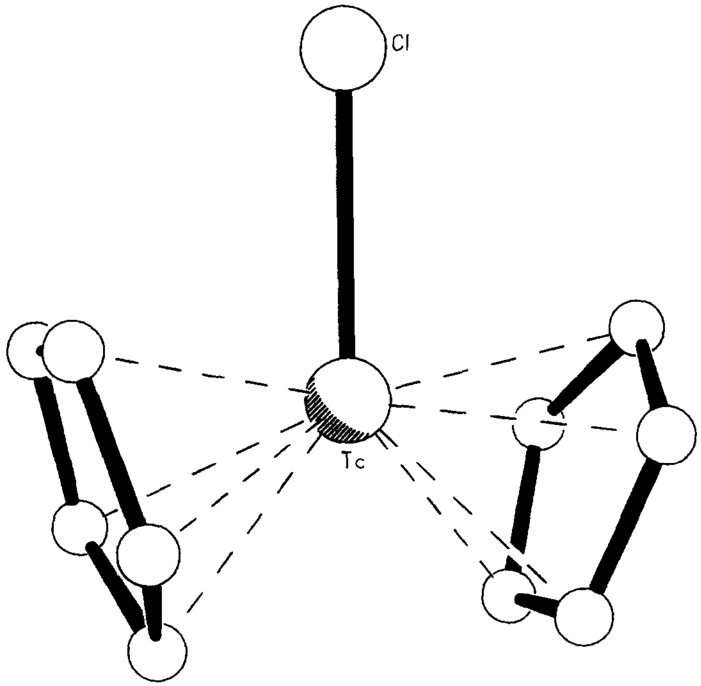

Fig. 35. $[TcCl(\eta^5\text{-}Cp)_2]$.

complex is the binuclear $[Tc_2(\mu\text{-bdn})(CO)_8]$ [244] with the *trans*-butadiene ligand bridging the two technetium centers (Tc···Tc separation of 3.117(1) Å).

11. HALIDE-BASED TECHNETIUM COMPLEXES

11.1. Pure halide species

This section briefly describes the structure of nine complexes containing only halide ligands in the coordination sphere. Moving from Tc compounds of low molecular complexity, as is the case of $[TcCl6]^{2-}$ in $(n\text{-}Bu_4N)_2[TcCl_6]$ [245] and $[NH_2(CH_3)_2]^+[DMAAH]^+[TcCl_6]\cdot PPh_3O$ [206] or $[TcBr_6]^{2-}$ present in $(H_3O)_2[TcBr_6]$ [246], towards the dimeric species $[Tc_2Cl_6]^{2-}$ present in $K_2[Tc_2Cl_6]$ [247,248], we get into the crowded hexanuclear clusters $[Tc_6Cl_6(\mu\text{-}Cl)_6]^{2-}$ [249,250], $[Tc_6Cl_{14}]^{3-}$ [249], $[Tc_6Br_6(\mu_3\text{-}Br)_5]^{2-}$ [246] and to the octanuclear clusters $[Tc_8Br_4(\mu\text{-}Br)_8]$ [246] and $\{[Tc_8Br_2I_2(\mu\text{-}Br)_4(\mu\text{-}I)_4]I_2\}^{2-}$ [251]. The last represents the first mixed-halide cluster to be structurally characterized.

The structure of $[n\text{-}Bu_4N]_2[TcCl_6]$ has heavy statistical disorder, with the octahedral dianion showing mean Tc–Cl distances of 2.3 Å. In $[H_3O]_2[TcBr_6]$ the octahedral anion is isostructural with a whole number of Tc(IV) halogenide complexes [159,252] and the Tc–Br distances average 2.506 Å. The structure of $K_2[Tc_2Cl_6]$, in which the approach of the two Tc atoms (2.044(1) Å) is very close, is described as containing infinite chains of $[Tc_2Cl_8]$ units sharing some Cl atoms in such a way that the formula can be more informatively written as $K_2[Tc_2Cl_4Cl_{4/2}]$. The uniquely short Tc–Tc distance is consistent with the assignment of a Tc≡Tc triple bond, based on a $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration. In $[Tc_6Cl_6(\mu\text{-}Cl)_6]^{2-}$ the structure of the technetium framework is a trigonal prism, six halogens are bonded to two Tc atoms forming bridges along the edges of the polyhedron, while the remaining six are extra terminal or non-bridging. The structure is of the type $(\mu_3\text{-}X)_6M_6Y_6$ (X = bridging anionic ligand; Y = anionic terminal ligand) using the usually adopted notation [253]. In contrast, the anion $[Tc_6Br_6(\mu_3\text{-}Br)_5]^{2-}$ represents an octahedral halogenide cluster, and in the octanuclear $[Tc_8Br_4(\mu\text{-}Br)_8]$ eight Tc atoms form a prism, the bases of the prism being rhombi with the short diagonal of the rhombi corresponding to the single Tc–Tc bonds (2.70 Å), the sides of the rhombi to the Tc–Tc bond with formal multiplicity about 0.5 (3.40 Å), and the side edges of the prism to formally quadruple ones (2.14 Å). Its structure-type is M_8-cube of the type $(\mu_3\text{-}X)_8M_8Y_4$.

11.2. Mixed-ligand species

Binuclear, asymmetric and dissymmetric μ-oxo technetium complexes, in which the two Tc atoms are in intimate electronic communication, are synthesized by reaction of $[TcOCl_4]^-$ in neat picoline. The two types of neutral complexes are isomers differing only in the arrangement of equatorial ligands, with the configurations being Cl_4 and $(4\text{-pic})_4$ for the dissymmetric case and $Cl_3(4\text{-pic})$ and $(4\text{-pic})_3Cl$ for the asymmetric one. The geometry of both compounds, $[(4\text{-pic})Cl_3(4\text{-pic})Tc\text{-}O\text{-}TcCl(4\text{-pic})_3Cl]$ (Fig. 36) [254] and $[Cl(4\text{-pic})_4Tc\text{-}O\text{-}Tc(4\text{-pic})Cl_4]$ [255], is essentially octahedral around each Tc atom, with the equatorial ligands on the opposite metal atoms being staggered relative to one another. The Tc–O–Tc moiety is almost linear with the μ-oxo bonds exhibiting a small *trans* influence on the axial ligands. These uncommon low-symmetry compounds possess a mixed valency (III/IV) for the two Tc nuclei. ESCA analyses for Tc 3d electrons reveal only a single peak for both Tc atoms, suggesting that the Tc ions differ by no more than a single oxidation state [254].

The reaction of $[TcOCl_4]^-$ with 4-picoline and phosphine-acceptors of different cone angles [256,257], such as PPh_3 or PMe_2Ph, results in Tc(III) complexes that vary for the phosphine coordination. The bulky PPh_3 acts only as reductant by extracting the oxo group from the starting material and does not participate in the coordination, giving the *mer*-$[TcCl_3(4\text{-pic})_3]$ complex [258]. Conversely, the less encumbering PMe_2Ph allows a crossing of the energy threshold for facile coordination to the *mer*-$[TcCl_3]$ moiety, affording the mixed *mer*-$[TcCl_3(4\text{-pic})(PMe_2Ph)_2]$ species [258].

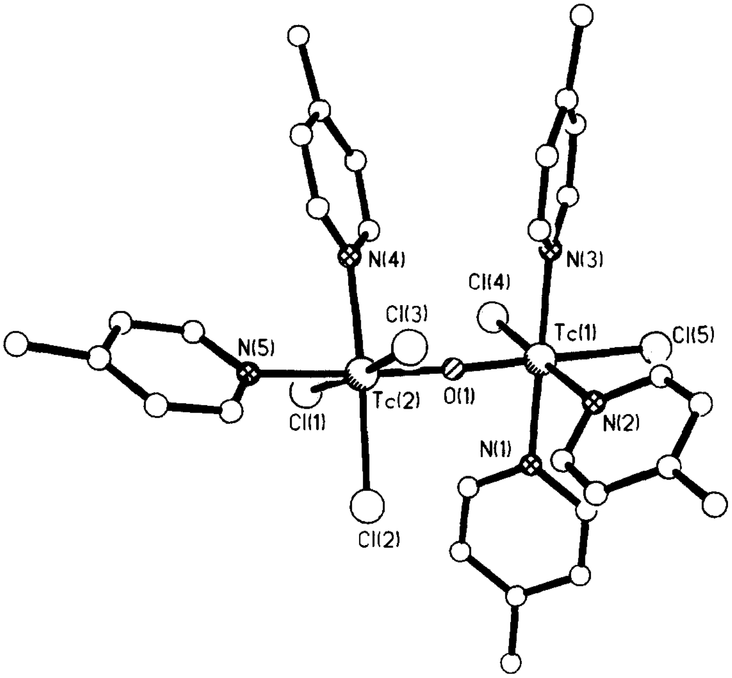

Fig. 36. [(4-pic)Cl_3(4-pic)Tc-O-TcCl(4-pic)$_3$Cl].

One of the rare examples of a Tc(V) complex without the Tc=O group is represented by $[TcCl_4(abt)]^-$ [259], which is obtained via ligand-exchange reaction by treatment of $[TcO(abt)_2]^-$ [56] with HCl in MeOH. Synthesis of the Tc-tetrahalo species presumably proceeds via protonation of the oxygen atom in $[TcO(abt)_2]^-$, which is subsequently lost as water. On the other hand, the starting material presents an abnormally long Tc=O bond (1.73 Å) which is consistent with the oxygen being susceptible to protic attack.

In the similar complex $[TcCl_4(pyrimt)]^-$ [260], distortion from octahedral coordination is ascribed to the small N–Tc–S bite angle (67.1(2)°) of the four-membered chelate ring, while in the dimeric Tc(III) species *cis*-$[Tc_2Cl_4(ac)_2(DMAA)_2]$ [261] the complex retains the octahedral geometry of the parent aquo-compound.

12. MISCELLANEOUS

Despite the great emphasis concerning cationic Tc(I)-isonitrile species due to the utilization of the [^{99m}Tc-MIBI] (Cardiotec®) derivative as a myocardial imaging agent [207], only a brief report regarding structural details on this class of compounds was communicated in 1985 [262]. The crystal structure of the prototype complex $[Tc(CN\text{-}t\text{-}bu)_6]^+$ (Fig. 37) shows the metal octahedrally coordinated by six equivalent isocyanide ligands. The easy synthesis of the $[Tc(CNR)_6]^+$ monocations makes them potentially useful starting materials for the preparation of low-oxidation-state technetium compounds, but its inherent kinetic inertness diminishes this potential somewhat. In fact, only a few examples dealing with the reactivity of $[Tc(CNR)_6]^+$-type complexes are so far available [222,263,264], and only the crystal structure of $[Tc(CN\text{-}t\text{-}bu)_4(bpy)]^+$ [265] has been published.

A re-investigation on the hexakis(isothiocyanato)technetate anion has been performed after the first determination published in 1980 [266,267]. The analysis of the crystal structure shows the Tc(IV) atom situated on a site of 4/*m* symmetry in an octahedral environment. The $[Tc(NCS)_6]^{2-}$ complex [268] undoubtedly shows the isothiocyanate groups being N-coordinated with a mean Tc–N single bond of 2.00 Å. Such a distance is marginally less than the Tc^{III}–N length (mean, 2.045 Å) exhibited by the $[Tc(NCS)_6]^{3-}$ anion [267].

The formation of bis(*μ*-oxo)dimers in the oxidation state 4+ is a dominant theme in "Tc-aminocarboxylate" chemistry. Two previously reported structures are concerned with polydentate EDTA and NTA ligands [162,163] and consist of neutral bis(*μ*-oxo)dimers. By treating an aqueous solution of the labile Tc(V) complex $[TcO(eg)(TCTA)]^{2-}$ with $NaBH_4$, the originally turquoise solution rapidly becomes

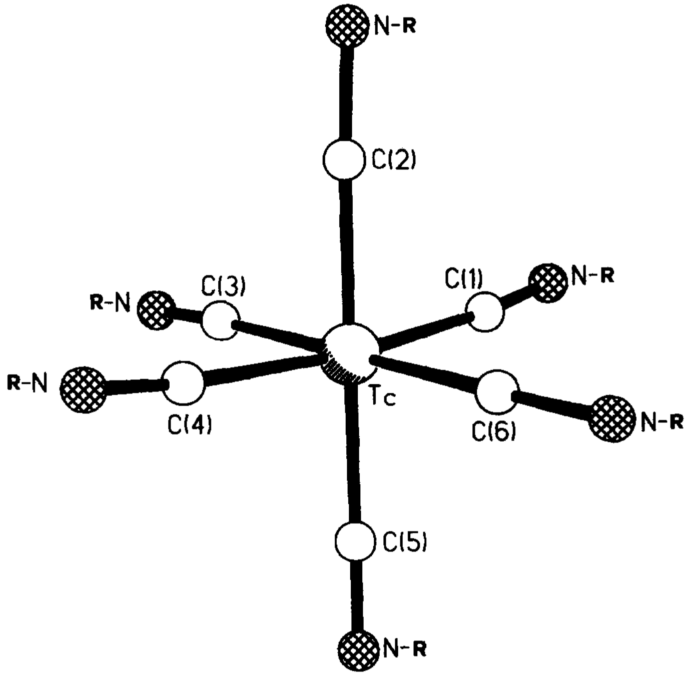

Fig. 37. $[Tc(CN\text{-}R)_6]^+$ (R = *t*-bu).

deep gold. The gold-coloured product is oxidized to the deep-blue Tc(III/IV) dimer, which can be crystallized as $Ba_2[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)](ClO_4)\cdot 9H_2O$ (Fig. 38) [269]. This complex further undergoes a reversible one-electron oxidation with potassium persulfate to form the already known Tc(IV/IV) dimer. The short Tc–Tc distance of 2.402(1) Å indicates the presence of a metal–metal multiple bond [270]. Such a distance is longer than that exhibited by the two Tc(IV/IV) bis(μ-oxo) dimers by 0.07 and 0.04 Å for the EDTA and NTA derivatives, respectively.

13. ADDENDUM

Thirty-three crystal structures have recently appeared in the literature and are briefly summarized in this section.

The $TcO(N_2S_2)$ moiety is still the subject of investigations, and four more complexes have been prepared by varying the ligand framework in $[TcO(DBDS)]^-$ [271], [TcO(BP-BAT-TE)] [272], [TcO(BAT-TE)] [272] and $[TcO(Et_2ddd)]^-$ [273]. The third complex is the neutral analog of the already reported cationic species [39] (Section 3.2), while the last compound represents a model for the synthesis of a new renal ^{99m}Tc agent.

The anionic $[TcO(dab)_2]^-$ complex [274] contains the $TcON_4$ inner core in

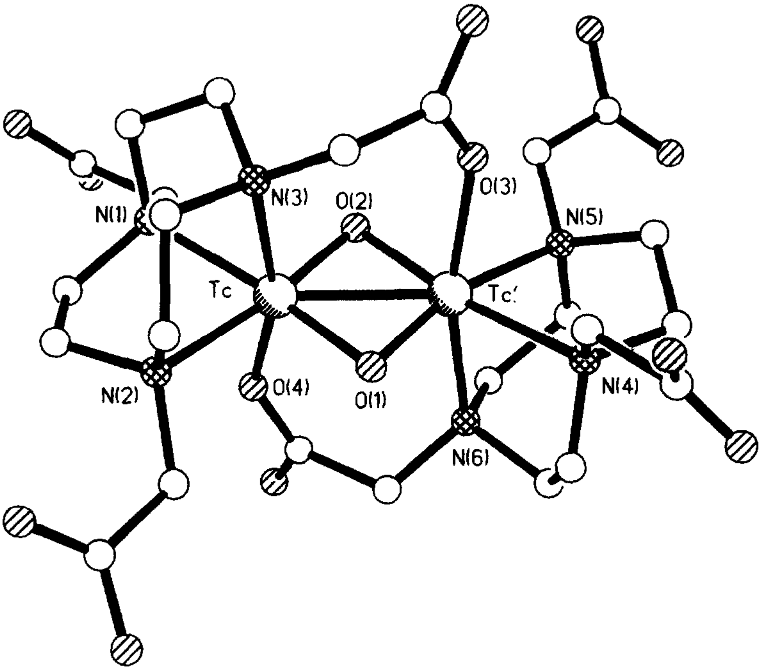

Fig. 38. $[(TCTA)Tc(\mu\text{-}O)_2Tc(TCTA)]^{3-}$.

the usual square-pyramidal configuration. When the reaction is performed in MeOH without a reducing agent, the unique cationic and trigonal prismatic Tc(VII) species $[Tc(dab)_3]^+$ (Fig. 39) [274] is obtained.

Three Tc-nitrido complexes join the growing class of multiple Tc–nitrogen-bonded species: two are dimeric compounds with a $Tc(\mu\text{-}O)_2Tc$ core, *i.e.* $\{(\mu\text{-}O)_2[TcN(Et_2dtc)]_2\}$ [275] and $\{(\mu\text{-}O)_2[TcN(pydtc)]_2\}$ [275], while the third is a monomeric mixed-ligand complex with the technetium atom having a square-pyramidal geometry, $[TcN(Et_2dtc)(dtco)]$ [275].

The third example of a Tc(V) phenylimido derivative is shown by $[TcCl_3(NPh)(dppe)]$ [276], in which the chloride ligands adopt a facial arrangement and the Tc–N–C angle (175.7°) is indicative of linear coordination for the phenylimido unit. The crystal structure of the previously communicated $[TcCl(NNPh)(dppe)_2]^+$ complex [97,277] has been fully reported, together with the neutral five-coordinate $[TcCl(NNC_6H_4\text{-}Cl)_2(PPh_3)_2]$ [277] derivative.

The following five structures are further representatives of Tc complexes whose chemistry has been revisited: $[TcO(bt)(SPhsal)]$ [278], *cis*-$[Tc(tdt)(dmpe)_2]^+$ [279], $[Tc(SCP)_2(dmpe)_2]^{3+}$ [280], $[Tc_2(\mu\text{-}ac)_4]^{2+}$ [281] and $[TcOBr_4]^-$ [282].

In the three dinuclear Tc(III) μ-oxo complexes, $\{(\mu\text{-}O)[TcX(bpy)_2]_2\}^{2+}$ (X=

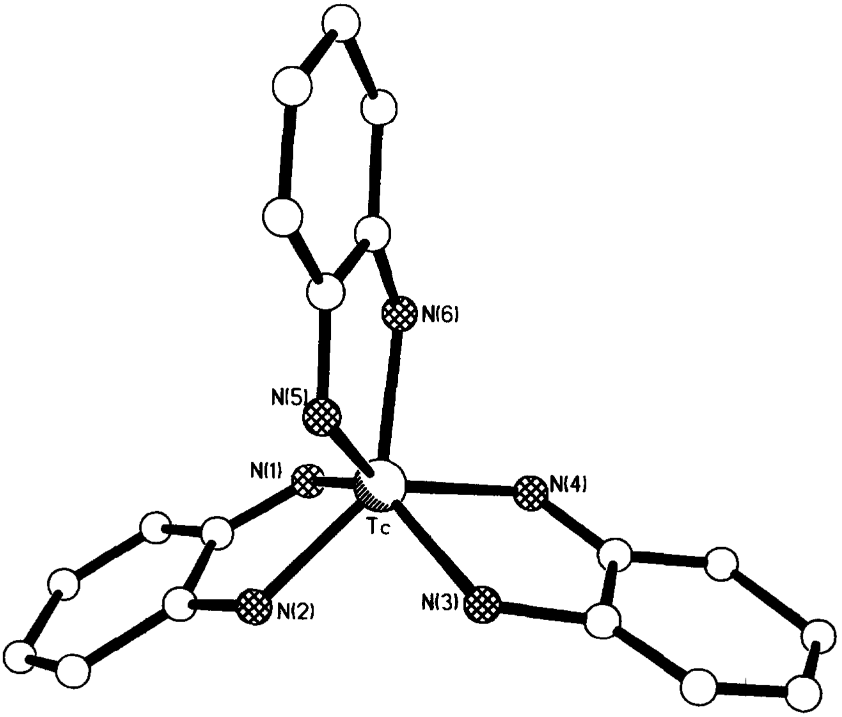

Fig. 39. $[Tc(dab)_3]^+$.

Cl,Br) and $\{(\mu\text{-O})[TcCl(phen)_2]_2\}^{2+}$ [283], steric factors cause the position *cis* rather than *trans* to the μ-oxo to be occupied by the halide ligand.

Novel technetium chemistry is instead exhibited by the first homoleptic thioether Tc complex $[Tc(9S3)]^{2+}$ [284], obtained by reduction of pertechnetate with the crown thioether in refluxing MeCN in the presence of tin chloride. Two 9S3 ligands coordinate facially in a tridentate fashion with mean Tc–S bond value of 2.38 Å. Two mixed halide-thioether Tc(V) complexes, namely $(\mu\text{-O})[TcOCl_2(dtdo)]_2$ and $[TcOCl_2(hdto)]$ [285], confirm the growing interest in Tc-thioether chemistry where the versatility of such a ligand is able to stabilize several Tc oxidation states.

Two interesting examples of air-stable technetium organometallic complexes are shown by $[Tc(NPh)_3(\eta^1\text{-Cp})]$ [286] and $[Tc_2(NAr)_6]$ [287]. The former complex exhibits only minor deviations from tetrahedral geometry, with the three Tc–N–C angles deviating remarkably from linearity (range 157.3–166.2°) and the Cp ring unambiguously η^1-coordinated. The dimer represents the first homoleptic Tc-imido complex which adopts an unprecedented "ethane-like" structure.

In the neutral complexes $[Tc(HBpz_3)(CO)_3]$ and $[Tc(HBMe_2pz_3)(CO)_3]$ [288], closely related to the already reported $[Tc(HBpz_3)(PPh_3)(CO)_2]$ derivative [209], the Tc(I) ion is facially coordinated by the three nitrogen atoms of the pyrazolylborate ligands, which represent a further example of a chelate stabilizing technetium in several oxidation states.

Unusual structures are represented by TcO_2F_3 [289], in which the open chains of fluorine-bridged TcO_2F_4 units are *trans* to the oxygens, and by the $[Tc_6X_8]$ (X = chalcogenide) clusters of ternary Tc chalcogenides [290]. In the polynuclear species, the six Tc atoms form nearly regular octahedra with the eight chalcogenide atoms placed over the octahedral faces.

Four complexes containing polydentate functionalized phosphines end the survey. $[TcNCl_2(PNP)]$ [291] and $[Tc(PS')_2(OPS')]$ (Fig. 40) [292] exhibit trigonal bipyramidal geometry. The latter structure shows three thiolate groups of the bidentate ligand on the basal plane and two π-acid phosphines in the axial positions, the third phosphine being oxidized out of the coordination sphere. Two Tc(V)-nitrido complexes, the square-pyramidal $[TcNCl_2(POOP)]$ [291] and the octahedral $[TcNCl(PNH_2)_2]^+$ [293] confirm the capability of the Tc-nitrido moiety to coordinate soft rather than hard donors.

14. CONCLUSIONS

This review reports on structural data of technetium complexes appearing in the literature between 1986 and 1992. It describes over 240 Tc compounds for which a single-crystal X-ray structure determination has been performed.

In Table 1, technetium structures are summarized as a function of oxidation states, coordination number and charge. The statistics include all Tc X-ray determinations since the first structurally characterized complex in 1965, with the exception

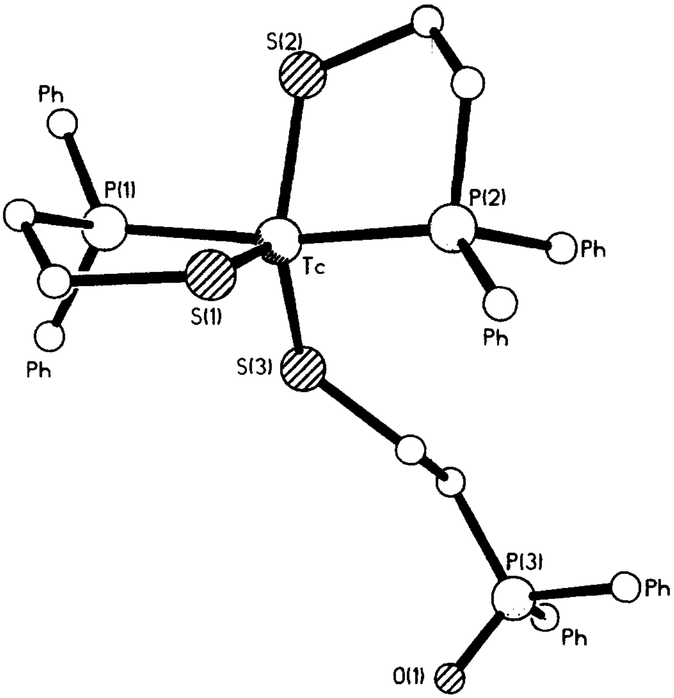

Fig. 40. $[Tc(PS')_2(OPS')]$.

TABLE 1

Coordination number and charge of Tc complexes vs. oxidation state. Numbers refer to Tc-complex entries

	Oxidation state								
	-I	0	I	II	III	IV	V	VI	VII
Coordination number									
4								1	2
5	1				7		78	6	3
6		1	20	17	56	19	57	5	2
7			1	1	7				1
8							1		
Charge									
−2					1	4	8	2	1
−1				3	1	6	31	4	2
0	1	1	15	10	43	7	70	5	4
+1			5	2	19	1	25		1
+2			1	3	1		2		

of polynuclear, mixed-valent and organometallic compounds, along with polycharged complexes.

As evidenced by Table 1, oxidation states V and III are by far the most investigated ones, covering one-half and one-fourth of the total number, respectively. Moreover, as expected for an element of Group 7, on the basis of spin-paired configurations, odd oxidation states are greatly favoured (81.8%) with respect to even ones. Further classic trends for transition metals are confirmed by the higher coordination number exhibited by complexes in lower oxidation states, and by the overall charge, which privileges anionic derivatives for electron-deficient metal configurations and cationic species for electron-rich ones.

Of Tc complexes, 54.5% are neutral, with a roughly symmetric entry for negatively and positively charged compounds. In particular, monoanionic and monocationic molecules reach 17.1 and 19.8%, respectively. Among Tc(III) complexes it is interesting to note that monocationic compounds represent almost one-third of the entries.

Figure 41 depicts the ligating atom species in Tc compounds as a function of the oxidation state. The most frequent coordinated atom is nitrogen (28.3%), followed by oxygen (21.3%), sulfur (18.3%), phosphorus (12.3%) and chlorine (12.2%). Grouping the donor atoms, pnictides sum to 42%, chalcogenides to 40%, and halogenides to 14.4%. Nitrogen also represents the most versatile donor atom, largely irrespective of the oxidation state; so do halides, which are homogeneously distributed among all oxidation states. Conversely, oxygen generally prefers high oxidation

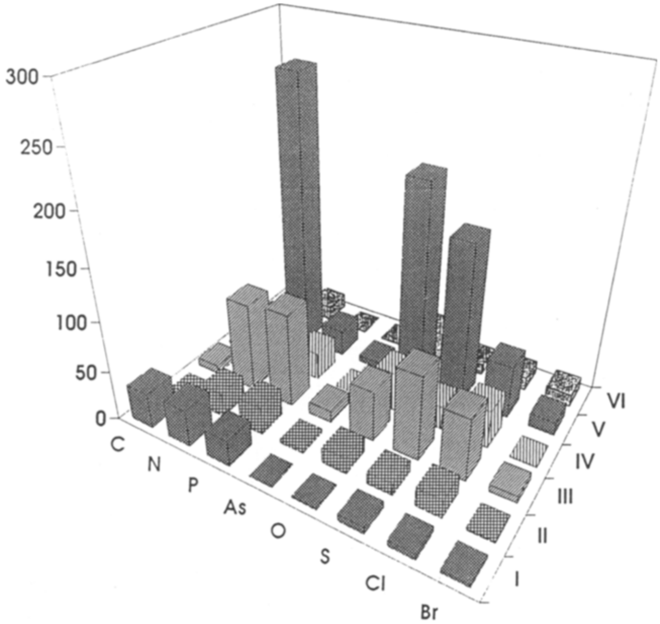

Fig. 41. Distribution of coordinating atoms *vs.* oxidation state in Tc complexes.

states (higher than IV), while sulfur contributes to stabilizing intermediate oxidation states (III–V) and phosphorus describes a gaussian distribution centered on oxidation state III.

Table 2 lists technetium–donor bond lengths as a function of the oxidation state. In this case also, all technetium complexes (from 1965) are listed, with the exceptions above detailed for Table 1, along with Tc complexes of Section 5, for which a well-defined oxidation state is often not available.

Careful analysis of Table 2 reveals a wide range in several Tc–L bond lengths. For example, considering only the Tc(V) oxidation state, the interval width (in parentheses) exhibited by $Tc–N_{anionic}$ (0.49 Å), $Tc–N_{neutral}$ (0.28 Å), $Tc–O_{anionic}$ (0.26 Å), $Tc–O_{neutral}$ (0.37 Å) and Tc–Cl (0.30 Å) distances does not allow an accurate description of the metal–donor interaction. In these cases the long-end values account for the structural *trans* effect operated by the Tc-oxo and Tc-nitrido moieties onto *trans*-coordinated atoms, while steric requirements of polydentate ligands may be responsible for the remarkable deviations from the mean values. Most noteworthy, sulphur has never been found *trans* to Tc-oxo and Tc-nitrido moieties and, consequently, the interval for the Tc–S distances (0.24 Å) is ascribed primarily to the chemical variety of the coordinated sulphur (thiolato, thiocarbamato or thioether).

Nevertheless, some "standard" bond lengths, irrespective of both Tc oxidation state and complex-coordination number, can be obtained: Tc≡N, 1.61 Å; Tc≡O, 1.66 Å (1.74 Å in *trans*-$[TcO_2]^+$ and 1.68 Å in $[Tc_2O_3]^{4+}$); Tc–NO, 1.73 Å; Tc–NS, 1.75 Å. In contrast, the Tc–O mean distance in linear μ-oxo moiety appears to be sensitive to the metal oxidation state, being 1.82 and 1.91 Å for Tc(III) and Tc(V) complexes, respectively.

Owing to the versatility of nitrogen donors, particular attention has been focused on the Tc–N interaction. Among the $Tc–N_{sp}{}^2$ bonds, three different mean distances can be drawn, which are dependent on the nature of the nitrogen donor:

i. $Tc–N_{py}$, 2.15 Å (such a value reaches 2.39 Å when the structural *trans*-effect is operating in Tc(V) species);

ii. $Tc–N_{imino}$, 2.085 Å;

iii. $Tc–N_{aminato}$, 1.95 Å.

The $Tc–N_{sp3}$ distances show a mean value of 2.16 Å for $Tc(V)^-$ and 2.22 Å for Tc(I) species, in accordance with the pure σ nature of the Tc–N bond.

Conversely, Tc–E interactions (E = P,As) appear to be dominated by π-back-bonding from Tc to E [183], which causes a shortening of the Tc–E bond with decreasing oxidation state. However, there are complications from Table 2 for E = P, since the related complexes may differ for geometry, coordination number and/or charge, whereas π-back-donation becomes evident for E = As, with Tc–As mean distances 2.47, 2.51 and 2.56 Å for Tc(II), Tc(III) and Tc(V), respectively. In contrast, as expected for a ligand that binds primarily through ionic interactions, the Tc–X (X = Cl,Br) mean distance shortens with increasing metal oxidation state.

TABLE 2

Summary data for Tc–L bond lengths

Tc–L	Oxidation state						
	I	II	III	IV	V	VI	VII
Tc–C	1.82–2.14		1.86–2.08		2.09–2.12		2.16
Tc–$N_{neutral}$	2.10–2.25[a]	2.00–2.12[b]	2.03–2.25	2.09–2.15	2.00–2.49		
Tc–$N_{anionic}$			1.95–2.19	2.00–2.01	1.88–2.16		1.98–2.03
Tc–NO	1.73–1.74	1.69–1.74	1.77				
Tc–NS	1.73–1.78	1.75	1.70–1.80				
Tc≡N					1.59–1.63[c]	1.58–1.65	1.61–1.69
Tc–P	2.36–2.47	2.38–2.46	2.27–2.52	2.47–2.57	2.40–2.52		
Tc–As		2.47	2.49–2.52		2.54–2.58		
Tc–$O_{neutral}$		2.10–2.13	1.99–2.11		2.32–2.69	2.44	
Tc–$O_{anionic}$	2.16	2.06–2.14	1.97–2.11[d]	1.94–2.10	1.89–2.15	1.95–2.41	1.93–2.47[e]
Tc≡O					1.59–1.70[f]		1.60–1.72
Tc=O$[TcO_2]^+$					1.71–1.75		1.64 (*cis*)
Tc=O$[Tc_2O_3]^{4+}$					1.66–1.73		
Tc–O–Tc			1.81–1.87	1.91–1.92	1.90–1.92	1.84–1.95	
Tc–S	2.41–2.54	2.37–2.42	2.23–2.54	2.29–2.43	2.22–2.46	2.43–2.46	2.37–2.39
Tc–Se					2.46–2.53		
Tc–Cl	2.39–2.50	2.29–2.44	2.29–2.48	2.31–2.41	2.31–2.61[g]	2.34–2.37[h]	2.35
Tc–Br	2.54–2.58	2.56	2.44–2.59	2.36–2.50	2.46-2.57	2.39–2.52	

[a] Tc–N (2.05 Å) in $[TcH(N_2)(dppe)_2]$ [294).

[b] Tc–N (2.93 Å in $[Tc(tren\text{–}py_3)]^{2+}$ [153].

[c] Tc≡N (1.54 Å) in $[TcN(Et_2dtc)(dtco)]^-$ [275].

[d] Tc–O (2.34 Å) in *cis*–$[Tc_2Cl_4(ac)_2(DMAA)_2]$ [261].

[e] Tc–O (1.72 Å) in $[Me_3SnOTcO_3)]_n$ [157].

[f] Tc=O (1.73 Å) in $[TcO(abt)_2]^-$ [56].

[g] Tc–Cl (2.73 Å) in $[TcNCl(en)_2]^+$ [82].

[h] Tc–Cl (2.74 Å) in $[TcNCl_5]^{2-}$ [87].

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APPENDIX: ACRONYMS AND ABBREVIATIONS

abt	2-aminobenzenethiolate (2-)
ac	acetate (1-)
acac	acetylacetonate (1-)
aeca	*N*-(2-aminoethyl)carbamic acid
14-ane-N_2S_2	1,4-dithia-8,11-diazacyclotetradecane(2-)
AO	3-amino-3-methyl-2-butanone oxime
apa	*N*,*N'*-3-azapentane-1,5-diylbis(3-(1-iminoethyl)-6-methyl-2*H*-pyran-2,4-(3H)-dionate(3-)
$AsPh_3$	triphenylarsine
BATO	boronic acid adducts of technetium dioximes
BAT-TE	ethane-1,2-bis(*N*-1-amino-3-ethylbutyl-3-thiolate) (3-)
BDI	butane-2,3-dione imine-oxime
bdn	butadiene
bdt	benzenedithiolate (2-)
bmepa	2-benzylmercaptoethyl-bis(2-pyridylmethyl)amine
BPA-BAT	*N'*-benzylpiperazinyl-bis-aminothiolate (3-)
BP-BAT-TE	biphenyl-2,2'-bis (*N*-1-amino-2-methylpropane-2-thiolate) (3-)
bpy	2,2'-bipyridine
bt	benzenethiolate (1-)
bt-Cl	*p*-chlorobenzenethiolate (1-)
n-Bu_4N	tetra-butylammonium
4-*t*-butpy	4-tert-butylpyridine
BX	*n*-butylxanthate (1-)
$C_6H_5CS_2$	dithiobenzoate (1-)
cat	catecholate (2-)
cat-Cl_4	tetrachlorocatecholate (2-)
cat-NO_2	4-nitro-1,2-catecholate (2-)
CDO	cyclohexanedione dioxime
CN-i-pr	isopropylisonitrile
CN-*t*-bu	*tert*-butylisonitrile
CNR	alkylisonitrile
Cp	cyclopentadienide (1-)
18-crown-6	(1,4,7,10,13,16-hexaoxacyclooctadecane)

cyclam	1,4,8,11-tetraaza-cyclotetradecane
dab	diaminobenzene (2-)
DBcat	3,5-di-*tert*-butylcatecholate (2-)
DBDS	*N*,*N*′-bis(mercaptoacetyl)butane-1,4-diaminate (4-)
depe	1,2-bis(diethylphosphino)ethane
diars	*o*-phenylenebis(dimethylarsine)
dien	diethylenetriamine
DMAA	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide
DMG	dimethylglyoxime
dmpe	1,2-bis(dimethylphosphino)ethane
DMSO	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dtco	dithiocarbonate (1-)
dtdo	5,8-dithiadodecane
dto	dithiooxalate (2-)
ecbap	[*N*-(2-ethoxycarbonyl-3-oxo-but-1-en(1)yl)-2-aminophenolate] (2-)
ECD	*N*,*N*′-1,2-ethylenediyl bis-L- ,diethyl ester (3-)
edt	ethanedithiolate (2-)
e=dt	ethenedithiolate (2-)
EDTAH$_2$	ethylenediaminetetraacetate (2-)
eg	ethaneglycolate (2-)
emaH$_2$	*N*,*N*′-ethylenebis(2-mercaptoacetamido) (2-)
ema-morph	*N*-[2-(2-(thioacetyl)amino)ethyl]-2-[(2-morpholino)ethylthio]acetamido (3-)
en	ethylenediamine
En(AO)$_2$	3,3,8,8-tetramethyl-4,7-diazadecane-2,9-dione dioximate (3-)
epa	*N*,*N*′-ethylenebis(2-phenoxyacetamide) (4-)
Et$_4$daodt	1,1′,8,8′-tetraethyl-3,6-diazaoctan-1,8-dithiolate (2-)
Et$_2$ddd	diethyl-2,9-dithio-3,8-dioxo-4,7-diazadecanedioate (4-)
Et$_2$dtc	diethyldithiocarbamate (1-)
EtOH	ethanol
Et$_2$tcb	*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinate (1-)
FDA	Food and Drugs Administration
glusal	*N*-salicylideneglucosaminate (2-)
HBMe$_2$pz$_3$	hydridotris(3,5-dimethylpyrazolyl)borate (1-)
HBpz$_3$	hydridotris(pyrazolyl)borate (1-)
hbt	2-(2-hydroxyphenyl)benzothiazole (1-)
hbtH	2-(2-hydroxyphenyl)benzothiazoline
hdto	1,8-dihydroxy-3,6-dithiaoctane (1-)

HM-PAO	hexamethylpropyleneamineoxime (3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione) dioxime
hph	hydrazidophthalazino (1-)
HNNC(Ph)S	thiobenzoylhydrazine
ind	indole (1-)
[I-131]OIH	iodine-131 hippurate
MAG_2	bis-mercaptoacetylglycine (4-)
MAG_3	tris-mercaptoacetylglycine (4-)
MAG_3-OMe	tris-mercaptoethylglycine mono methyl ester (4-)
map	2,3-bis(mercaptoacetamido)propanoato (4-)
MeCN	acetonitrile
Me_5Cp'	pentamethylcyclopentadienide (1-)
Me_6daodt	1,1′,8,8′-tetramethyl-5,5′-dimethyl-3,6-diazaoctan-1,8-dithiolate(3-)
Me_4daodt	1,1′,8,8′-tetramethyl-3,6-diazaoctan-1,8-dithiolate (2-)
Me_2dtc	dimethyldithiocarbamate (1-)
Me_4EtCp'	tetramethylethylcyclopentadienide (1-)
MeOH	methanol
meph	*o*-mercaptophenolate (2-)
Mequin	2-methyl-8-quinolinolate (1-)
quinaph	1-(8′-quinolyniminomethyl)-2-naphtholate (1-)
$Me_2Pn(AO\text{-}Me)_2$	3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate (3-)
Me_4pnNMe_3Cp'	tetramethyl(propyltrimethylammonium) cyclopentadienide
Metu	*N*-methylthiourea
Me_2tu	*N*,*N*′-dimethylthiourea
Me_4tu	tetramethylthiourea
mns	1,1-dicyanoethene-2,2-diselenolate (2-)
mnt	1,1-dicyanoethene-dithiolate (2-)
MRP20	*N*-[2-(1H-pyrrolylmethyl)]-*N*′-[4-(pentene-3-one-2)] ethane-1,2-diamine (3-)
MRP40	*N*-(2-mercaptoacetyl)-*N*′-[4-(pentene-3-one-2)] ethane-1,2-diamine (3-)
mt	methanethiolate (1-)
mtbm	monothiobenzylmethanate (1-)
NAr	2,6-diisopropylphenylimido (2-)
$NaBH_4$	sodium borohydride
NaOMe	sodium methoxide
[N-Et]Me_4daodt	1,1′,8,8′-tetramethyl-3-ethyl-3,6-diazaoctan-1 ,8-dithiolate (3-)
$[N\text{-}Et_2]_2Me_4$daodt	1,1′,8,8′-tetramethyl-3,6-diethyl-3,6-diazaoctan-1,8-dithiolate (2-)

[NMe]Me$_4$daodt	1,1′,8,8′-tetramethyl-3-methyl-3,6-diazaoctan-1,8-dithiolate (3-)
[N-Me$_2$]$_2$daodt	3,6-dimethyl-3,6-diazaoctan-1,8-dithiolate (2-)
NNPh	phenyldiazenido (2-)
NNC$_6$H$_4$Br	*p*-bromophenyl diazenido (1+)
NNC$_6$H$_4$Cl	*p*-chlorophenyl diazenido (1+)
NNPh$_2$	1,1-diphenylhydrazido (2-)
NPh	phenylimido (2-)
Ntol	tolylimido (2-)
NTA	nitrilotriacetate (2-)
OMe	methanolate (1-)
(4-OMesal)$_3$TAME	tris(4-methoxysalicylideneiminatemethyl)ethane (3-)
OPh$_2$bu	*N*,*N*′-bis(2-hydroxybenzyl)-1,3-diaminobutane (2-)
OPh$_2$Me$_2$pn	*N*,*N*′-bis(2-hydroxybenzyl)-2,2-dimethyl-1,3-diaminopropane (2-)
OPh$_2$pn	*N*,*N*′-bis(2-hydroxybenzyl)-1,3-diaminopropane (2-)
OPhsal	*N*-(2-oxidophenyl)salycilideneiminate (2-)
OPMe$_2$Ph	dimethylphenylphosphinoxide
OPPh$_3$	triphenylphosphineoxide
OPS′	(2-diphenylphosphino)ethanethiolate oxide (1-)
OU-BAT	1,1′,9,9′-tetramethyl-4,5-phenyl-3,7-diazanonan-1,9-dithiolate (oxidized form) (3-)
ox	oxalate (2-)
PCHO	(2-diphenylphosphino)benzaldehyde
PCOO	(2-diphenylphosphino)propionate (1-)
Pent(AO)$_2$	3,3,11,11-tetramethyl-4,10-diazatridecane-2,12-dione dioximate (1-)
PEt$_3$	triethylphosphine
PEtPh$_2$	ethyldiphenylphosphine
PEt$_2$Ph	diethylphenylphosphine
phen	1,10-phenanthroline
Phdtc	phenyldithiocarbamate (1-)
PhN=C(OEt)S	*O*-ethyl(phenylimino)thiocarbonate (1-)
PhNNCON$_2$HPh	(phenylazo)formic acid-2-phenylhydrazido (1+)
Phsal	*N*-phenylsalicylideneiminate (1-)
4-pic	4-picoline
PIC	*N*-(2-((2-mercaptoacetyl)amino)ethyl)-2-pyridinecarboxyamido (3-)
PIP	*N*,*N*′-bis(2-mercapto-2-methylpropyl)homopiperazine(2-)
piv	pivalate (1-)
PMe$_3$	trimethylphosphine
PMe$_2$Ph	dimethylphenylphosphine

P_2N_2	*N*,*N*′-bis[2-(diphenylphosphino)-phenyl] propane-1,3-diaminate (2-)
Pn(AO-Me)$_2$	3,9,-diethyl-4,8-diazaundecane-2,10-dione dioximate (3-)
Pn(AO)(AO-Me)	3,3,9,-trimethyl-4,8-diazaundecane-2,10-dione dioximate (3-)
PNH	(2-diphenylphosphino)benzeneaminate (1-)
PNP	bis(diphenylphosphinoethyl)propylamine
PO	(2-diphenylphosphino)phenolate (1-)
POOP	1,8-bis(diphenylphosphino)-3,6-dioxaoctane
P_2O_2	1,2-bis[(2-diphenylphosphino)-phenyl]ethaneglycolate (2-)
PPh_3	triphenylphosphine
i-prOH	isopropylic alcohol
(i-pr)$_2$NEt	ethyldiisopropylamine
PS	(2-diphenylphosphino)thiophenolate (1-)
PS′	(2-diphenylphosphino)ethanethiolate (1-)
PS_3	tris(o-marcaptophenyl)phosphinate (3-)
Ptol$_3$	tris(*m*-tolyl)phosphine
py	pyridine
pydtc	pyrrolidinildithiocarbamate (1-)
pyrimt	pyrimidine-2-thiolate (1-)
quin	8-quinolinolate (1-)
quinaph	1-(8′-quinolyniminomethyl)-2-naphtholate (1-)
9S3	1,4,7-trithiacyclononane
sacac$_2$en	*N*,*N*′-ethylenebis (acetylacetonethioiminate) (2-)
S_2CO	thiocarbonato (1-)
S_2COEt	ethylthiocarbonate ester (1-)
SCP	$^{-}SCH_2P+(CH_3)_2(CH_2)_2P(S)(CH_3)_2$
S_2CPh	dithiobenzoate (1-)
sal	salicylaldehydate (1-)
sal$_2$pn	*N*,*N*′-propane-1,3-bis(salycilideneiminate) (2-)
sal$_2$pnOH	*N*,*N*′-2-hydroxypropane-1,3-bis(salycilideneiminate) (2-)
salthz	*N*-(2-hydroxy-benzylidene-2-thiazolyliminate (1-)
sal$_2$tren	*N*,*N*′-3-azapentane-1,5-diylbis(salicylideneiminate) (3-)
SMe-OPhdtcz	S-methyl 3-(2′-hydroxyphenyl-methylene) dithiocarbazate (2-)/(1-)
SMe-Me$_2$dtcz	S-methyl 3,3′-dimethyl-methylenedithiocarbazate (1-)
SMe-Ondtcz	S-methyl 3-(2′-hydroxy-1-naphthylmethylene) dithiocarbazate (2-)
SPhsal	*N*-(2-marcaptophenyl)salycilideneiminate (2-)
tactdd	1,4,8,11-tetraazacyclotetradecane-5,7-dionate (2-)
tactdo	1,4,8,11-tetraazacyclotetradecane-5-onate (1-)
tad	1,5,8,12-tetraazadodecane
TAN	1,4,7-triazacyclononane

TCTA	1,4,7-triazacyclononane-*N*,*N*′,*N*′-triacetate (2-/3-)
tdt	toluenedithiolate (2-)
terpy	2,2′:6′,2″-terpyridine
tet	1,4,8,11-tetraazaundecane
THMT	tris-(oxymethyl)(trimethylammonio)methane (3-)
tibt	2,4,6-triisopropylbenzenethiolate (1-)
tmbt	2,3,5,6-tetramethylbenzenethiolate (1-)
TMG	1,1,3,3-tetramethylguanidine
tquin	8-quinolinethiolate (1-)
tren-py$_3$	tris[1-(2-pyridyl)-2-azabuten-4yl]amine
trimbt	2,4,6-trimethylbenzenethiolate (1-)
TTOD	5,8,11,14-tetrathiaoctadecane
tu	thiourea
U-BAT	1,1′,9,9′-tetramethyl-4;5-phenyl-3,7-diazanonan-1,9-dithiolate (3-)