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COORDINATION CHEMISTRY REVIEWS

2. Technetium 1992

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CONTENTS

INTRODUCTION

This survey covers the coordination chemistry of technetium that was published in 1992, with some additional papers from the tail end of 1991. Its format is similar to that of the 1990 survey [1]; a review of the 1991 literature has also recently been published [2]. The literature has been searched by using *Current Contents* and also by use of the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]. Although not fully comprehensive, this article does provide the reader with a significant coverage of papers published; I apologise to authors whose work has not been included. One aspect not covered directly is that of medical applications of technetium chemistry. However, new complexes which have been prepared and studied with the expectation of possible applications have been discussed. Organometallic complexes are outside the scope of this review; technetium(I) carbonyl complexes are included where they additionally involve inorganic ligands of interest to the coordination chemist.

Complexes have been arranged according to the formal oxidation state of the technetium centre. The dominant features of technetium(V) chemistry are those of oxo- and nitrido-species; for these complexes, the presence of the Tc=O or Tc≡N moiety has taken preference over the identity of the donor atoms is other ligands present for the purposes of categorization. Section 2.8 deals with dimetallic species.

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Caution: ^{99}Tc is a weak β^- emitter (E = 0.292 MeV, $t_{1/2}$ 2.12 x 10^5 yr).

A review article concerning transition metal nitrido complexes has been published [4] and includes significant details of technetium compounds.

2.1 *TECHNETIUM(VII)*

An overview of the structure of the technetium(VII) oxide Tc_2O_7 has been presented. This article focuses on the use X-ray diffraction results and infrared spectroscopic data to probe Tc_2O_7 in the solid, liquid and gas phases. Differences in structure as a function of state are discussed [5].

The extraction of technetium(VII) as a function of the concentration of HNO_3 at temperatures of 25, 50 and 70°C using the amine (^{n}octyl)$_3$N and the organophosphorus compound tributylphosphate has been assessed. Mechanistic aspects have also been discussed [6].

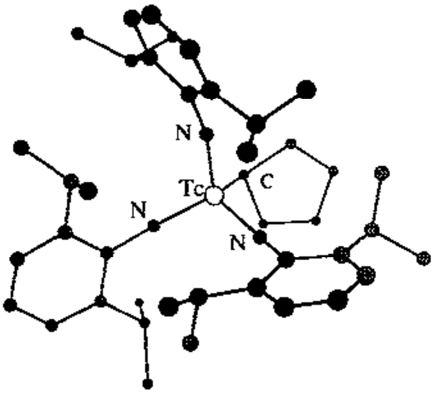
The anion $[TcO_4]^-$ appears in several crystallographic studies, for example in a structural investigation of {*N,N',N''*-tris(2-methyl-(2-mercaptopropyl)-1,4,7-triazacyclononane)}tin(IV) pertechnate with chloroform solvate [7] and in the complex $[Tc(\mu\text{-OAc})_4][TcO_4]_2$ [8] (see section 2.8); see also $[TcL_3][TcO_4]$ where H_2L = 1,2-diaminobenzene which is described below.

As part of a study of the synthesis in the vapour state and the mass spectrometric properties of some halides and oxyhalides (X = Cl or F) of technetium, the technetium(VII) complexes TcO_3Cl, TcO_3F, TcO_2Cl_3 and TcO_2F_3 have been reported [9].

The oxidation of $[TcOCl_2L]$ or the reaction of $[TcO_4]^-$ with L^- in acidified ethanol where L^- = hydrotris(1-pyrazolyl)borate generates the technetium(VII) complex $[TcO_3L]$. This has been characterized by elemental analysis, mass spectrometric data, and IR and NMR spectroscopies [10].

The reaction of $[TcI(NC_6H_3\text{-}2,6\text{-}^iPr_2)_3]$ with potassium cyclopentadienide, KCp, leads to the elimination of KI and the formation of $[Tc(\eta^1\text{-}Cp)(NC_6H_3\text{-}2,6\text{-}^iPr_2)_3]$ (**1**). The η^1-bonding mode of the organic ligand and the retention of tetrahedral coordination at the metal centre have been confirmed by the results of a crystallographic study. The Tc-N bond distances are 1.753(2), 1.761(2) and 1.748(2)Å. Use of an excess of KCp in the reaction leads to $K[Cp_2TcNC_6H_3\text{-}2,6\text{-}^iPr_2)_3$ instead of (**1**). In solution, the ^{1}H NMR spectrum of (**1**) exhibits just one signal in the Cp region (δ +6.70) even though the ligand is η^1-bonded; the resonance begins to broaden at 220 K [11]. The reaction of $[TcO_4]^-$ with 1,2-diaminobenzene (H_2L) in methanol yields the salt $[TcL_3][TcO_4]$. On the other hand, in the presence of a reducing agent (sodium dithionite) in an alkaline medium, the anionic complex $[Tc^VOL_2]$ forms. These complexes have been characterized by IR and electronic spectroscopies, conductivity measurements, elemental analysis and single crystal X-ray diffraction studies. In the IR spectrum, absorptions can be assigned to the mode ν(NH), consistent with the formulation of L^{2-}. The technetium(VII) cation $[TcL_3]^+$ has an octahedral structure in the solid state and Tc-N bond distances lie in the range 1.948(1) to 2.03(2)Å. The chelating ligands subtend angles at the metal centre (∠N-Tc-N) of 77.22(7), 75.5(7) and 75.7(6)° [12].

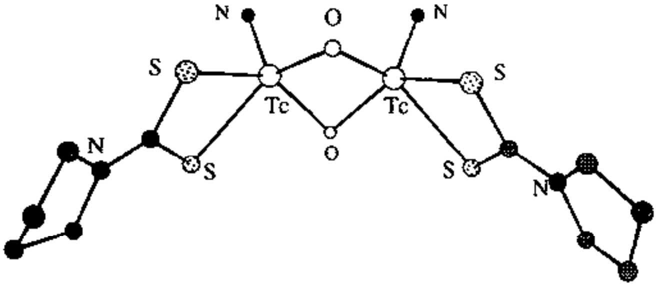
The technetium(VII) complexes $[TcLO_3]$ where $L^- = [CpCo\{P(O)(OR)_2\}_3]^-$ (R = Me, Et or Bu) will be described in section 2.3.1 along with a related technetium(V) species [21].



(1)

2.2 TECHNETIUM(VI)

The vapour state synthesis and the mass spectrometric properties of some halides and oxyhalides (X = Cl or F) of technetium have been described. Complexes studied include the technetium(VI) complexes $TcOF_4$ and TcO_2Cl_2 [9]. Following on from studies of the analogous chloro species, $[Tc^{VI}NBr_4]^-$ diamagnetically diluted with $[Tc^{V}OBr_4]^-$ has been the subject of a single crystal EPR spectroscopic and ^{15}N powder ENDOR investigations. The results are discussed in terms of the bonding in the system. The EPR spectra typify a $4d^1$ configuration and indicate that the single electron resides in an in-plane π-type orbital. The results of this new study have been compared with those obtained previously for the chloro complex [13]. A series of technetium(VI) complexes has been included in an EPR spectroscopic study in which the EPR parameters have been related to the structures of the anions concerned, namely $[TcNF_4]^-$, $[TcNCl_4]^-$, $[TcNCl_5]^{2-}$, $[TcNBrCl_3]^-$, $[TcNBr_2Cl_2]^-$, $[TcN(CN)Cl_3]^-$ and $[TcOCl_5]^-$ [14].



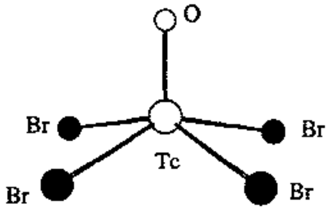
(2)

The ions $[TcNCl_5]^{2-}$ and $[\{TcN(H_2O)_3\}_2(\mu\text{-}O)_2]^{2+}$ have been used as precursors to the technetium(VI) oxo complexes $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$, $[\{TcN(S_2CNC_4H_8)\}_2(\mu\text{-}O)_2]$ (2), $[\{TcN(CN)_2\}_2(\mu\text{-}O)_2]^{2-}$ and $[\{TcN(L)\}_2(\mu\text{-}O)_2]^{2-}$ (H_2L = ethane-1,2-diol). Infrared data have been analysed for the new complexes; for example, (2) exhibits two absorptions 1062(s) and 1055(m) cm^{-1} assigned to ν(Tc≡N) and consistent with a non-centrosymmetric geometry. This structure has been confirmed crystallographically; the Tc-N bond distances are 1.65(2) and 1.59(2)Å. In the oxo-bridged unit, the Tc-O distances range from 1.934(13) to 1.947(12)Å and the angles Tc-O-Tc are 81.8(5) and 81.9(5)°. The crystal structure of $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ has also been determined and is similar to that of (2). In both, the coordination geometry about each technetium centre is square pyramidal. UV-VIS and EPR spectroscopic data have also been presented for the complexes [15].

2.3 TECHNETIUM(V)

2.3.1 Oxo complexes

The vapour phase syntheses of and mass spectrometric data for a range of technetium(VII) and (VI) complexes have already been mentioned in the previous sections. This same work [9] includes the technetium(V) oxo complexes $[TcOCl_3]$, $[TcOF_2Cl]$ and $[TcOFCl_2]$ as well as technetium pentafluoride. The salt $[Ph_4As][TcOBr_4]$ has been prepared from $[Bu_4N][TcO_4]$, HBr and Ph_4AsBr , and its crystal structure has been determined. The crystal lattice contains discrete $[TcOBr_4]^-$ anions, (3), and each has C_{4v} symmetry. The bond lengths are Tc=O = 1.613(9)Å and Tc-Br = 2.460(1)Å [16].



(3)

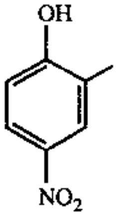
The protonation of the technetium(V) species $[Tc(O)_2(CN)_4]^{3-}$ leads to the formation of $[Tc(O)(OH)(CN)_4]^{2-}$ and $[Tc(O)(H_2O)(CN)_4]^-$. The mononuclear anion $[Tc(O)(OH)(CN)_4]^{2-}$ cannot be isolated since association occurs to give $[Tc_2(O)_3(CN)_8]^{4-}$. The new complexes have been characterized by UV-VIS and IR spectroscopies and mass spectrometry. The anion $[Tc(O)(H_2O)(CN)_4]^-$ (used as the $[bpyH_2]^{2+}$ salt) undergoes ligand exchange reactions, *e.g.* with NCS^-. In this case the product is $[Tc(O)(NCS)(CN)_4]^{2-}$ for which X-ray crystallographic data confirm that the CNS^- ligand lies *trans* to the oxo group. The solution equilibrium given in equation (i) has been studied [17]. The kinetics of ligand exchange in the cation $[Tc(O)_2(py)_4]^+$ as defined in equation (ii) have been investigated by use of ^1H NMR spectroscopy. The rate law is found to be first order in the complex and zero order in pyridine. A rate constant (298 K) of $0.04 \pm 0.02\ s^{-1}$ has been estimated; the estimated values of the activation parameters $\Delta H^‡$ and $\Delta S^‡$ are $101 \pm 9\ kJ\ mol^{-1}$ and $68 \pm 35\ J\ K^{-1}\ mol^{-1}$ respectively [18].

$$trans\text{-}[Tc(O)(H_2O)(CN)_4]^- + CNS^- \rightarrow trans\text{-}[Tc(O)(CNS)(CN)_4]^{2-} + H_2O \qquad (i)$$

$$[Tc(O)_2(py)_4]^+ + 4\,L \rightarrow [Tc(O)_2L_4]^+ + 4\,py \qquad \text{where } L = D_5(py) \qquad (ii)$$

The reaction of $[TcO_4]^-$ with 1,2-diaminobenzene (H_2L) in methanol yields a technetium(VII) complex which was described in section 2.1. When the medium is alkaline and the reaction is carried out in the presence of a reducing agent (sodium dithionite), the product is the technetium(V) complex anion $[TcOL_2]^-$, isolated and structurally characterized as the tetrabutyl ammonium salt. In the IR spectrum, an absorption at 891 cm^{-1} is assigned to the mode $\nu(Tc{=}O)$. The solid state structure shows the technetium(V) centre to be within a square pyramidal array of donor atoms with the oxo ligand in the apical site. The Tc=O bond length is 1.668(7)Å and the Tc-N distance lie in the range 1.97(1) to 1.99(1)Å [12].

The product of the reaction of $[TcOCl_4]^-$ with the ligand terpy depends upon the conditions used. In dichloromethane, the complex $[Tc(terpy)(O)Cl_3]$ is formed in which terpy functions as an *N,N'*-donor with one pyridine ring free from a role in the coordination sphere. In boiling ethanol, and with a Tc:terpy ratio of 2:1, the product is the cation $[Tc(terpy)(O)Cl_2]^+$ (precipitated as the $[TcO_4]^-$ salt) and here, terpy provides an *N,N',N''*-donor set. An excess of the ligand (and still running the reaction in EtOH) leads to the formation of an oxygen-bridged dimer and, again, the ligand terpy, makes use of all three nitrogen donor atoms. The reaction of $[TcO_4]^-$ and terpy in a mixture of ethanol and HCl provides a route to $[TcOCl_3(terpy.HCl)]$, a complex that can also be accessed from $[TcOCl_4]^-$. All the new complexes have been characterized by elemental analysis and IR, UV-VIS and ^1H NMR spectroscopies [19].



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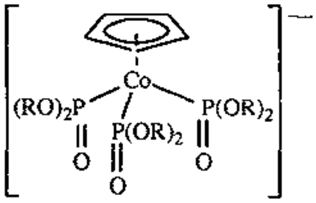


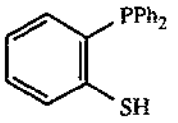
R = Me, Et or Bu

(5)

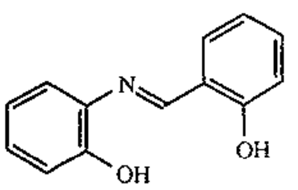
The structure of the compound $[Bu_4N][Tc(O)L_2]$, for which H_2L = (**4**), has been determined by X-ray diffraction. In the anion, the technetium(V) centre is in a square pyramidal environment, with the oxo group in the apical site (Tc=O = 1.634(4)Å). For the two catecholate ligands, the Tc-O distances are in the range 1.952(4) to 1.979(5)Å. The nitro-group of each of the basal ligands lies in the same plane as the rest of the atoms contained in L^{2-} [20]. The anion (**5**) is a tripodal *O,O',O''*-ligand, the sodium salt of which reacts with $[NH_4][TcO_4]$ in the presence of concentrated HCl to yield the technetium(V) complex $[Tc(O)(5)Cl_2]$ for R = Et in ligand (**5**). Treatment of $[Tc(O)(5)Cl_2]$ (R = Et) with concentrated HNO_3 leads to oxidation and the formation of the technetium(VII) species $[Tc(5)O_3]$ (R = Et); this complex can be obtained directly from

$[NH_4][TcO_4]$ by using HNO_3 in place of HCl. The analogous complexes $[Tc(5)O_3]$ for R = Me and Bu have been prepared from $[NH_4][TcO_4]$ in a similar manner. These new derivatives of the ligand (**5**) have been characterized by mass spectrometric and spectroscopic means and this includes the use of ^{99}Tc NMR spectroscopy for the technetium(VII) complexes [21].

During the reaction of the complex $[Tc(O)L_4](PF_6)_3$ ($L = (Me_2N)_2C{=}S$) with dppe in dmf, rearrangement of the tetramethylthiourea to dimethyldithiocarbamate ligands is observed. Two products have been isolated and these are the technetium(V) complex $[Tc(O)L_2(Me_2NCS_2)](PF_6)_2$ and the technetium(II) species $[Tc(dppe)_2(Me_2NCS_2)](PF_6)$ (see section 2.6). A mechanism has been suggested for the ligand rearrangement. The structure of $[Tc(O)L_2(Me_2NCS_2)](PF_6)_2$ has been elucidated. The cation has a square pyramidal geometry about the metal centre; the apical Tc=O bond is of length 1.661(6)Å. The Tc-S bonds are in the range 2.328(2) to 2.353(2)Å with chelate angles of 74.0° which distort the basal array away from a true square planar arrangement [22]. Technetium(V) oxo-complexes with dithioetherdithiol ligands have also been reported [23].



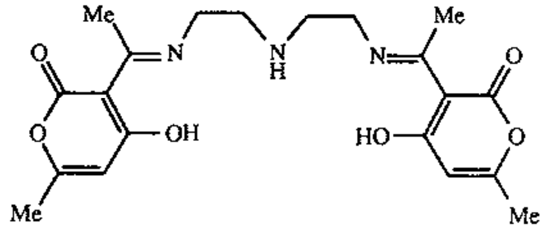
(6)



(7)

Technetium(V) and technetium(III) complexes involving the conjugate base of the ligand HL, (**6**), have been prepared from technetium(V) precursors; the lower oxidation state complex $[TcL_3]$ is described in section 2.5. The two technetium(V) products are $[Tc(O)L_2Cl]$ and the nitrido-containing complex $[Tc(N)L_2]$. The UV-VIS spectroscopic properties of the new complexes have been detailed and cyclic voltammetric studies have also been carried out [24].

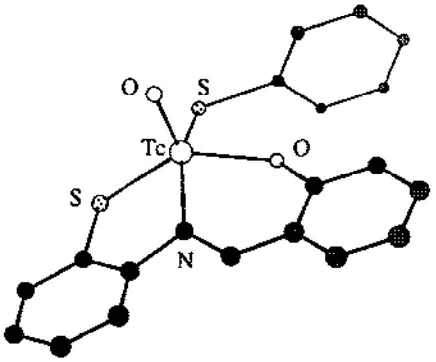
The reactions of bpy or phen with $[Tc(O)LCl]$ (H_2L = (7)) lead to the formation of the mixed ligand complexes $[Tc(O)L(bpy)]^+$ and $[Tc(O)L(phen)]^+$. Spectroscopic data are in accord with octahedral complexes containing L^{2-} acting as a tridentate ligand. It is proposed that the three donor atoms of L^{2-} are in a *mer*-arrangement. This places the oxo-group *trans* to one *N*-donor atom of the bpy (or phen) ligand. When $[Tc(O)LCl]$ (H_2L = (7)) reacts with bis(2-pyridyl)ketone (L') in ethanol, addition of EtOH across the unsaturated ketonic group occurs and the product is $[Tc(O)L(L'.EtOH)Cl]$ [25]. A pentadentate ligand with an *O,N,N',N'',O'*-donor set is derived from H_3L = (**8**). This ligand has been prepared by a Schiff's base condensation reaction and its reaction with $[TcOCl_4]^-$ and $NaO_2CMe.3H_2O$ in methanol and chloroform yields the technetium(V) complex $[Tc(O)L]$. This may also be synthesized from $[Tc(O)Y_2]^-$ in which Y^- is ethylene glycolate. The new complex $[Tc(O)L]$ has been characterized from IR, UV-VIS and NMR (^1H and ^{13}C) spectroscopies and by the results of a single crystal X-ray diffraction study. The technetium(V) centre is octahedrally sited with the oxo-group *trans* to one of the oxygen donor atoms of L^{3-}. In the presence of the $\{Tc{=}O\}^{3+}$ unit, the central NH functionality of the ligand is rendered sufficiently acidic for the ligand to be triply deprotonated [26].



(8)

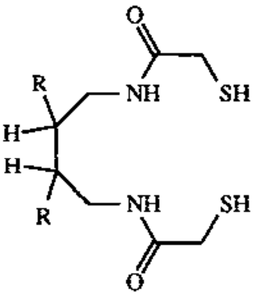
Technetium(V) complexes containing the ligand L^- where HL is a substituted benzimidazolyl-alcohol or -thiol have been reported. In the presence of Et_3N, the reaction of $[TcOCl_4]^-$ and HL (HL = 2-benzimidazolyl-CH(SH)R; R = H or Me) leads to the formation of $[Tc(O)L_2(H_2O)]Cl$. In contrast, the corresponding system for HL' = 2-benzimidazolyl-CH(OH)R (R = H, Me or Ph) yields six coordinate complexes of the type [Tc(O)L'$_2$Cl] where $[L']^-$ functions as an *N,O*-donor. In the same study, the complex [Tc(O)L"$_2$Cl] has been prepared where HL" = 2-(2-hydroxyphenyl)benzothiazole. The products have been characterized by use of vibrational and electronic spectroscopic techniques and by elemental analysis, and the influence of the donor atom on the complex geometry has been discussed [27].

The crystal structure of the complex [Tc(O)(SPh)L] (**9**) in which the ligand L^{2-} is *N*-(2-sulfidophenyl)salicylideneimidato) (an *N,O,S*-donor) has been determined crystallographically. The technetium(V) centre is in a square pyramidal environment with the oxo-group in the apical site; the metal atom lies 0.66Å above the mean plane of the four basal donor atoms [28].



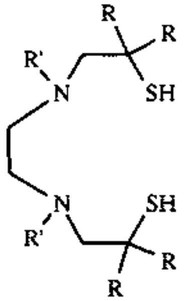
(9)

Several technetium(V) oxo-complexes featuring *N,N',S,S'*-ligands have been reported. For H_4L = (**10**), complexation with technetium(V) gives rise to the anions $[Tc(O)L]^-$, isolated as either the tetraphenylphosphonium or tetraphenylarsonium salts. Mass spectral, UV-VIS and IR spectroscopic data are consistent with the formulation of these as 5-coordinate species. For R = H, the solid state structure has been crystallographically confirmed; the Tc=O bond distance is 1.657(3)Å. The basal plane of the two sulfur and two nitrogen donor atoms is "ruffled" and the metal atom lies 0.67Å above the mean N_2S_2-plane [29]. The reactions of the four ligands in the family **(11)** with $[TcOCl_4]^-$ lead to the formation of the cationic complexes $[Tc(O)L]^+$, $[Tc(O)L']^+$, $[Tc(O)(H_2L'')]^+$ and $[Tc(O)(H_2L''')]^+$. These have been characterized by elemental analysis, conductivity and magnetic measurements, and IR and ^1H NMR spectroscopies. The influence on the complexes of varying the solution pH has been investigated; at pH 12.5, the cations $[Tc(O)(H_2L'')]^+$ and $[Tc(O)(H_2L''')]^+$ are deprotonated to give neutral complexes containing either $[HL'']^-$ or $[HL''']^-$. The crystal structures of the tetrafluoroborate salts of $[Tc(O)L]^+$ and $[Tc(O)(H_2L'')]^+$ **(12)** have been elucidated. In each of these cations, a square based pyramidal arrangement around the technetium(V) centre has been confirmed; the metal is raised above the plane of the *N,N',S,S'*-donor set by 0.774(1)Å in the case of $[Tc(O)L]^+$ and 0.7731(3)Å in **(12)** [30]. A further example of an *N,N',S,S'*-ligand is seen in the complex $[Tc(O)(H_2O)L]Cl$ in which $H_2L = (HS)CR{=}CHCMe{=}NCH_2CH_2N{=}CMeCH{=}CR(SH)$ (R = Me) and in $[Tc(O)LCl]$ (same H_2L but with R = Ph). In solution, these complexes show solvent dependent UV-VIS and ^1H NMR spectra and this is attributed to exchange involving the axially bound ligand. The crystal structure of $[Tc(O)(H_2O)L]Cl$ (R = Me) has been determined and a distorted octahedral geometry with a *trans*-$\{O{=}Tc{-}OH_2\}$ core is thus confirmed [31].



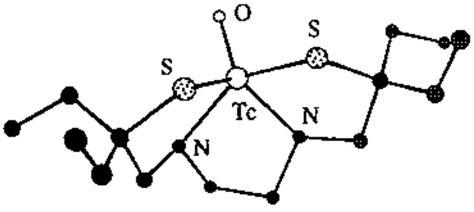
R = H or Ph

(10)



H_2L R' = Et, R = Me
H_2L' R = R' = Me
H_4L'' R' = H, R = Et
H_4L''' R' = H, R = Me

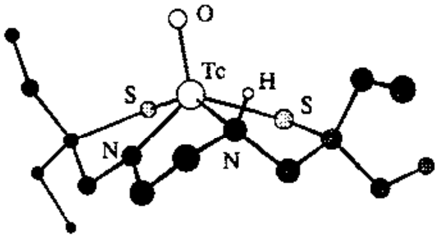
(11)



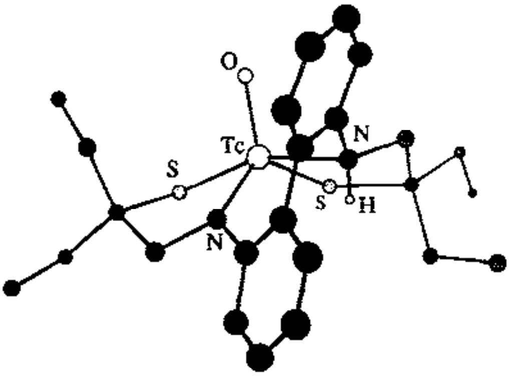
(12)

Neutral and lipophilic complexes $[^{99}TcO(HL)]$, **(13)** and **(14)**, in which H_4L is $HSCEt_2CH_2NHCH_2CH_2NHCEt_2SH$ or a related ligand with a biphenyldiamine-backbone have been prepared by the reactions of $[^{99}TcO_4]^-$, tin(II) tartrate and H_4L. Both **(13)** and **(14)** have been structurally and spectroscopically characterized. The presence of the biphenyl-unit produces a central 7-membered chelate ring in complex **(14)**. In the solid state, both complexes adopt a square pyramidal geometry, but the orientation of the remaining nitrogen-attached hydrogen atom in the

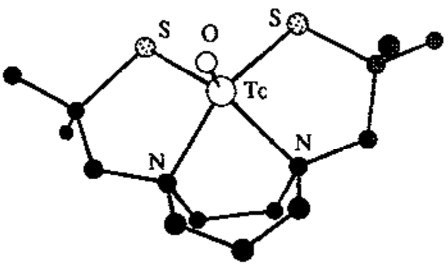
N,N',S,S'-ligand differs in the two complexes. This feature is indicated in the diagrams of structures (**13**) and (**14**). The results of NMR spectroscopic studies indicate that the solid state structures are retained in solution.. The effects of compound lipophilicity on brain uptake is illustrated through these new technetium(V) complexes [32]. With the aim of producing new ^{99m}technetium(V) complexes which are of potential use as myocardial imaging agents, Ohmomo *et al* have utilized an *N,N',S,S'*-ligand with a piperazine unit which is conformationally restricted. In this work, the complex [(**15**)](PF$_6$) has been synthesized and characterized by IR, UV-VIS and NMR spectroscopies and single crystal X-ray diffraction methods. The technetium(V) centre is in a square pyramidal environment with the *N,N',S,S'*-donor atoms residing in the basal plane of the 5-coordinate array [33].



(**13**)



(**14**)



(**15**)

The preparation and characterization of the new ligand $PhP(=S)(NMeNH_2)_2$ (H_2L) have been described. It complexes with ^{99m}technetium(V) to yield the compound [Tc(O)LCl] in which L^{2-} functions as an *N,N′,S*-donor. [Tc(O)LCl] is formed in good yields and is stable over a wide pH range. Its potential application as a ^{99m}Tc imaging agent has been discussed [34].

A synthetic investigation dealing mainly with rhenium(VI) oxo-complexes which are of relevance to technetium renal imaging agents has been reported. As an integral part of this study, molecular mechanics parameters have been developed, and their availability permits investigations of the anionic complex $[Tc(O)(HL)]^-$ (HL^{4-} = tetra-anion derived from mercaptoacetyltriglycine) and related systems. Moving from $[Tc(O)(HL)]^-$ to the dianion $[Tc(O)L]^{2-}$ provides results that illustrate that this system is conformationally flexible. The data have been placed into the context of the renal system [35].

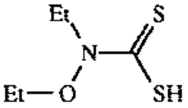
A further oxo-complex is $[Tc(O)Cl_2\{N(CH_2C_6H_4\text{-}2\text{-}PPh_2)_3\}][BPh_4]$; this compound forms part of a series of nitrido and other complexes involving the ligands (**23**) and is described in section 2.3.2 [44].

2.3.2 *Nitrido complexes*

Technetium nitrido complexes have been included within a general review of transition metal nitrido compounds [4].

The reaction of $[Tc(N)Cl_2(S_2CNEt_2)]$ with $K_2[SCOCOS]$ leads to the formation of a mixed ligand complex with concomitant reduction of the technetium from oxidation state VI to V. The product, $[Tc(N)(S_2CNEt_2)(SCOCOS)]^-$ can also be prepared from $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ (see section 2.2). The anion $[Tc(N)(S_2CNEt_2)(SCOCOS)]^-$ has been isolated and characterized as the tetraphenylarsonium salt, and a monomeric species has been confirmed from the results of a single crystal X-ray diffraction study. The technetium(V) centre is in a square pyramidal coordination sphere with an apical Tc≡N group (Tc≡N is 1.54(2)Å). For the $[C_2S_2O_2]^{2-}$ ligand, the Tc-S bond distances are 2.377(5) and 2.374(6)Å, compared with 2.424(5) and 2.396(5)Å for the Tc-S bonds involving the $[S_2CNEt_2]^-$ ligand [15]. The reaction of $[TcO_4]^-$ with HCl, PPh_3 and $H_2NN(Me)C(S)SMe$ gives rise to an intermediate species which, when treated with NaL (HL = (**16**)) yields the complex $[Tc(N)L_2]$. This synthesis has been carried out both at the tracer level (*i.e.* 10^{-9}–10^{-11} mol dm^{-3} ^{99m}Tc) and on a millimolar scale (*i.e.* 10^{-3} mol dm^{-3} ^{99}Tc) and at the millimolar level of reaction, the intermediate has been shown to be $[Tc(N)Cl_2(PPh_3)_2]$. This is an unusual example of a preparation that gives the same technetium-containing product at two very different concentration levels. The new complex $[Tc(N)L_2]$, which has a square pyramidal geometry, has been characterized fully, including by a crystal structure determination although details of the latter are not given. Electrochemical studies have been carried out [36]. In another related report, Pasqualini *et al.* discuss an improved method of preparing ^{99m}Tc-radiopharmaceuticals which contain the $\{Tc{\equiv}N\}^{2+}$ core unit; the route starts from $[^{99m}TcO_4]^-$ and $H_2NN(R)C(S)SMe$ (R = H or Me) in reactions that take place in the presence of HCl and a tertiary phosphine. $H_2NN(R)C(S)SMe$ is both a source of N^{3-} and of a ligand that can later be exchanged to give the required radiopharmaceutical [37]. Further studies describe conditions for preparing $[^{99m}TcNCl_4]^-$

from $[^{99m}TcO_4]^-$, azide and HCl; ligand exchange reactions involving the complex $[^{99m}Tc(N)Cl_2\{P(CH_2CH_2CN)_3\}_2]$ have been described [38]. Technetium(V) nitrido-complexes with dithioetherdithiol ligands have also been reported [23].



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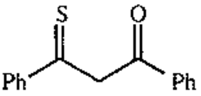
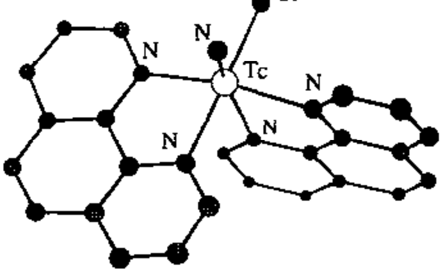


(17)

Ligand (**17**), HL, reacts with $[TcNCl_4]^-$ to give the technetium(V) complex $[Tc(N)L_2]$. This compound has been the subject of elemental and FAB mass spectral analysis and of UV-VIS spectroscopic studies [39].

Technetium(V) nitrido-complexes with other *N*-donor ligands include several with pyridyl-derived ligands; two are described here and one other, namely *cis*-$[Tc(N)Br(bpy)_2]^+$, is detailed at the end of this section along with related complexes. The complex *cis*-$[Tc(N)Cl(phen)_2]^+$ (**18**) (see also reference [43] discussed below) is of particular interest because its structural characterization addresses the question of the so-called 'bond-stretch isomerism', an issue that has received much attention of late. The two salts *cis*-$[Tc(N)Cl(phen)_2]Cl.H_2O$ and *cis*-$[Tc(N)Cl(phen)_2](PF_6)$ have been prepared; slight differences in the physical properties of the two systems have been noted. The crystal structures of both salts have been determined. In $[Tc(N)Cl(phen)_2](PF_6)$, the cation possesses a pseudo-two-fold axis of symmetry and this gives rise to an enantiomeric disorder (0.85:0.15). These data may be incorrectly interpreted in terms of a particularly long Tc≡N bond length thus leading to a suggestion of the occurrence of 'bond stretch isomerism'. The complex cation in *cis*-$[Tc(N)Cl(phen)_2]Cl.H_2O$ exhibits no pseudo-symmetry and there is no bond length ambiguity. The final analysis yields Tc≡N bond distances of 1.603(5) and 1.593(5)Å for the two cations; Tc-Cl = 2.412(2) and 2.405(2)Å respectively. There are however real distortional differences between the two cations and these are discussed. Experimental results are complemented by theoretical studies [40]. The synthesis of ligand (**19**) has been detailed; it reacts with $[Tc(N)Br_2(PPh_3)_2]$ in acetonitrile to yield $[Tc(N)Br_2(\mathbf{19})]$ (R = Me). The results of a single crystal X-ray diffraction study of $[Tc(N)Br_2(\mathbf{19})]$ show it to be an octahedral complex and illustrate that the



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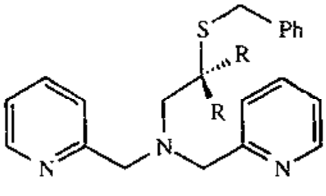
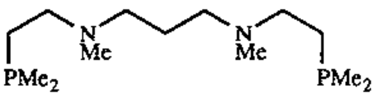


R = H or Me

(19)

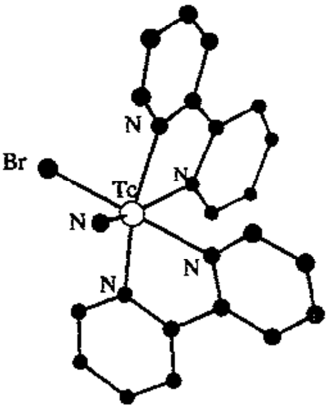
ligand behaves as an *N,N',N''*-donor and the thioether moiety dangles free. The three nitrogen donor atoms of **(19)** are in a *fac*-arrangement and, accordingly, the bromide ligands are *cis* to one another. Important bond lengths are $Tc{\equiv}N$ = 1.61(1)Å and $Tc\text{-}N_{(19)}$ = 2.116(9), 2.166(9) and 2.47(1)Å; the one long $Tc\text{-}N_{(19)}$ value corresponds to the bond which is *trans* to the nitrido group. This feature is in keeping with the strong *trans*-influence of N^{3-}. In solution, ^{1}H NMR spectroscopic studies show that an equilibrium exists between the complex in a structure analogous to that found in the solid state and one in which the thioether-*S* donor atom displaces a bromide ligand. Parallel chemistry for **(19)** with R = H has also been reported [41].

The crystal structure of a technetium(V) complex containing a cyclic tetraamine ligand has been determined. The complex is $[Tc(N)L(H_2O)]Cl$ (L^- = 1,4,8,11-tetraazacyclotetradecan-5-onato) and, in the cation, the technetium centre is six-coordinate with the water molecule coordinated *trans* to the nitrido group. The long $Tc\text{-}O_{water}$ bond length of 2.560Å reflects the strong *trans* influence of N^{3-}. Notably, the angles $N{\equiv}Tc\text{-}N$ average 101(3)° and these obtuse values indicate that the geometry of the cation is part way between being square pyramidal and fully octahedral [42].



(20)

A series of complexes involving bisphosphine ligands has been prepared by Dilworth and coworkers. Two members of the family are $[Tc(N)(dppe)_2Cl]^+$ and $[Tc(N)(dmpe)_2Cl]^+$; these have been synthesized from $[TcNCl_4]^-$ and the bisphosphine ligand, and isolated as either the tetraphenylborate or hexafluorophosphate salts. A similar reaction is seen when $[TcNCl_4]^-$ reacts with the ligand **(20)**; here the product is $[Tc(N)(\mathbf{20})Cl]^+$. In contrast, when the bisphosphine is more sterically demanding, a pathway to a dinuclear species is observed. This is exemplified by the reaction of $[TcNCl_4]^-$ with $^iPr_2PCH_2CH_2P^iPr_2$ which leads to the formation of a complex the structure of which is proposed to involve two octahedrally coordinated technetium(V) centres bridged by two chloride ligands: $[\{Tc(N)(^iPr_2PCH_2CH_2P^iPr_2)Cl\}_2(\mu\text{-}Cl)_2]$. The crystal structure of $[Tc(N)(dmpe)_2Cl][BPh_4]$ has been elucidated and an octahedral coordination sphere for the metal centre has been confirmed. The *trans* relationship between the nitrido and chloro ligands leads to a long Tc-Cl bond (2.608(3)Å), but even though lengthening is to be expected due to the *trans* influence of N^{3-}, this distance is noted for the fact that it the longest such reported to date. The authors, however, point out that the pseudo-symmetry of the system caused problems with the refinement [43]. The situation should be compared with that experienced in dealing with the structure of $[Tc(N)Cl(phen)_2]$ [40] (see above). Dilworth and coworkers have also looked at the reactions of $[TcNBr_4]^-$ and $[TcNCl_4]^-$ with bpy and phen (see also reference [40] discussed above). Spectroscopic data are consistent with the formation of *cis*- (rather than *trans*) cations of the type $[Tc(N)(L)_2X]^+$ (L = bpy or phen; X = Br or Cl). However difficulties were experienced in obtaining analytically pure materials when the cations were precipitated as halide salts from ethanol. Unexpectedly, recrystallization from a mixture of acetone and diethyl ether of the product of the reaction of $[TcNBr_4]^-$ and bpy led to the isolation of the mixed oxidation state compound $[Tc^{V}(N)(bpy)_2Br]_2[Tc^{II}Br_4]$, the identity of which has been confirmed by X-ray diffraction. The cation $[Tc^{V}(N)(bpy)_2Br]^+$ **(21)** has a distorted octahedral geometry; for one of two independent molecules, selected bond distances are Tc≡N = 1.621(20)Å, Tc-N_{bpy} = 2.104(19) to 2.415(19)Å (the longest bond being associated with the *trans* influence of N^{3-}), and Tc-Br = 2.529(4)Å. The tetrahedral $[TcBr_4]^{2-}$ anion is particularly unusual and is detailed in section 2.6. $[TcNCl_4]^-$ also reacts with the Schiff's base **(22)**, H_2L, to give [Tc(N)(L)] in good yield [43].



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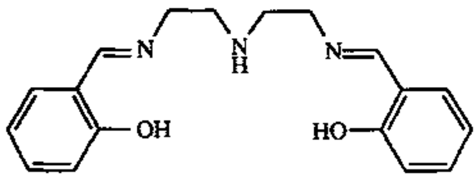

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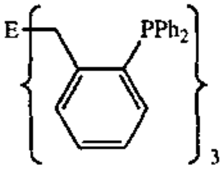


E = N or P

(23)

The technetium(V) complex $[Tc(N)L_2]$ where HL = 2-$SHC_6H_4PPh_2$ (6) was mentioned in section 2.3.1 as one of a group of technetium(III) and technetium(V) products containing the *P*,*S*-donor ligand L^- [24]. The preparations of the technetium(V) complex cations *cis*-$[Tc(N)Br(\mathbf{23})]^+$ (isolated as the PF_6^- or BF_4^- salts) have been reported along with technetium(III) complexes of the type *cis*-$[Tc(X)(Y)(\mathbf{23})]^+$ (X = Y = Cl; X = Cl, Y = NNC_6H_4Cl). Attempts to synthesize *cis*-$[Tc(O)_2(\mathbf{23})]^+$ were not successful but $[Tc(O)Cl_2(\mathbf{23})]^+$ for E = N has been isolated as the tetraphenylborate salt. Electrochemical studies on the systems have been carried out. The *cis*-chloro technetium(III) cations show reversible one electron reductions at -0.13V (*vs* SCE) in dmf, the potential being independent of E in the ligand. The other complex cations proved more difficult to reduce [44].

2.3.3 *Miscellaneous complexes*

The reaction of $[Bu_4N][TcOCl_4]$ in methanol with 1-acetyl-2-phenylhydrazine and dppe leads to the formation of the technetium(V) complex $[TcCl_3(NPh)(dppe)]$. This exhibits an absorption of the infrared spectrum at $1110cm^{-1}$, assigned to a ν(Tc≡N) mode. The complex has also been characterized by ^1H NMR spectroscopy, mass spectrometry and a crystal structure determination. The chloride ligands are in a *fac*-arrangement; the Tc-N bond distance is 1.687(9)Å. When PPh_3 is used in the synthesis in place of dppe, the product is $[TcCl_3(NPh)(PPh_3)_2]$ (a previously reported complex). This reacts with pyridine to give $[TcCl_3(NPh)(PPh_3)(py)]$ which has been spectroscopically and mass spectrometrically characterized [45].

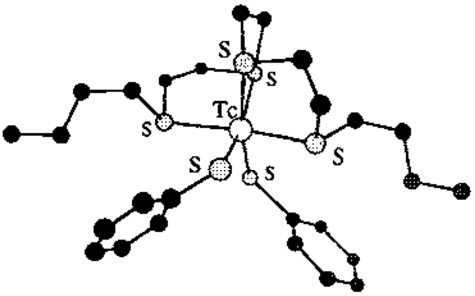
2.4 *TECHNETIUM(IV)*

The luminescence spectra of the mixed halides $[TcCl_nBr_{6-n}]^{2-}$ (n = 1 to 5) have been recorded and the results discussed [46].

2.5 *TECHNETIUM(III)*

The preparation of the technetium(III) complex $[Tc(acac)_2(MeCN)_2]^+$ from $[Tc(acac)_3]$ and MeCN in the presence of HCl or $HClO_4$ has been detailed, and the kinetics of the process have been investigated. $[Tc(acac)_2(MeCN)_2]^+$ has been characterized by elemental analysis, IR and UV-VIS spectroscopies, ion exchange chromatography and electrophoresis. The new cation appears to have a potential application as a precursor to various mixed ligand technetium(III) complexes [47].

Two thioether ligands, 5,8,11,14-tetrathiaoctadecane (L) and 3,6,9,12-tetrathiatetradecane (L'), have been incorporated into complexes of technetium(III). Prepared from $[TcO_4]^-$, the new complexes are $[Tc(L)(SPh)_2][PF_6]$ and $[Tc(L')(SR)_2][PF_6]$ (R = Ph, ^iPr and $4\text{-}MeOC_6H_4$). Their spectroscopic properties have been recorded, and $[Tc(L)(SPh)_2][PF_6]$, $[(\mathbf{24})][PF_6]$, has been the subject of a crystallographic study. The metal centre in cation (**24**) is in a greatly distorted octahedral environment; the two thiolate ligands are mutually *cis* [48]. Some reactions of thiols with *trans*-$[Tc(OH)(O)(diars)_2]^{2+}$ (diars = $1,2\text{-}(Me_2As)_2C_6H_4$) have been investigated. The initial technetium(II) products can be oxidized to yield $[Tc(SR)_2(diars)_2]^+$. For R = Me or CH_2Ph, *trans*-complexes result, but for R = Ph, both *cis*- and *trans*-cations are formed. Complex characterization has been by use of mass spectral data, UV-VIS spectroscopy, and electrochemical and spectroelectrochemical techniques. The crystal structure of *trans*-$[Tc(SMe)_2(diars)_2][PF_6]$ has been determined. The technetium(III) atom lies on an inversion centre; selected distances are Tc-S = 2.292(2)Å and Tc-As = 2.496(2)Å. These values compare with Tc-S = 2.410(2)Å and Tc-As = 2.471(2)Å in the technetium(II) complex $[Tc(SPh)_2(diars)_2]$, the structure of which is also reported in this study. Comparisons between the electrochemical and spectroscopic data for the new diars complexes and related dmpe species indicate that in *trans*-$[Tc(SR)_2L_2]^+$ (R = alkyl), greater π-acceptance is effected by L = diars than by L = dmpe [49]. The same authors have looked at complex formation involving the ligand (**26**), H_2L. The reaction between (**26**) and the technetium(V) cation $[Tc(OH)(O)(dmpe)_2]^{2+}$ leads to the formation of the technetium(III) complex $[Tc(L)(dmpe)_2]^+$. Isolated as the hexafluorophosphate salt, $[Tc(L)(dmpe)_2]^+$ has been characterized by elemental analysis, UV-VIS spectroscopy, mass spectrometry and single crystal X-ray diffraction. The technetium(III) centre is in a coordination geometry that is in between octahedral and trigonal prismatic, each ligand behaving as an *S,S'*-chelate. The ligand bite angle is 84.49(4)°. Electrochemical studies reveal that $[Tc(L)(dmpe)_2]^+$ can be reversibly reduced with Tc(III)/Tc(II) and Tc(II)/Tc(I) couples at −0.600 and −1.217 V, respectively (*vs* Ag/AgCl). In addition, a quasi-reversible Tc(IV)/Tc(III) couple was observed at +0.680 V [50].



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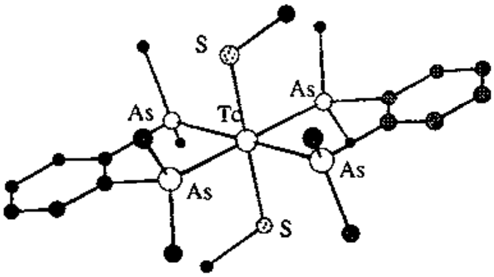

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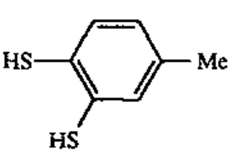

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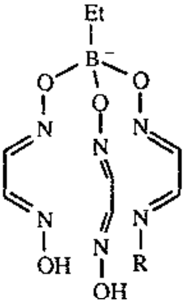


(27)

Technetium(III) complexes of the type *cis*-$[Tc(X)(Y)(23)]^+$ (X = Y = Cl; X = Cl, Y = NNC_6H_4Cl) were described in section 2.3.2 along with related technetium(V) species [44].

The reaction of $EtB(OH)_2$ with dimethylglyoxime and $[^{99m}TcCl_3(MeCN)(PPh_3)_2]$ results in the formation of the complexes $[^{99m}TcCl(L)]$ (HL^- = (27) with R = H or OH). For R = H, a crystallographic analysis of the new complex reveals that the technetium centre if 7-coordinate. The new species have been compared with previously reported and related complexes [51].

Technetium(V) complexes involving the conjugate base of the ligand HL, (6), were described in section 2.3.1. The technetium(III) complex $[TcL_3]$ has also been prepared and fully characterized by Dilworth *et al.* The structural details of the complex have been compared with those of the rhenium(III) analogue [24]. In independent work, Bolzati *et al* have also prepared $[TcL_3]$ for HL = (6) and in addition have studied the analogous complex $[TcL'_3]$ where HL' = $2\text{-}Ph_2PC_6H_4OH$. The method of synthesis is the reaction of an excess of either HL or HL' with $[NH_4][TcO_4]$. In this study, the complexes $[TcL_3]$ and $[TcL'_3]$ have been characterized by elemental analysis, ^1H NMR, IR and electronic spectroscopies, and conductivity and magnetic susceptibility measurements. For $[TcL_3]$, $\mu_{eff} = 3.0\ \mu_B$ and for $[TcL'_3]$, $\mu_{eff} = 2.7\ \mu_B$; these values are consistent with a d^4 configuration for the metal centre. Many of the features of the solid state structures of $[TcL_3]$ and $[TcL'_3]$ are very similar. In each complex, the metal centre is in a distorted octahedral coordination sphere with a *mer* arrangement of donor atoms. Selected distances are Tc-S = 2.258(1), 2.489(2) and 2.297(1)Å for $[TcL_3]$ and Tc-O = 2.074(3), 2.000(3) and 1.990(3)Å in $[TcL'_3]$, the variation within the three bond distances of a given type being due to the particular relationship of a bond with other S or P donor atoms [52].

2.6 *TECHNETIUM(II)*

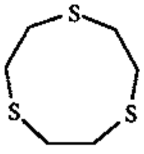
A range of technetium(II) complexes has been included in an EPR spectroscopic study in which the EPR parameters have been related to the structures of the complexes concerned. The systems studied were $[Tc(NO)Cl_5]^{2-}$, $[Tc(NO)Br_4]^-$, $[Tc(NO)I_4]^-$, $[Tc(NO)Cl_3(PPhMe_2)_2]$, $[Tc(NO)(H_2O)(NH_3)_4]^{3+}$ along with related thionitrosyl complexes [14].

In section 2.3.2, reactions of $[TcNBr_4]^-$ with phen and bpy were described. It was noted that recrystallization of the product from the reaction of $[TcNBr_4]^-$ and bpy from a mixture of acetone and diethyl ether led to the isolation of $[Tc^V(N)(bpy)_2Br]_2[Tc^{II}Br_4]$ instead of a simple bromide salt. The crystal structure determination of $[Tc(N)(bpy)_2Br]_2[TcBr_4]$ allows information about the newly discovered technetium(II) anion $[TcBr_4]^{2-}$ to be detailed. The ion possesses almost regular tetrahedral symmetry. The Tc-Br bond lengths are 2.399(4), 2.401(5), 2.388(4) and 2.417(4)Å and Br-Tc-Br angles range from 106.1(2) to 112.1(2)° [43].

An EPR spectroscopic investigation of $[Tc(bpy)_3](PF_6)_2$ has been carried out; the complex contains a trigonally distorted octahedral, low spin technetium(II) cation. The ligand field splitting within the $^2T_2$ manifold has been estimated. Spin-orbit coupling is reduced as a consequence of extensive metal-ligand covalent interactions [53]. Related to $[Tc(bpy)_3]^{2+}$ is $[Tc(phen)_3]^{2+}$, and this cation has been prepared in the form of $[^{99}Tc(phen)_3]Cl_2$ through the borohydride reduction of pertechnetate ion in the presence of excess phen. The product has been characterized by use of mass spectrometry, IR and UV-VIS spectroscopies and magnetic measurements. Additionally, its biodistribution in mice has been assessed. It is possible to obtain $[^{99}Tc(phen)_3]Cl_2$ in a state of radiochemical purity of 92.5% [54].

The reduction of $[TcO_4]^-$ in a hot alcoholic solution during reaction with dppe and $H_2C_2O_4$ (H_2ox) leads to the formation of $[Tc(dppe)_2(ox)]$. In its UV-VIS spectrum, this complex exhibits two intense absorptions at 323 and 497 nm, both of which are assigned to CT bands. Infrared and ^1H NMR spectroscopic details are also given, and the solid state structure of $[Tc(dppe)_2(ox)]$ has been determined by X-ray diffraction methods. This species appears to be the first example of a technetium complex containing mixed phosphorus- and oxygen-donor chelating ligands. Recrystallization of $[Tc(dppe)_2(ox)]$ from EtOH leads to the formation of three different crystal forms although only one was found to be stable in the X-ray beam. For this form, the Tc-P bond distances lie in the range 2.404(5) to 2.442(5)Å and Tc-O lengths are 2.12(1) and 2.14(1)Å. Within the oxalate chelate ring, $\angle$O-Tc-O = 75.6(5)°, while the dppe ligands subtend angles at the metal centre of 80.7(2) and 80.6(2)° [55]. Earlier (section 2.3.1) the reaction of $[Tc(O)L_4](PF_6)_3$ (L = $(Me_2N)_2C{=}S$) with dppe was outlined. Concomitant with the reaction is a rearrangement of the tetramethylthiourea to render dimethyldithiocarbamate ligands. One product of the reaction is the technetium(II) cation $[Tc(dppe)_2(Me_2NCS_2)]^+$, the structure of which has been elucidated. The cation is a distorted octahedron, with Tc-S bond distances of 2.448(7) and 2.439(6)Å and an acute dithiocarbamate chelate bite angle of 71.0(2)°. The Tc-P distances fall in the range 2.413(6)—2.473(6)Å [22].

The first homoleptic thioether complex of technetium has been prepared by reacting **(28)** with $[NH_4][TcO_4]$ in MeCN under reflux in the presence of hydrated tin(II) chloride and tetrafluoroboric acid. The product is the technetium(II) complex $[Tc(\mathbf{28})_2](BF_4)_2$. The characterization of this complex has included IR spectral analysis which confirmed the absence of a Tc=O bond. The effective magnetic moment of 1.8 μ_B is consistent with a low spin d^5 configuration. The crystal structure of the complex has been determined. The technetium(II) centre in the dication $[Tc(\mathbf{28})_2]^{2+}$, **(29)**, has been shown to be in an octahedral environment and the average Tc-S bond distance is 2.38Å. Electrochemical studies have been carried out [56].



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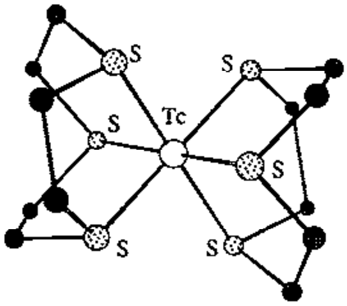

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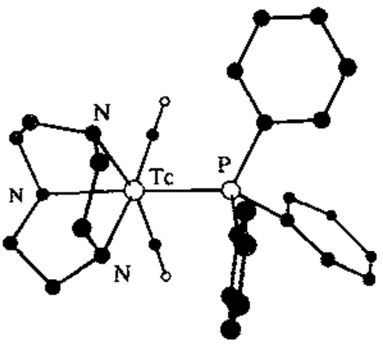
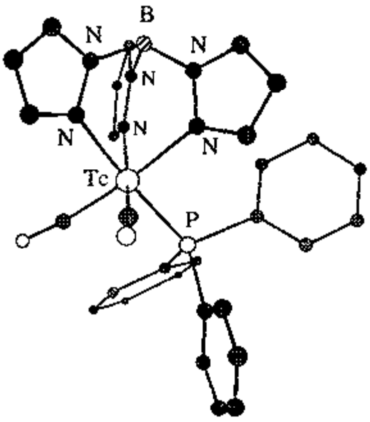
2.7 *TECHNETIUM(I)*

The reaction between S_2Cl_2 and *cis*-[Tc(N)Cl(phen)$_2$](PF$_6$) leads to the formation of the thionitrosyl complex *cis*-[Tc(NS)Cl(phen)$_2$](PF$_6$). The related nitrosyl complex *cis*-[Tc(NO)(NH$_3$)(phen)$_2$](PF$_6$)$_2$ has been prepared by treating [NH$_4$]$_2$[TcCl$_6$] or [NH$_4$][TcO$_4$] with hydroxylamine hydrochloride in the presence of phen. Both the new complexes have been fully characterized, including by the use of electrochemical measurements. The infrared spectrum of [Tc(NO)(NH$_3$)(phen)$_2$](PF$_6$)$_2$ (KBr pellet) exhibits (amongst others) a strong absorption at 1715 cm^{-1} which is assigned to the mode ν(N=O). The structural parameters for *cis*-[Tc(NO)(NH$_3$)(phen)$_2$]$^{2+}$ are instructive and have been discussed in terms of the bonding in the complex. In particular, note is made of competition between the nitrosyl and phen ligands for the metal d_π-orbitals. The bond parameters involving the nitrosyl ligand are: Tc-N$_{NO}$ = 1.739(9)Å, N-O = 1.160(9)Å and $\angle$Tc-N-O = 171.9(8)°. The infrared spectrum of [Tc(NS)(NH$_3$)(phen)$_2$](PF$_6$) exhibits a strong absorption at 1173 cm^{-1} which is assigned to the thionitrosyl stretching mode. The structure of the hexafluorophosphate salt of *cis*-[Tc(NS)Cl(phen)$_2$]$^+$ has been determined and the N-S bond distance for the linear nitrosyl ligand is 1.538(6)Å. Overall, the experimental data for [Tc(NS)Cl(phen)$_2$]$^+$ point towards there being significant back bonding from technetium(I) to the $N{\equiv}S^+$ unit [57].



(30)



(31)

The use of phosphine complexes as precursors to new technetium species has been a feature in several substitution reactions described in previous sections. Low valent technetium chemistry also makes use of phosphine substitution reactions. For this purpose [Tc(CO)$_3$Cl(PPh$_3$)$_2$] has been synthesized and shown to be a profitable starting material. This technetium(I) compound can be prepared from [TcOCl$_4$]$^-$ and triphenylphosphine under an atmosphere of carbon monoxide. The crystal structure of [Tc(CO)$_3$Cl(PPh$_3$)$_2$] has been determined. The technetium(I) centre is octahedrally coordinated and the two PPh$_3$ ligands are mutually *trans*. The complex [Tc(CO)$_3$Cl(PPh$_3$)$_2$] reacts with 1,4,7-triazacyclononane, L, to yield [Tc(CO)$_2$(PPh$_3$)(L)]Cl [(**30**)]Cl, and with potassium hydridotris(pyrazolyl)borate, KL', to give [Tc(CO)$_2$(PPh$_3$)(L')] (**31**).

The new complexes have been fully characterized, including by crystallographic methods [58]. Dinitrogen is a labile ligand in the complex [Tc(H)(N_2)(dppe)$_2$] and it exchanges readily with carbon monoxide, isonitriles and phosphites (*e.g.* P(OMe)$_3$). In boiling methanol, and in the presence of sodium or pyridine, [Tc(H)(N_2)(dppe)$_2$] abstracts CO from the solvent and forms [Tc(H)(CO)(dppe)$_2$]. The hydride ligand is also an active site for exchange as seen in the reactions of complexes [Tc(H)(L)(dppe)$_2$] (L = CO, P(OMe)$_3$ or RCN; R = various) with MeCN which yield [Tc(MeCN)(L)(dppe)$_2$]$^+$, isolated as the PF_6^- salts. The new complexes have been characterized spectroscopically and part of the study includes the use of ^{99}Tc NMR spectroscopy. The shift range observed for the technetium(I) species is from δ –1080 to –3517 (*vs* δ 0 for [TcO_4]$^-$). For some of the complexes, ^{99}Tc-^{31}P spin-spin coupling has been resolved; for example in [Tc(H)(^{t}BuNC)(dppe)$_2$], J_{TcP} = 605 Hz [59].

The technetium carbonyl [$^{99}Tc_2(CO)_{10}$] reacts quantitatively with $NOPF_6$ in acetonitrile to give [^{99}Tc(CO)$_5$(MeCN)](PF_6). Like the phosphine and dinitrogen complexes described above, the acetonitrile derivative [Tc(CO)$_5$(MeCN)]$^+$ has also been shown to be a useful starting material for the synthesis of low valent technetium complexes by using a ligand exchange route. The technetium(I) cation [^{99}Tc(CO)$_5$(MeCN)]$^+$ reacts with tridentate ligands, L, such as 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane and 1,4,7-trithiacyclononane (**28**) to give the respective complex cation [^{99}Tc(CO)$_3$(L)]$^+$. Complexes involving the ligands bpy and 4,4'-Me$_2$bpy have also been prepared, including the cations [^{99}Tc(CO)$_2$(bpy){P(OR)$_3$}$_2$]$^+$ (R = Me or ^{i}Pr) [60].

2.8 DIMETALLIC COMPLEXES

Like CO, PF_3 acts as a π-acid and stabilizes low oxidation state transition metal centres. This is apparent in the isolation of [$Tc_2(PF_3)_{10}$], a complex that forms when technetium vapour and PF_3 are cooled together to 77 K. The compound is volatile; at 293 K, its vapour pressure is (7 ± 3) x 10^{-3} Pa. [$Tc_2(PF_3)_{10}$] decomposes above 470 K. It has been characterized by IR spectroscopy and mass spectrometry [61].

It has been possible to isolate single crystals of the metal-metal quadruply bonded complex [$Tc_2(\mu$-OAc)$_4$][TcO_4]$_2$ from a sample of [$Tc_2(\mu$-OAc)$_4$]Cl$_2$. The new compound has been structurally studied. The TcTc bond distance is 2.149(1)Å. The two [TcO_4]$^-$ ions are associated with the axial sites of the [$Tc_2(\mu$-OAc)$_4$]$^{2-}$ dimer. The electronic structure of the system has been investigated at the extended Hückel molecular orbital level [8].

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