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COORDINATION CHEMISTRY REVIEWS

6. Technetium 1993

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CONTENTS

INTRODUCTION

This review covers the coordination chemistry of technetium, published during 1993; the format of the article is similar to that of the 1992 survey [1]. 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 aims to give the reader a significant coverage of papers published. Organometallic complexes have been excluded from this review with the exception of selected technetium(I) carbonyl complexes with *N*-donor ligands. Another aspect not covered directly is that of medical applications of technetium chemistry, but compounds prepared and studied with the expectation of possible applications have been included. A review article (232 refs.) concerning the medical applications of coordination complexes and including significant discussion of technetium-based radiopharmaceuticals has appeared [3].

Complexes have been arranged according to the formal oxidation state of the technetium centre. Technetium(V) chemistry is dominated by oxo- and nitrido-species, and here, the presence of the Tc=O or Tc≡N moiety has taken preference over the identity of the donor atoms in other ligands present in the complexes for the purposes of categorization (see section 6.3).

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

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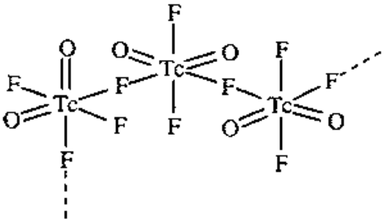
6.1 TECHNETIUM(VII)

The technetium(VII) compounds Tc_2O_7, $TcO_3(OH)$ and $TcO_2(OH)_3$ are amongst a series of oxides studied mass spectrometrically; technetium oxide was exposed to low pressures of O_2 and water vapour in a platinum Knudsen cell reactor (1100°C) [4]. The Raman spectrum of $[TcO_4]^-$ in aqueous solution has been recorded and calibrated against $NaClO_4$; comparisons have been made with data for $[ReO_4]^-$ and $[IO_4]^-$ — results are discussed in terms of the sizes of the anions. The equilibrium bond polarisabilities have been estimated using refractive index data and the intensities of the Raman ν_2 bending modes [5].

The yellow oxyfluoride TcO_2F_3 has been prepared from XeF_6 and Tc_2O_7 (3:1) in anhydrous HF and characterised by X-ray diffraction studies and Raman spectroscopy. The solid state structure (**1**) possesses chains of octahedrally sited Tc(VII) centres, linked by fluoride bridges. The oxo groups lie *trans* to bridging F atoms and are mutually *cis* at each technetium centre [6].



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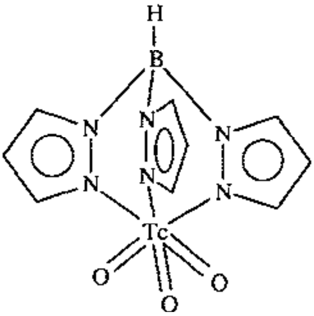
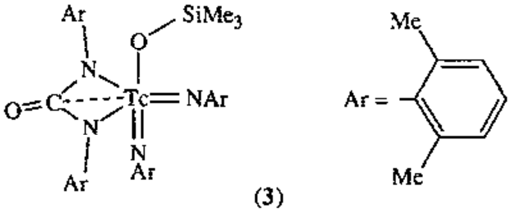


(2)

The reactions of Tc_2O_7 with $K(HBpz_3)$ or $Na(HBpz^*_3)$ in thf lead to the formation of $[TcO_3(HBpz_3)]$ (2) and $[TcO_3(HBpz^*_3)]$. The structures have been proposed on the basis of IR, ^1H NMR and UV-VIS spectroscopies and mass spectrometric data [7].

The syntheses of the technetium(VII) imido complexes $[Tc(NAr)_3(OSiMe_3)]$ where Ar = $2,6\text{-}R_2C_6H_3$, R = Me or ^iPr have been reported. These compounds react with Me_3SiI to yield $[Tc(NAr)_3I]$, with $[R']^-$ to give $[Tc(NAr)_3R']$ (R' = alkyl), or with fluoride ion to give $[Tc(NAr)_3O]^-$. The X-ray crystal structures of $[Tc\{N(2,6\text{-}^iPr_2C_6H_3)\}_3(OSiMe_3)]$ and $[Tc\{N(2,6\text{-}^iPr_2C_6H_3)\}_3I]$ have been determined and show that the Tc(VII) centre is tetrahedrally sited. The urylene complex (3) has been formed from the reaction of the less sterically demanding $[Tc\{N(2,6\text{-}Me_2C_6H_3)\}_3(OSiMe_3)]$ with $2,6\text{-}Me_2C_6H_3NCO$ and crystallographically confirmed for the rhenium analogue [8].



(3)

The catalysis by Tc(VII) of the oxidation of hydrazine by HNO_3 has been studied. A chain process has been confirmed with a mechanism that follows a sequence of (a) an initial slow stage (slow attack of Tc(VII) on N_2H_4 giving Tc(VI) and then, after further reaction, Tc(IV), (b) a fast stage with three steps which are summarised in equations (i) to (iii), and (c) a termination stage in which Tc(VII) is regenerated [9]. In an accompanying paper, Kemp *et al* also describe the results of a parallel study which replaces the HNO_3 by aqueous acidic perchlorate [10].

$$\mathrm{Tc(IV)} + NO_3^- \rightarrow \mathrm{Tc(VI)} + NO_2^- \qquad \text{(i)}$$

$$\mathrm{Tc(VI)} + N_2H_5^+ \rightarrow \mathrm{Tc(IV)} + N_2H_2 + 3H^+ \qquad \text{(ii)}$$

$$2N_2H_2 \rightarrow NH_3 + HN_3 \qquad \text{(iii)}$$

6.2 TECHNETIUM(VI)

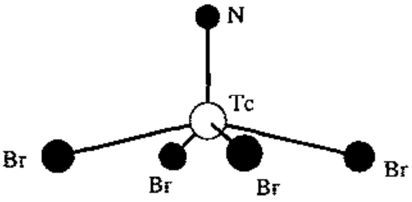
The mass spectrometric study described at the beginning of section 6.1 also includes the oxide TcO_3 [4].

Electron spin resonance and electronic spectroscopies have been used to investigate solutions containing $Cs_2[TcNCl_5]$ or its hydrolysis product $[\{TcN(OH)(H_2O)_2\}_2(\mu\text{-}O)]$ with a range of sulfur and phosphorus oxo acids (CF_3SO_3H to H_2SO_4, and H_3PO_4 to $H_4P_2O_7$) [11]. Baldas *et al* have also prepared caesium and rubidium crown-ether salts (15-crown-5 and 18-crown-6) of $[TcNCl_4]^-$ and $[TcNCl_4(H_2O)]^-$. A new refinement of the crystal structure of [Cs(8-crown-6)][$TcNCl_4$] has addressed some of the problems of an earlier disordered structure. The lattice contains an infinite sandwich of Cs^+/ether units, and polymeric anions featuring —Tc≡N—Tc≡N— chains with Tc≡N distances of 1.56Å and Tc----Tc separations of 4.275(4)Å. The ESR spectroscopic data evidence exchange interactions along the $(TcN)_x$ chains. The crystal structure of [Rb(15-crown-5)][$TcNCl_4(H_2O)$] has also been determined and reveals that here the anions are isolated entities in the solid state. The IR spectroscopic data are consistent with the solid state X-ray diffraction data —ν(Tc≡N) ≈ 1074 cm^{-1} for [Rb(15-crown-5)][$TcNCl_4(H_2O)$], in keeping with an isolated anion, but two bands assigned to ν(Tc≡N) are observed in the spectrum of [Cs(8-crown-6)][$TcNCl_4$] [12].

The preparation of $[^{99}TcN(Hedta)].3H_2O$ from $[^{99}TcNCl_4]^-$ has been described. The UV-VIS spectrum of this new complex is characterised by an absorption at λ_{max} = 505 nm (ε_{max} = 1060 $dm^3\ mol^{-1}\ cm^{-1}$); $[^{99}TcN(Hedta)]$ decomposes in alkaline conditions [13]. The reaction between $[^{99m}TcNCl_4]^-$ and ethylenediamine-*N,N'*-diacetic acid (H_2L) leads to the formation of the technetium(V) species $[^{99m}TcNL_2]^{2-}$ if stannous tartrate is present, but some $[^{99m}TcO_4]^-$ is produced if the reducing agent is absent. The exchange reaction between $[^{99}TcNCl_4]^-$ and H_2L at pH 6.5 follows a similar pattern in the absence of the reducing agent [14].

When $[Bu_4N][TcNCl_4]$ reacts with 1,4,8,11-tetrathiacyclotetradecane, 1,5,9,13-tetrathiacyclohexadecane, 1,5,9,13-tetrathiacyclohexadecane-3,11-diol and 1,4,7,10,13,16-hexathiacyclooctadecane, cationic thia-crown ether complexes are formed and some of their features have been crystallographically confirmed (see section 6.3.2). The counter-ion in some cases is $[TcNCl_4]^-$ [15].

The reactions of the technetium(IV) ions $[TcX_6]^{2-}$ (X = Cl or Br) with $(NSCl)_3$ lead to technetium(III) anions (described in section 6.5) which spontaneously decompose to nitrido technetium(VI) species. The structure of $[Ph_4P][TcNBr_4]$ has been determined at 185 K. The $[TcNBr_4]^-$ anion (4) has the expected square-based pyramidal geometry with the nitrido group in the axial site [16].



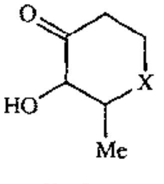
(4)

6.3 TECHNETIUM(V)

6.3.1 Oxo complexes

The mass spectrometric investigation described in section 6.1 also includes the oxide Tc_2O_5 [4].

The complexes $[TcOL_2Cl]$ where HL = (5) have been synthesised from $[TcOCl_4]^-$ under non-aqueous conditions. The anion $[TcOLCl_3]$ for HL = (5) with X = O has also been prepared. The new technetium(V) oxo complexes have been characterised by IR and ^{1}HNMR spectroscopies and from mass spectrometric data. The crystal structure of $[Bu_4N][TcOLCl_3]$ has been elucidated; the anion (6) has a distorted octahedral geometry. Acetonitrile-d_3 solutions of the complexes in which X = O have been treated with D_2O, and the initial hydrolysis occurs in a fast step; further (slow) hydrolysis follows [17].



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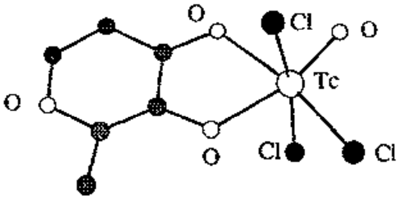
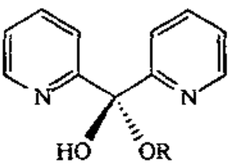
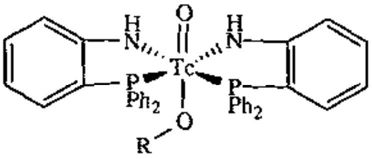


(6)

The complexes $[TcOLCl_2]$ [HL = (7)] are formed by reacting $[TcOCl_4]^-$ with di-2-pyridylketone in ethanol (under N_2 with trace amounts of water for R = Et) or in air (for R = H). During reaction, the coordinated diketone apparently undergoes addition of H_2O and EtOH at the carbonylic carbon, and in the final product, L^- is a *N,O,N'*-donor. The compounds $[TcOLCl_2]$ have been characterised by elemental analysis, and electronic, ^{1}H NMR and vibrational spectroscopies. Additional confirmation comes from an X-ray structure analysis of the rhenium analogue [18].



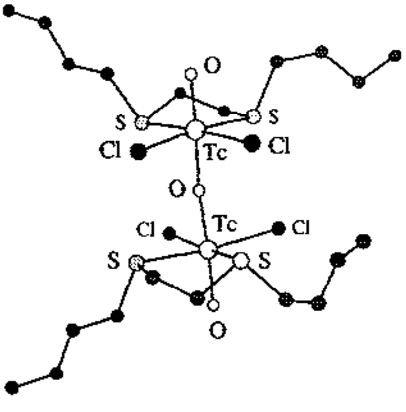
(7) R = H or Et



(8) R = Me or Et

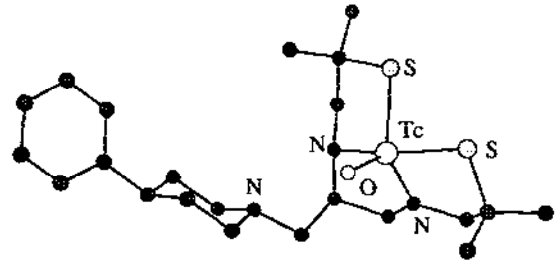
The syntheses and reactivities of the cations $[Tc(O)_2L_2]^+$ (L = en or 1,3-diaminopropane) have been described. Comparisons with the rhenium analogues reveal similarities between the rhenium and technetium species, in particular, with regard to stabilities in solution at varying pH, substitution kinetics, lipophilicity and protein binding [19]. With $2\text{-}PPh_2C_6H_4NH_2$, $[TcO_4]^-$ reacts to give the complexes (**8**) which have been characterised spectroscopically and by an X-ray diffraction study for R = Me. In the IR spectrum, absorptions assigned to ν(Tc=O) appear at 878 cm^{-1} for R = Me, or 857 cm^{-1} for R = Et, and bands at 3303 (R = Me) or 3294 cm^{-1} (R = Et) assigned to ν(NH) are consistent with the presence of the mono-deprotonated ligand [20].

Reactions between $[TcOCl_4]^-$ and a range of didentate thioethers in acetone yield the complexes $[\{TcOLCl_2\}_2(\mu\text{-}O)]$ where L is a dithiaalkane, or $[TcOL'Cl_2]$ where L' is a dithiadiol. The products have been characterised spectroscopically and by elemental analysis, and the crystal structures of $[\{TcOLCl_2\}_2(\mu\text{-}O)]$ for L = 5,8-dithiadodecane, and $[TcOL'Cl_2]$ for HL' = 3,6-dithiaoctan-1,8-diol have been determined. The mononuclear complex possesses a distorted octahedral technetium(V) centre in which the oxo group is *trans* to a deprotonated hydroxy group. The second OH group of the ligand is not coordinated. In the dinuclear complex, shown in structure (**9**), each Tc(V) centre is again octahedrally sited and the Tc=O groups lie *trans* to the oxo bridge [21].



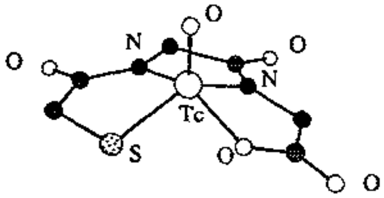
(9)

The reactions of a racemic bis(amino-thio)phenylpiperidine with $[^{99}TcO_4]^-$ and stannous tartrate or with a technetium(V) ethylene glycol precursor yield two neutral isomeric (*syn* and *anti*) complexes both of which have been fully characterised. The structure of the *syn*-isomer is shown in (**10**). Detailed ^{13}C and ^1H NMR spectroscopic studies have been carried out and are consistent with



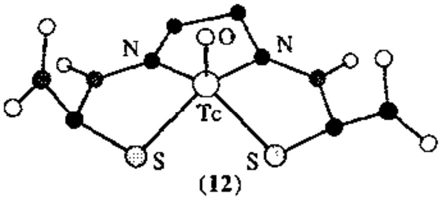
syn
(10)

the retention of the solid state structures in solution [22]. Technetium(V) gluconate reacts with mercaptoacetyl diglycine to give the anionic oxo-complex (**11**). The IR spectrum of (**11**) is characterised by an absorption at 960 cm^{-1} assigned to the mode ν(Tc=O), and the UV-VIS spectrum shows an absorption at λ_{max} 345 nm (lg $\varepsilon_{max} = 3.16$); ^1H NMR spectroscopic data have also been recorded and the structure has been confirmed crystallographically. The technetium(V) centre lies 0.756Å above the plane of the *S,N,N',O*-donor set and pertinent bond lengths are Tc-O_{oxo} = 1.644Å and in the equatorial plane Tc-O = 2.016Å, Tc-S = 2.271Å, and Tc-N = 1.968Å (twice) [23]. Derivatives of mercaptoacetyltriglycine in which one or more gly moieties are replaced by D-ala, L-ala, D-ser or D-val have been prepared and labelled with ^{99m}Tc. In each complex, the technetium labelling generates two radioactive species; since the ligands are chiral, it seems reasonable that these are diastereomeric pairs of the oxotechnetium(V) complexes [24].



(11)

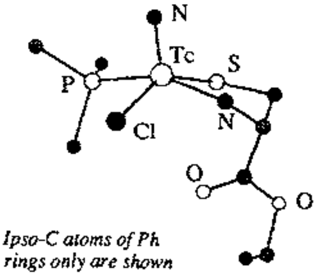
The ligands PhC(O)SCHRC(O)NHCH$_2$CH$_2$NHC(O)CHRSC(O)Ph (R = CH$_2$CO$_2$Me or CO$_2$Et) and PhC(O)SCH(CO$_2$Me)CH$_2$C(O)NHCH$_2$CH$_2$NHC(O)CH$_2$CH(CO$_2$Me)SC(O)Ph have been prepared and their potential as radiopharmaceuticals has been assessed. Complex formation with ^{99m}Tc takes place to give compounds that are stable for up to 6 hours. The salt [AsPh$_4$][^{99}TcOL] (H$_4$L = HSCH(CO$_2$Et)C(O)NHCH$_2$CH$_2$NHC(O)CH(CO$_2$Et)SH) has been structurally characterised; in the anion (**12**) the Tc-O bond length is 1.667(11)Å, and Tc-N and Tc-S distances are 2.002(12), 1.984(12)Å and 2.300(5), 2.286(5)Å respectively [25].



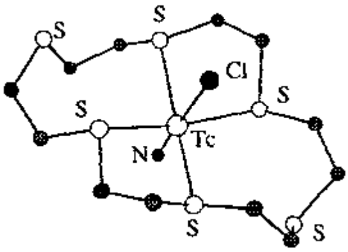
(12)

6.3.2 Nitrido complexes

The air-stable, diamagnetic complexes [TcNClL(PPh$_3$)] (HL = L-cysteine ethyl ether or L-cysteine) and [TcNL'$_2$] (HL' = cysteamine) have been prepared by adding the ligand to solutions of [TcNCl$_2$(PPh$_3$)$_2$] in CH$_2$Cl$_2$ and MeOH pre-heated to 40°C. Characterisation by elemental analysis and IR spectroscopy [ν(Tc≡N) 1060-1090 cm^{-1}, and confirmation of an uncoordinated carboxyl group] has been complemented by an X-ray diffraction study of [TcNClL(PPh$_3$)] (**13**) (HL = L-cysteine ethyl ether). Scintigraphic studies in rats have demonstrated a high renal uptake [26].

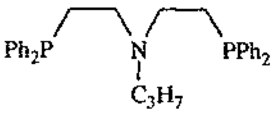


(**13**)

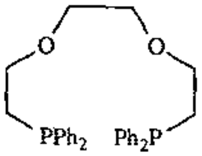


(**14**)

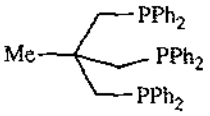
Reactions of [Bu$_4$N][TcNCl$_4$] with the macrocyclic ligands 1,4,8,11-tetrathiacyclotetradecane, 1,5,9,13-tetrathiacyclo-hexadecane, 1,5,9,13-tetrathiacyclohexadecane-3,11-diol and 1,4,7,10,13,16-hexathiacyclooctadecane have been investigated. The product types are represented in the structurally characterised compounds [TcNClL][TcNCl$_4$] (L = 1,4,8,11-tetrathiacyclotetradecane or 1,4,7,10,13,16-hexathiacyclooctadecane) and [TcNClL']Cl (L' = 1,5,9,13-tetrathiacyclohexadecane-3,11-diol). In the cation [TcNCl(1,4,8,11-tetrathiacyclotetradecane)]$^+$, the technetium(V) centre is in a distorted octahedral environment and the strong *trans*-influence of the nitrido ligand is reflected in a long Tc-Cl bond (2.718Å). The structure of [TcNCl(1,4,7,10,13,16-hexathiacyclooctadecane)]$^+$ is shown in (**14**); two of the six sulfur donor atoms in the macrocycle are not coordinated to the metal centre. In [TcNCl(1,5,9,13-tetrathiacyclohexadecane-3,11-diol)]Cl the Tc≡N bond is unusually long (1.95Å); the structure also shows that the OH groups of the ligand are pendant [15].



(**15**)



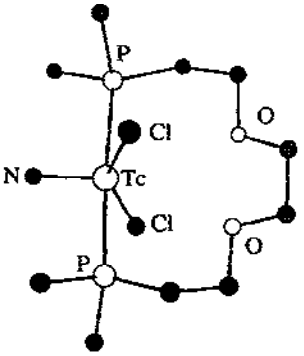
(**16**)



(**17**)

The technetium(V) nitrido complexes [TcNCl$_2$L] where L = (**15**)-(**17**) have been synthesised from [TcNCl$_4$]$^-$ or [TcNCl$_2$(PPh$_3$)$_2$]. The new products react with *O*-ethyl dithiocarbonate to yield [TcN(S$_2$CO)L] and with K[S$_2$CNEt$_2$] to give [TcN(S$_2$CNEt$_2$)$_2$L]$^+$ and [TcN(S$_2$CNEt$_2$)$_2$]. The crystal structures of [TcNCl$_2$(**15**)] and [TcNCl$_2$(**16**)] have been elucidated.

The former possesses a square pyramidal technetium(V) centre (Tc≡N = 1.60Å) whilst the latter, shown in structure (**18**), exhibits an unusual trigonal bipyramidal geometry (Tc≡N = 1.60Å) [27].



Ipso-C atoms of Ph rings shown.

(**18**)

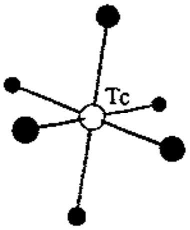
The reaction between $[^{99m}TcNCl_4]^-$ and ethylenediamine-*N,N'*-diacetic acid (H_2L) gives the technetium(V) species $[^{99m}TcNL_2]^{2-}$ (see section 6.2). The UV-VIS and IR spectroscopic characteristics, and electrophoretic and chromatographic properties of the product have been reported [14].

6.3.3 *Sulfido complexes*

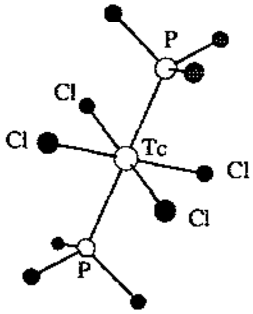
Treating $[TcCl_6]^{2-}$ with H_2edt ($HSCH_2CH_2SH$) leads to the formation of the anion $[TcS(edt)_2]^-$ (see also section 6.8) — this is one of two examples of the first complexes with terminal Tc=S groups. The second is $[TcSCl_2(HBpz_3)]$ which is the product of the reaction between the oxo-analogue of this compound and B_2S_3 [28].

6.4 *TECHNETIUM(IV)*

The crystal structures of the 1,1-dimethyl-3-oxobutyltris(4-methylphenyl)phosphonium salt of the hexachlorotechnetium(2–) anion (**19**) and the complex *trans*-bis(trimethylphosphine)-tetrachlorotechnetium (**20**) have been determined [29].



(**19**)



(**20**)

6.5 TECHNETIUM(III)

An investigation of the base hydrolysis of the complex [Tc(acac)$_3$] in NaOH solutions of varying concentrations (0.1–1M) and at various temperatures has concluded that the rate of decomposition of this technetium(III) compound follows the law given in equation (iv) where (at 298 K) $k_1 = (1.67 \pm 0.11) \times 10^{-5}$ dm^3 mol^{-1} s^{-1} and $k_2 = (1.71 \pm 0.14) \times 10^{-5}$ dm^6 mol^{-2} s^{-1} [30].

$$-\frac{d[\mathrm{Tc(acac)_3}]}{dt} = \left\{k_1[\mathrm{OH^-}] + k_2[\mathrm{OH^-}]^2\right\}[\mathrm{Tc(acac)_3}] \qquad \text{(iv)}$$

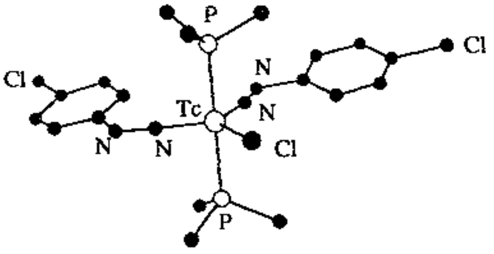
The preparation and characterisation of the complex [Tc(*S*acac)$_2$(en)(PPh$_3$)$_2$][PF$_6$].2H$_2$O have been described; IR, UV-VIS and ^{1}H NMR spectroscopic data are presented, and biodistribution studies have shown that there is a significant uptake into the heart but that hepatic elimination and clearance from the blood are slow [31].

Several technetium(III) complexes with nitrogen donor ligands have been reported. The reactions of [TcCl$_6$]$^{2-}$ and [TcBr$_6$]$^{2-}$ with (NSCl)$_3$ lead to the formation of [Tc(NS)X$_4$]$^-$ (X = Cl or Br), the equatorial ligands in which are kinetically labile; taking the thionitrosyl group as a neutral ligand, the anions are categorised as technetium(III) species. This allows the preparation of the mixed halide complexes [Tc(NS)Cl$_n$Br$_{4n}$]$^-$ and the anion [Tc(NS)(NCS)$_4$]$^-$. Electron spin resonance spectroscopic data have been recorded for the new products. Spontaneous decomposition occurs to give technetium(VI) nitrido complexes as illustrated in equation (v) and this formulation has been confirmed by the results of an X-ray diffraction study (see section 6.2) [16].

$$8[\mathrm{Tc(NS)X_4}]^- \rightarrow 8[\mathrm{TcNX_4}]^- + \mathrm{S_8} \qquad \text{(v)}$$

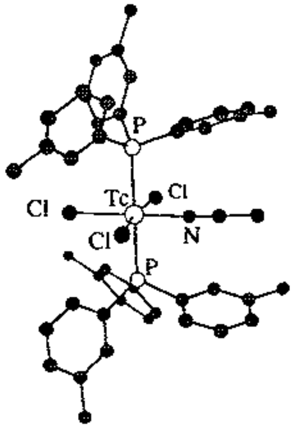
The treatment of [TcOCl$_4$] with hydrazines yields diazenido compounds which further react with PPh$_3$ to give the complexes [TcCl(NNR)$_2$(PPh$_3$)$_2$] (R = Ph, 4-ClC$_6$H$_4$ or 4-MeC$_6$H$_4$) and [TcCl$_2$(NNR)(PPh$_3$)$_2$] (R = 4-NO$_2$C$_6$H$_4$). Other preparative routes involve the use of [TcO$_4$]$^-$ as the precursor. The crystal structure of [TcCl(NNC$_6$H$_4$-4-Cl)$_2$(PPh$_3$)$_2$] (**21**) has been determined and reveals a trigonal pyramidal technetium(III) centre with axial PPh$_3$ ligands. Derivatisation with dppe in place of the monodentate phosphine leads to the complex cations [TcCl(NNR)(dppe)$_2$]$^+$ (R = Ph, 4-ClC$_6$H$_4$ or 4-NO$_2$C$_6$H$_4$) and an octahedral coordination sphere has been confirmed by an X-ray diffraction analysis of [TcCl(NNPh)(dppe)$_2$][PF$_6$].H$_2$O. The dppe *P*-donor atoms occupy the equatorial plane; the bond parameters for the (bent) PhNN$^-$ ligand are ∠Tc-N-N = 163°, Tc-N = 1.917Å and N-N = 1.25Å [32].

Reduction of the technetium(IV) complex [TcCl$_4$(PPh$_3$)$_2$] with zinc in acetonitrile and in the presence of PPh$_3$ leads to the formation of the technetium(III) compound [TcCl$_3$(MeCN)(PPh$_3$)$_2$]. For crystallographic confirmation of the structure, crystals of the analogous complex [TcCl$_3$(MeCN){P(C$_6$H$_4$-3-Me)$_3$}$_2$] (**22**) have been grown and studied; the technetium(III) centre is in a distorted octahedral site with *mer*-chloride and *trans*-phosphine ligands. The complex [TcCl$_3$(MeCN)(PPh$_3$)$_2$] reacts with bpy, phen and terpy (terpy = 2,2':6',2"-terpyridine) to yield technetium(II) species $[TcL_3]^{2+}$ (L = bpy or phen) or $[Tc(terpy)_2]^{2+}$ (see section 6.6). The results of electrochemical studies have also been reported [33]. The technetium(III) complex cation $[Tc(phen)_3]^{3+}$ has been prepared and characterised [34].



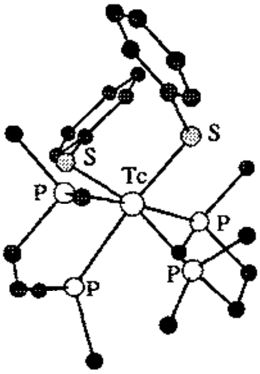
Ipso C-atoms only shown for Ph rings

(21)

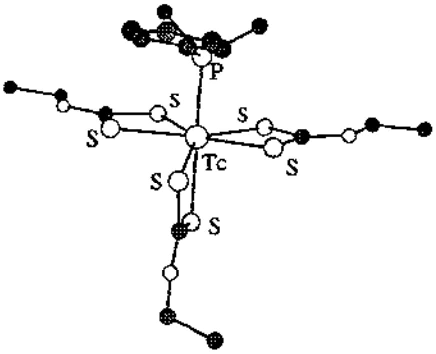


(22)

Moving to ligands with sulfur and phosphorus ligands takes us to the reactions of the technetium(V) dication *trans*-$[Tc(OH)(O)(dmpe)_2]^{2+}$ with HSC_6H_4-4-X (HL with X = H, Cl, Me, OMe or ${}^tBu$) under basic conditions which lead to the formation of *cis*-$[TcL_2(dmpe)_2]^+$. These technetium(III) complex cations have been characterised from mass spectrometric data, the results of electrochemical studies and electronic spectra. In each complex, the visible region of the spectrum shows CT bands that are diagnostic of a *cis* geometry. The crystal structure of the $[PF_6]^-$ salt of *cis*-$[Tc(SPh)_2(dmpe)_2]^+$ **(23)** has been determined; pertinent bond lengths are Tc-S(av.) = 2.29Å, Tc-$P_{trans\text{-}P}$ = 2.42Å and Tc-$P_{trans\text{-}S}$ = 2.49Å [35]. Further investigations of sulfur-donor ligands have included ethylxanthate and *O,O'*-dimethyldithiophosphate ligands. Potassium ethylxanthate and ammonium *O,O'*-dimethyldithiophosphate react with $[TcCl_3(PPhMe_2)_3]$ to give $[Tc(EtOCS_2)_3(PPhMe_2)]$ and $[TcCl_2\{P(OMe)_2S_2\}(PPhMe_2)_2]$ respectively. Structural data for



(23)

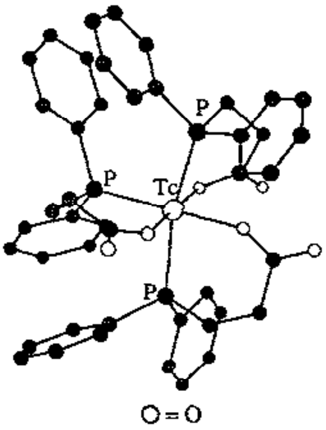


(24)

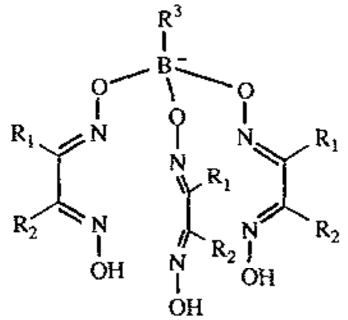
both have been obtained; in $[TcCl_2\{P(OMe)_2S_2\}(PPhMe_2)_2]$ the technetium(III) centre is octahedrally coordinated with the chloride ligands being mutually *trans*, whilst $[Tc(EtOCS_2)_3(PPhMe_2)]$ **(24)** has a pentagonal bipyramidal geometry with the phosphine ligand occupying an axial site [36].

In the presence of $[TcO(OH)(dmpe)_2]^{2+}$ and in acidic solution, an excess of dmpe reacts with dithiocarbamates to give the zwitterion $^-SCH_2P^+Me_2CH_2CH_2P(S)Me_2$ (L). The technetium(III) complex $[TcL_2(dmpe)_2]^{3+}$ has been isolated as the hexafluorophosphate salt and characterised by elemental analysis, UV-VIS spectroscopy and X-ray diffraction. The technetium centre is octahedrally sited with distances (average) of Tc-S = 2.299Å and Tc-P = 2.437Å. Electrochemical data have been recorded for the complex; it exhibits a reversible Tc(III)/Tc(II) couple at –0.311 V (vs. Ag/AgCl) and a chemically irreversible Tc(II)/Tc(I) couple at –1.310 V [37].

Technetium(III) complexes containing a series of ligands which function as *P,O*-donors have been prepared; they are of the general type $[TcL_3]$ in which HL = $Ph_2PCH_2CH_2CO_2H$, $Ph_2PCH_2CO_2H$ or 2-PPh_2-$C_6H_4CO_2H$, or NaL = $Et_2PCH_2CH_2CO_2Na$. The products have been characterised by elemental analysis, IR, UV-VIS and ^1H NMR spectroscopies and mass spectrometry, and the structure of *mer*-$[Tc(Ph_2PCH_2CH_2CO_2)_3]$ **(25)** has been confirmed by X-ray crystallography. Further reactions involving ^{99m}Tc have been studied, and the biodistributions in rats injected with $[^{99m}TcL_3]$ have been assessed — there is a low (but significant) brain uptake [38].



(25)

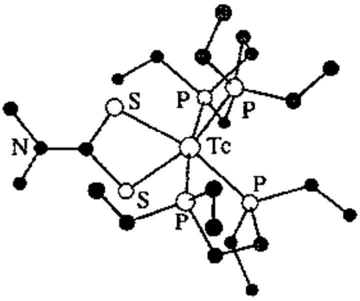


$R^1 = R^2 = Me$; R^1-$R^2 = (CH_2)_4$
R^3 = Me, Et, Bu, ^iBu, Ph, OH
(26)

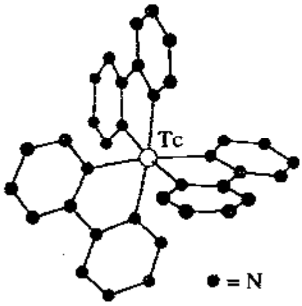
Previous reviews in this series [1] have described BATO-compounds of technetium and 1993 saw another contribution to this area — complexes of the BATO ligands H_3L^- **(26)** of the type $[Tc(H_2L)X]$ (X = Cl, Br or OH) have been prepared. A seven-coordinate geometry is proposed; the complexes have been investigated by CV d.c. polarography and controlled-potential coulometry/bulk electrolysis in dmf solution. For X = Cl or Br, each complex exhibits a 2-electron reduction whilst for X = OH, two consecutive 1-electron reductions are observed. However, it would appear that the redox changes are inaccessible biologically [39].

6.6 TECHNETIUM(II)

The synthesis, characterisation (including elemental analysis, mass spectrometry and UV-VIS spectroscopy) and electrochemical properties of the technetium(II) species $[TcL(depe)_2]^+$ (depe = $Et_2PCH_2CH_2PEt_2$; L^- = dimethyldithiocarbamate, diethyldithiocarbamate and pentamethylene-dithiocarbamate) have been reported. An octahedral environment for the metal centre has been confirmed crystallographically in $[TcL(depe)_2]^+$ **(27)** where L^- is dimethyldithiocarbamate; the hexafluorophosphate salt was studied and some bond distances are Tc-S = 2.449(6)Å, $Tc\text{-}P_{trans\text{-}P}$ = 2.43(2)Å and $Tc\text{-}P_{trans\text{-}S}$ = 2.38(2)Å. Each complex shows a reversible Tc(II)/Tc(I) couple between −0.517 and −0.544 V (vs. Ag/AgCl) and a reversible Tc(III)/Tc(II) couple in the range +0.298 to +0.312 V (in 0.5M Et_4NClO_4/dmf) [40]. The rates of reactions between the outer-sphere reductant $[Tc(dmpe)_3]^+$ (or its rhenium analogue) and the ions $[NpO_2]^{2+}$ and $[PuO_2]^{2+}$ in basic carbonate media have been investigated; the self-exchange rates for the Ac(VI)/(V) (Ac = actinide) couple have been determined by use of Marcus cross relations [41].



(27)

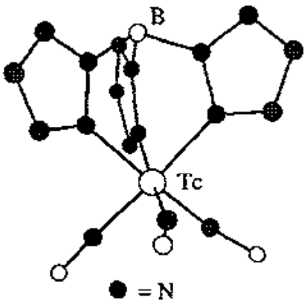


(28)

The technetium(III) complex $[TcCl_3(MeCN)(PPh_3)_2]$ (see section 6.5) reacts with bpy, phen and terpy (terpy = 2,2':6',2"-terpyridine) to give $[TcL_3]^{2+}$ (L = bpy or phen) or $[Tc(terpy)_2]^{2+}$. Characterisation of these the technetium(II) species includes an X-ray diffraction analysis of $[Tc(bpy)_3][PF_6]_2$. In the cation **(28)**, the technetium(II) centre is octahedrally coordinated as expected and the Tc-N bond lengths are 2.077 Å [33].

6.7 TECHNETIUM(I)

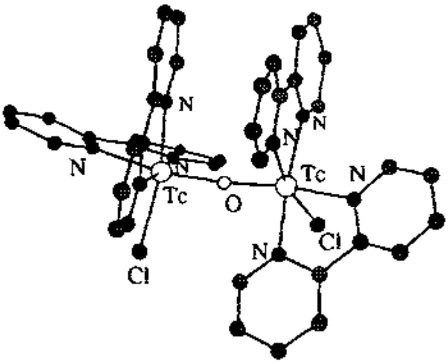
The preparations of the technetium(I) pyrazolylborate compounds $[Tc(HBpz_3)(CO)_3]$ **(29)** and $[Tc(HBpz^*{}_3)(CO)_3]$ have been described. Both compounds have been studied using IR, UV-VIS and ^1H and ^{13}C NMR spectroscopies and mass spectrometry, and additionally, by X-ray crystallography. Octahedral coordination is confirmed with a *fac*-configuration as expected [42].



(29)

6.8 DINUCLEAR COMPLEXES AND HIGHER NUCLEARITIES

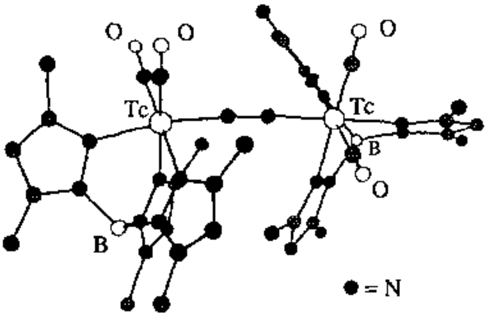
The oxo-bridged complex $[\{TcOLCl_2\}_2(\mu\text{-}O)]$ (9) (L = 5,8-dithiadodecane) and related species were described earlier [21]. Other oxo-species have been reported and here the technetium centres are in intimate electronic communication. These have been prepared from the reactions of $[TcOX_4]^-$ (X = Cl or Br) with bpy or phen (L) in dmf and have the general formula $[\{TcL_2X\}_2(\mu\text{-}O)]X_2$. The IR spectra of the complexes exhibit absorptions in the range 723-730 cm^{-1} assigned to the mode $\nu(TcO)$. The crystal structures of $[\{Tc(phen)_2Cl\}_2(\mu\text{-}O)]Cl_2$, $[\{Tc(bpy)_2Cl\}_2(\mu\text{-}O)]Cl_2$.bpy and $[\{Tc(bpy)_2Br\}_2(\mu\text{-}O)]Br_2$.bpy have been determined and that of the $[\{Tc(bpy)_2Cl\}_2(\mu\text{-}O)]^{2+}$ dication is shown in **(30)**. Each possesses octahedral technetium centres and the angles Tc-O-Tc lie in the range 171.6 to 173.0°. Electrochemical studies have been carried out. Further work shows that at low pH, dioxygen slowly oxidises $[\{Tc(phen)_2(OH)\}_2(\mu\text{-}O)]^{2+}$, but the process is rapid if the oxidising agent is HNO_3 or H_2O_2. The oxidation product is a mixed technetium(III)/technetium(IV) complex which exhibits a low energy absorption band at 959 nm [43].



(30)

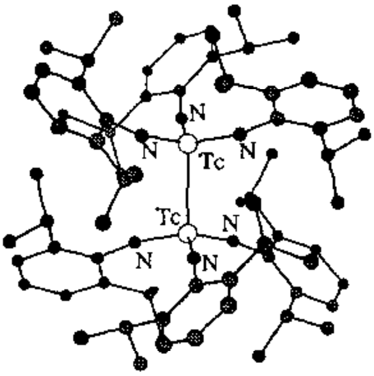
Following from the work described in section 6.7, Joachim *et al* have successfully used $[Tc(HBpz^*_3)(CO)_3]$ as a precursor to a novel example of a dinitrido-bridged ditechnetium complex. Photolysis of $[Tc(HBpz^*_3)(CO)_3]$ in thf in the presence of N_2 leads to the formation of

$[\{Tc(HBpz^*_3)(CO)_2\}_2(\mu\text{-}N_2)]$ (**31**), the structure of which has been crystallographically confirmed (N-N = 1.160Å, ∠Tc-N-N = 174.0°). The results of IR, UV-VIS and ^1H NMR spectroscopic studies are also reported [44].

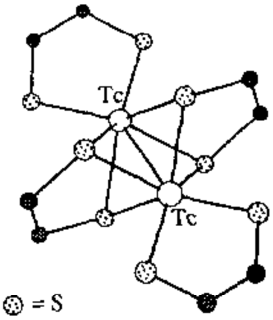


(**31**)

The reaction of 2 equivalents of MeMgCl with $[(ArN)_2Tc(\mu\text{-}NAr)_2Tc(NAr)_2]$ (Ar = 2,6-$Me_2C_6H_4$) leads to the formation of $[Me_2(ArN)Tc(\mu\text{-}NAr)_2Tc(NAr)_2]$. On further treatment with MeMgCl, another two ArN groups can be displaced to give $[Me_2(ArN)Tc(\mu\text{-}NAr)_2Tc(NAr)Me_2]$. This unprecedented result has been confirmed by the results of an X-ray diffraction study, and additionally, ^1H NMR spectroscopic data are reported [45]. Related work centres on the reaction of sodium with $[Tc(NAr')_3I]$ where Ar' = 2,6-$^iPr_2C_6H_4$; the product is the dinuclear compound $[Tc_2(NAr')_6]$ (**32**) and interestingly, the Tc-Tc bond cannot be cleaved (and so the reaction reversed) by treating $[Tc_2(NAr')_6]$ with I_2. The ^1H NMR spectrum of compound (**32**) shows that the imide groups are equivalent and a crystallographic study reveals that the complex possesses an ethane-like structure with the Tc-Tc bond lying along a crystallographic S_6 axis. The Tc-Tc bond length of 2.744(1)Å is consistent with single bond character; the compound is diamagnetic.



(**32**)



(**33**)

Treating $[TcCl_6]^{2-}$ with H_2edt ($HSCH_2CH_2SH$) leads to the formation of the anion $[TcS(edt)_2]^-$ (see also section 6.3.3) with a terminal Tc=S group. Additionally, the dinuclear complex [Tc(edt)$_2$L$_2$] (33) (with H_2L = HSCH=CHS) is produced in the reaction. It is suggested that this product may play an important role in the formation of the $(Tc=S)^{3+}$ unit observed in $[TcS(edt)_2]^-$. The crystal structure of (33) has been elucidated and shows that each technetium centre is in a trigonal prismatic environment if the Tc-Tc connection is excluded from the geometrical description; the ethane-1,2-dithiolato ligands are in the two bridging sites whilst the unsaturated ligands are chelating, one to each technetium atom [28].

Several technetium chalcogenide clusters have been prepared by heating (at 800°C) M_2CO_3 (M = alkali metal) with technetium and sulfur or selenium under argon for 8 hours. Black crystals were extracted with water and ethanol from the cooled melt. The products have been formulated as $[K_4Tc_6S_{12}]$, $[K_4Tc_6Se_{12}]$, $[Rb_4Tc_6S_{13}]$, $[Rb_4Tc_6Se_{12}]$, $[Cs_4Tc_6S_{13}]$ and $[Cs_4Tc_6Se_{13}]$. The structure of each cluster features an octahedral Tc_6-core residing within a cubic S_8- or Se_8-cage, and these Tc_6E_8-units are linked via E or E_2 bridges. The alkali metal cations occupy interstitial sites [47].

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