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COORDINATION CHEMISTRY REVIEWS

Technetium 1994

Catherine E. Housecroft

Contents

1. Introduction

This review covers the coordination chemistry of technetium, published in 1994, and follows the format of the 1993 survey [1]. The literature has been searched using *Current Contents* and the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]. Although not fully comprehensive, this article gives a significant coverage of papers published, although organometallic complexes have been excluded. Medical applications of technetium chemistry are not covered *per se*, but compounds prepared and studied with the expectation of possible applications have been included.

Complexes are organized according to the formal oxidation state of the technetium centre. Technetium(V) chemistry is dominated by oxo- and nitrido-species, and here, for categorization purposes, the presence of the Tc=O or Tc≡N moiety takes preference over the donor atoms in other ligands. *Caution*: ^{99}Tc is a weak β-emitter (E=0.292 MeV, $t_{1/2}$ 2.12×10^5 yr).

A special issue of *Radiochim. Acta* prefaced by Yoshihara [3] and dealing with the behaviour and utilization of technetium has appeared. Within this issue, Lieser

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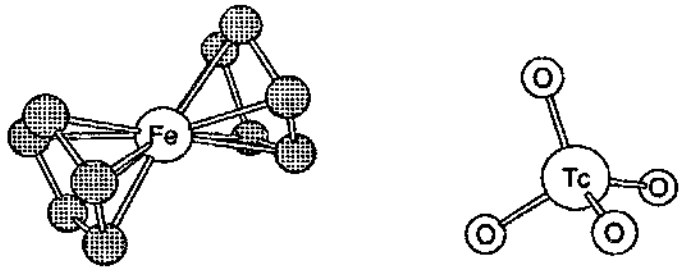
has addressed the formation of ^{99}Tc in nuclear reactors, and has included discussions of the generation of ^{99}Mo and ^{99}Tc nuclides for medicine, and the entry of ^{99}Tc into the environment [4].

2. Technetium(VII)

Gaseous technetium oxide bromides and iodides have been produced in a Knudsen cell at temperatures up to 900°C when solid technetium oxides TcO_x are exposed to Br_2 or I_2 and O_2. Mass spectrometry was used to identify the two dominant products as TcO_3Br and TcO_3I-the iodide is less stable than the bromide. Minor components of the product mixtures were the technetium(VII) compound TcO_2Br_3 and technetium(VI) species TcO_2Br_2 [5].

Two papers describe the ferrocenium salt $[Cp_2Fe][TcO_4]$ (**1**). It may be prepared by ion-exchange of $[Cp_2Fe]^+$ for $[H_3O]^+$ ions in $HTcO_4$ in water. Structural data show that the compound contains isolated cations and anions in the solid state, although fast dynamic electron transfer is observed [6,7].



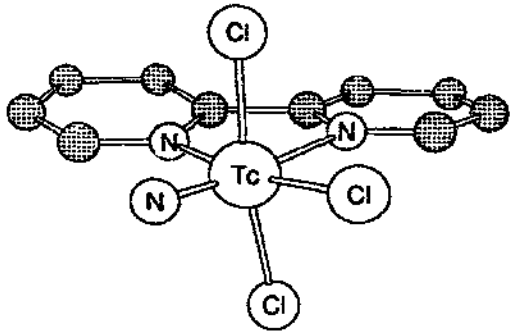
(1)

The extraction of technetium(VII) from nitric acid solution using *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (cmpo) and tributyl phosphate (tbp) in *n*-dodecane or decalin has been investigated. By using the mixed cmpo-tbp system, an enhancement of the technetium extraction was achieved [8]. The transportation of technetium(VII) and rhenium(VII) from feed solutions (pH 0-1.36) to distilled water or 0.5 M $NaHCO_3$ solution using a tbp-decalin membrane supported on a microporous PTFE sheet has been studied. Of the two, the sodium hydrogen carbonate solution provided a greater rate of transport, and a pH of 1 proved to be the most suitable. A permeability coefficient of 11×10^{-4} cm s^{-1} was determined for technetium(VII) at pH 0.74 with a $NaHCO_3$ strip solution [9].

3. Technetium(VI)

The reaction of $[NBu_4][TcNCl_4]$ with bpy leads to the formation of $[Tc^{VI}NCl_3(bpy)]$ if the reaction is carried out in MeCN. In MeOH, the product is

$[Tc^{V}NCl(bpy)]^{2+}$. A *mer*-conformation for $[TcNCl_3(bpy)]$ (**2**) is suggested by the results of EPR spectroscopy and this has been confirmed by an X-ray diffraction study. The coordination environment is a distorted octahedron; the Tc-N(nitrido) bond distance is 166.9(4) pm, and the Tc-N(bpy) bond *trans* to the nitrido ligand is lengthened (237.1(4) pm) as a result of the *trans*-effect [10].



(2)

4. Technetium(V)

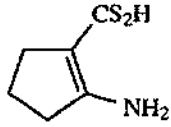
4.1. Oxo complexes

The electrolytic reduction of pertechnetate in aqueous solution containing cyanide ions leads to the formation of $[TcO_2(CN)_4]^{3-}$ as well as $[Tc(CN)_6]^{5-}$ [11]; (see also section 7).

The high-yield syntheses of triakyl ammonium salts of $[TcO(SPh)_4]^-$ from $[TcBr_3(NPh)(PPh_3)_2]$ have been reported. An absorption at 936 cm^{-1} in the IR spectrum of the product is assigned to the $\nu(Tc{=}O)$ mode [12]. Further imido complexes from this study are described in section 4.3. The complex $[NBu_4][TcOCl_4]$ reacts with the diimines 2,3-bis(2-pyridyl)pyrazine (L) and 2,3-bis(2-pyridyl)quinoxaline (L′) in EtOH to give $[TcOCl_2(X)L]$ (X = Cl or OEt), $[Cl_3OTc(\mu\text{-}L)TcOCl_2(OEt)]$ and $[TcOCl_2(X)L']$ (X = Cl or OEt). IR and ^1H NMR spectroscopic data are consistent with the coordination of ligand L through one pyrazine and one pyridine N atom, whereas it is proposed that L′ bonds through two pyridine *N*-donor sites, thereby producing a 7-membered chelate ring [13].

Complex formation of ligand HL = (**3**) and its *N*- and *S*-alkyl derivatives HL′ with technetium(V) has been investigated and products of the type $[TcOClL'_2]$ have been isolated and characterized by ^1H NMR and IR spectroscopies. The ligands act as *N,S*-donors [14].

With the aim of developing potential brain imaging agents, Mastrostamatis *et al.* have studied the reactions of the ligands (**4**), L, with $[^{99}TcOCl_4]^-$. Coordination of



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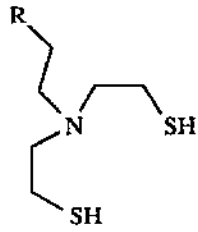
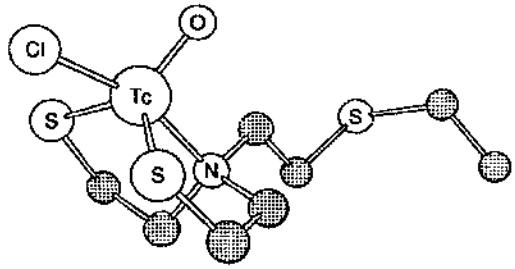


R = EtS or Et_2N

(4)

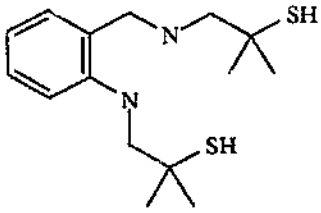
the tridentate ligands (**4**) to the $[TcO]^{3+}$ moiety leaves one coordination site vacant; this may be filled by chloride ion as the complexes [TcOLCl] but if L reacts with a technetium(V) gluconate precursor in the presence of 4-methoxythiophenol (HR′), the product is [TcOLR]. The new complexes have been characterized by UV, IR and ^1H NMR spectroscopies and single crystal X-ray diffraction studies for [TcOLCl] (R = EtS) (**5**) and [TcOLR′] ($R = Et_2N$). Studies of the biodistribution of these complexes in mice have revealed a high initial brain uptake and from the data it should be possible to design suitable structural modifications to enhance these properties [15]. The ^1H and ^{13}C NMR spectra of three of the series of complexes [TcOLCl] and [TcOLR] have been fully assigned [16].



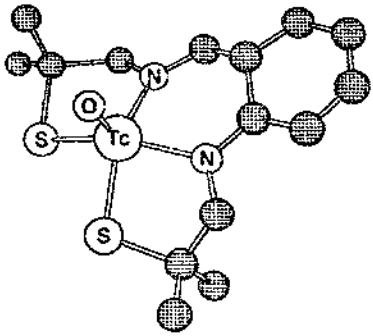
(5)

Ligand (**6**) H_2L possesses two amine substituents with different pK_a values. It reacts with $[^{99m}TcO_4]^-$ in the presence of stannous tartrate to give the technetium(V) complex [TcOL] (**7**) which has been structurally characterized by X-ray crystallography. In the pH range 9-10 and at 100°C, the reaction proceeds to give [TcOL′] (also structurally characterized) in which L′ is the oxidized imine derivative of (**6**). Intravenous injection into rats shows a significant uptake of the complexes into the brain [17].

The preparation and IR spectroscopic and structural characterization of [TcOL] in which L is *N,N′*-bis-1-(carboxy-2-mercaptoethyl)-1,2-diaminoethane have been reported. In the product, the technetium(V) centre is six-coordinate with a Tc=O bond distance of 165.7(3) pm; the ligand is bound in an *N,N′,S′,S′,O*-mode with the carboxylate oxygen atom sited *trans* to the oxo group [18]. The Schiff base



(6)

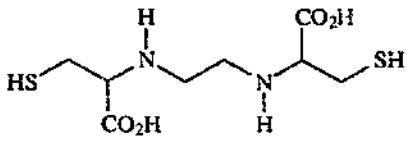


(7)

complex [TcO{2-OC_6H_4CMe=NN=C(S)SMe} {Me_2C=NN=C(S)SMe}] has been prepared from $[TcOCl_4]^-$ in acetone. Crystallographic characterization of the product confirms the involvement in the coordination sphere of the deprotonated phenolic oxygen atom which is sited *trans* to the oxo group. This renders one Schiff base tridentate (*N,O,S*) with the second ligand binding in a didentate *N,S*-mode [19].

Ligand (**8**) H_6L may coordinate to the $[TcO]^{3+}$ moiety in a triply deprotonated form to generate neutral complexes $[TcO(H_3L)]$ in which one carboxyl group is *syn* and the other *anti* with respect to the oxo-group. This complex gives broad ^1H NMR spectra at physiological pH and, this, coupled with a lack of crystallographic data, means that it has not been possible to completely characterize the complex. In the present study, Marzilli *et al.* have addressed the problem of the broad NMR spectroscopic signals and have prepared a related complex with a penicillamine rather than cysteine-based ligand. This reduces the complexity of the observed coupling. From 2D NMR spectroscopic data it has been possible to assign the ^1H NMR spectrum of the new complex, and, additionally, crystallographic data have been obtained. The results show that the coordination of the *anti*-carboxyl group is pH dependent, and the broadening of the spectrum of $[TcO(H_3L)]$ at pH 7 has been attributed to the combined effects of the carboxyl coordination and NH proton dissociation — the deprotonated amine site competes with the carboxyl group as a donor to the metal centre. The solution studies are complemented by molecular mechanics calculations [20].

The reaction of $[^{99}TcO_4]^-$ and ligand (**9**) H_4L leads to the formation of *rac*-



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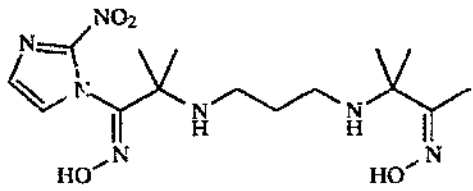

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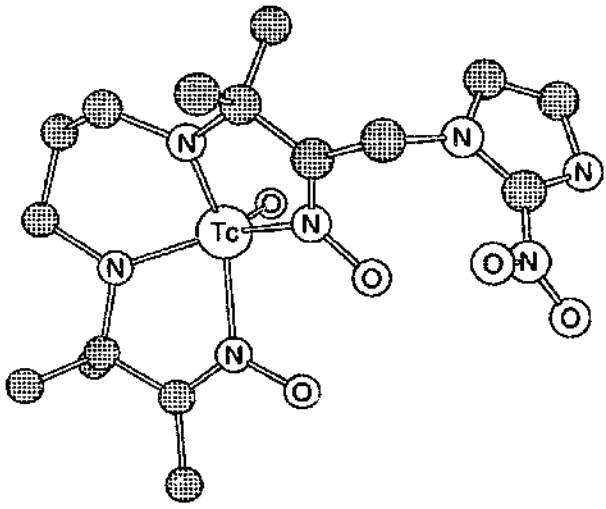


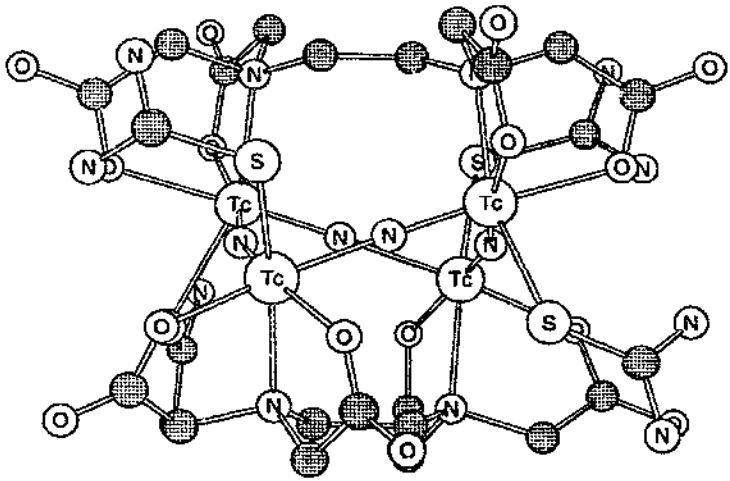
(10)

[TcO(HL)] (**10**), a complex that is also produced by treating $[^{99}TcO(L')_2]^-$ where H_2L' is ethane-1,2-diol. The product has been characterized by IR, UV-VIS and ^1H NMR spectroscopies, HPLC, mass spectrometry and a single crystal X-ray diffraction study. Electrochemical studies have shown that the redox properties of the NO_2 group are retained upon complex formation but the couple shifts to a more positive potential. Chiral HPLC has been used to resolve the enantiomers of [TcO(HL)], but racemization occurs rapidly in water ($t_{1/2} < 2$ min) [21].

4.2. Nitrido complexes

The reaction of the technetium(V) thiourea complex $[TcN(tu)_4Cl]Cl$ with $Na_2[edtaH_2]$ in aqueous solution results in the formation of $[\{TcN(tu)\}_4(edta)_2]\cdot 6H_2O$ (**11**) — the first example of a cyclic nitrido-bridged tetrameric technetium complex. The structure has been crystallographically elucidated; the bridges are asymmetrical with Tc-N distances in the ranges 168.1-169.5(7) and 197.7-200.9(7) pm. Compound (**11**) is soluble in water and a range of organic solvents (*e.g.* EtOH, MeCN, CH_2Cl_2, dmf) and in the IR spectrum, an absorption at 984 cm^{-1} is assigned to the $\nu(Tc\equiv N)$ mode [22].

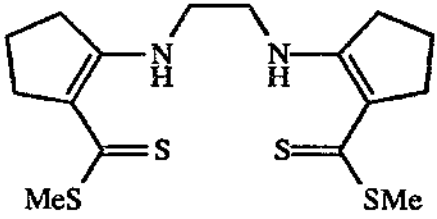
The synthesis of the complex $[^{99}TcNL]$ where H_2L=(**12**) from $[^{99}TcNCl_2(PPh_2)_2]$ has been described. The product has been characterized by elemental analysis, IR and NMR spectroscopies, conductivity measurements and an X-ray diffraction study. The metal centre is in a pseudo-square-based pyramidal environment with the nitrido ligand occupying the apical site and the ligand adopting an *N,N',S,S'*-mode. Pertinent bond distances are Tc≡N = 162.9(7), Tc-N = 208.2(7),



Six hydrate molecules omitted

(11)

210.1(8), Tc-S=236.39(29), 236.43(22) pm. The electrochemical properties of [^{99}TcNL] have also been investigated [23].



(12)

4.3. Imido complexes

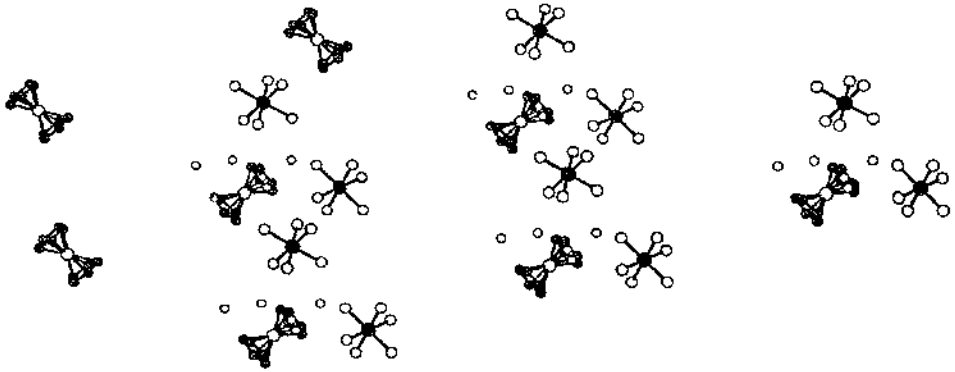
The imido complex $[TcBr_3(NPh)(PPh_3)_2]$ has been prepared from $K[TcO_4]$, PPh_3, 1-acetyl-2-phenylhydrazine and HBr, and in the presence of a tertiary amine and in methanol, it reacts with thiophenol to give $[R_3NH][TcO(SPh)_4]$. The chloro complex $[TcCl_3(NPh)(PPh_3)_2]$ reacts with a 4-fold excess of the sterically hindered 2,3,5,6-tetramethylbenzenethiol (HL) in the presence of a proton scavenger to yield $[Tc(NPh)L_3(PPh_3)]$. With a 5-fold excess of 2,6-dimethylbenzenethiol HL′ (again with a proton scavenger), the imido complex $[Tc(NPh)L'_4]$ is produced. When $[TcCl_3(NPh)(PPh_3)_2]$ is treated with $P(C_6H_4SH\text{-}2)_3$ in the presence of a proton sponge, reduction occurs and the product is the technetium(III) complex

$[Tc(PPh_3)\{P(C_6H_4S\text{-}2)_3\}]$, Infrared and mass spectrometric data are reported, as well as the ^1H NMR spectrum of $[Tc(PPh_3)\{P(C_6H_4S\text{-}2)_3\}]$ [12].

Further imido complexes are discussed in section 9, and technetium(V) complexes involving diazenido ligands are described along with related technetium(III) species in section 6.

5. Technetium(IV)

A new complex containing the anion $[TcCl_6]^{2-}$ has been prepared and structurally characterized-$[Cp_2Fe]_4[H_3O]_2[TcCl_6]_3$. The crystal lattice contains isolated cations and anions as figure (13) illustrates [24].



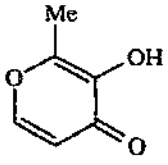
Hydrogen atoms are omitted.

(13)

6. Technetium(III)

A method of preparing mixed ligand β-diketonate complexes of technetium(III) has been detailed. The strategy is a ligand exchange reaction starting from $[Tc(acac)_2(NCMe)_2]^+$ and has been shown to be successful for the ligands such as $PhC(O)CH_2C(O)Ph$, $PhC(O)CH_2C(O)Me$ and $^tBuC(O)CH_2C(O)^tBu$ [25].

Treatment of $[TcCl(NNR)_2(PPh_3)_2]$ ($R=4\text{-}ClC_6H_4$) with $Na[Me_2NCS_2]$ leads to the formation of the complex $[Tc(NNR)(S_2CNMe_2)_2(PPh_3)]$. Similar ligand displacements have been carried out using, for example, salenH_2 and ligand (**14**). Using $[TcO_4]^-$ as the precursor, the technetium(V) complexes $[TcCl(NNR)_2(S_2CNMe_2)_2]$, $[Tc(NNR)_2L_2]Cl$ for HL=(**14**), $[TcCl(NNR)(bpy)_2][BPh_4]$, $[TcCl_2(NNR)L'(NH_3)]$ for H_2L'=(**15**), and $[TcCl(NNR)L''][BPh_4]$ for H_2L''=(**16**) have been prepared and characterized by IR and ^1H NMR spectroscopies and elemental analyses; the HPLC retention times of the products have been reported [26].



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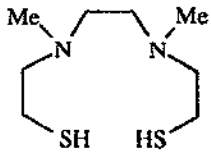
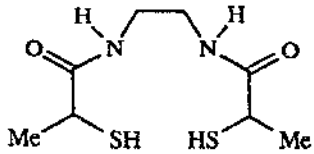


(15)



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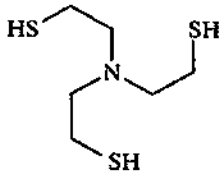

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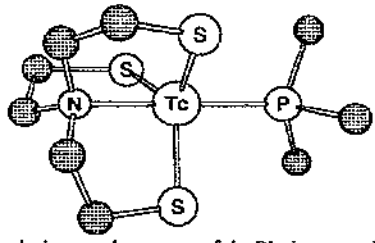


Only the ipso-carbon atoms of the Ph rings are shown

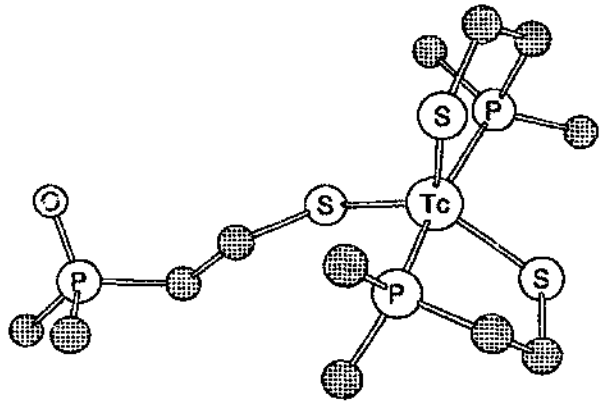
(18)

The reaction of $K[TcO_4]$ with H_3L (**17**) in the presence of PPh_3 leads to the formation of the technetium(III) complex $[TcL(PPh_3]$ (**18**), the single crystal structure of which has been determined. The metal centre is in a trigonal bipyramidal environment with the nitrogen donor and the PPh_3 ligand occupying the axial sites. Complex (**18**) may also be obtained from the reaction of $[TcCl_3(PPh_3)_2(NCMe)]$ with H_3L, but in this reaction, a minor product is $[TcL(PPh_3)_2]$. Only ^1H NMR spectroscopic data are available for this product, proposed to have an octahedral structure [27].

The technetium(III) complex $[Tc(PPh_3)\{P(C_6H_4S\text{-}2)_3\}]$ was mentioned in section 4 [12]. The formation of complexes involving other potentially *S,P*-donor ligands have also been investigated. The thiolates L^- ($HL=Ph_2PCH_2CH_2SH$ or $Ph_2PCH_2CH_2CH_2SH$) react with $[TcO_4]^-$ to yield neutral, diamagnetic, five-coordinate technetium(III) complexes $[TcL_2(L{=}O)]$. When HL is 2-$Ph_2PC_6H_4SH$, the six-coordinate complex $[TcL_3]$ is formed. The crystal structure determination of $[TcL_2\{Ph_2P(O)CH_2CH_2S\}]$ (**19**) confirms the oxidation of the phosphine group of one ligand and its pendant bonding mode in the complex. All the products have been characterized by elemental analyses, IR, UV-VIS and ^1H and ^{31}P NMR spectroscopies, mass spectrometry and cyclic voltammetric measurements [28].

7. Technetium(II)

When the technetium(III) complex $[TcCl_3(PMe_2Ph)_3]$ reacts with an excess of dmpe, reduction occurs and the product is the technetium(II) complex $[TcCl_2(PMe_2Ph)_2(dmpe)]$. A crystal structure determination confirms that the coordination sphere is octahedral, and the chloro ligands are mutually *trans* (Tc-Cl=



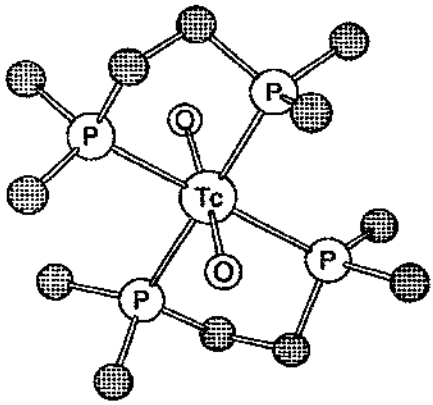
(19)

243.1(5)pm). The Tc-P bond distances lie in the range 239.8-243.5(4) pm and the data suggest that there is a decrease in the degree of Tc-P multiple bonding character as the oxidation state of the metal decreases [29].

The electrolytic reduction of pertechnetate in aqueous solution in the presence of π-acceptor ligands provides a method of preparing technetium complexes for several oxidation states — in the presence of cyanide ions, $[TcO_2(CN)_4]^{3-}$ and $[Tc(CN)_6]^{5-}$ are formed, and in the presence of 1,10-phenanthroline, the technetium(II) cation $[Tc(phen)_3]^{2+}$ is produced [11].

8. Technetium(I)

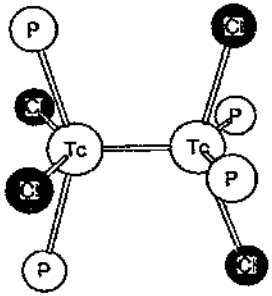
The preparation of $[Tc(CN)_6]^{5-}$ was mentioned above. Other technetium(I) complexes reported in 1994 included [TcCl(dppe)] formed by treating $[TcCl_4(PPh_3)_2]$ with zinc in the presence of dppe. The complex [TcCl(dppe)] is very air sensitive but is stable under helium or argon atmospheres. Under dinitrogen, it forms $[Tc(N_2)Cl(dppe)]$ but when heated in toluene, this complex loses N_2 again. With dihydrogen, [TcCl(dppe)] reacts to give $[Tc(H_2)Cl(dppe)]$, but again, the uptake of the diatomic molecule is reversible. $[Tc(H_2)Cl(dppe)]$ represents the first example of an η^2-H_2 complex of technetium and it has been characterized by ^{1}H NMR spectroscopy and crystallography. The H_2 ligand lies *trans* to the chloro group, but the molecule is disordered with respect to these sites [30]. The single crystal structures of *trans*-$[Tc(H_2O)_2(dppe)_2][BPh_4]$ (**20**) [31] and *trans*-$[TcCl(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}_2]$ (in which the nitrosyl and chloro ligands are disordered) [32] have been determined.



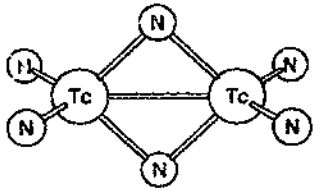
Only the ipso-carbon atoms of the Ph rings are shown
(20)

9. Dinuclear complexes with metal-metal bonds

The multiply bonded dimers $[Tc_2Cl_4(PR_3)_4]$ have been prepared and characterized for $PR_3 = PEt_3$, P^nPr_3, $PMePh_2$ and PMe_2Ph. The synthetic strategy involves the 2-electron chemical reduction of $[TcCl_4(PR_3)_2]$. Structural data for $[Tc_2Cl_4(PEt_3)_4]$, $[Tc_2Cl_4(PMePh_2)_4]$ and $Tc_2Cl_4(PMe_2Ph)_4]$ show that the molecules possess an eclipsed conformation with D_{2d} symmetry as shown in structure **(21)**. The Tc-Tc bond distances in the three compounds are 213.3(3) pm (PEt_3), 212.7(1) pm (PMe_2Ph) and 213.84(5) pm ($PMePh_2$). Taken with the spectroscopic results, these structural data suggest the presence of Tc≡Tc triple bonds with a $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration in the ground state. Electrochemical studies have shown that each dimer undergoes two reversible one-electron oxidation processes [33].



$Tc_2Cl_4P_4$ core only
(21)



Tc_2N_6 core only
(22)

The reduction of the imido complex $[Tc(NAr)_3I]$ (Ar = 2,6-$Me_2C_6H_4$) with sodium results in the formation of the dinuclear compound $[Tc_2(NAr)_4(\mu\text{-}NAr)_2]$, the core of which is shown in structure **(22)**. When the more sterically hindered

$[Tc(NAr')_3I]$ ($Ar' = 2,6\text{-}^iPr_2C_6H_4$) is reduced in a similar reaction, the product is $[Tc_2(NAr')_6]$ which possesses an ethane-like Tc_2N_6 core. Both ditechnetium compounds have been crystallographically characterized. Further reduction of $[Tc_2(NAr')_6]$ leads to cleavage of the metal-metal bond and the formation of $[Tc(NAr')_3]^{3-}$. This anion reacts with $HgBr_2$ to yield the heterometallic species $[(Ar'N)_3TcHgBr]$ and $[(Ar'N)_3TcHgTc(NAr')_3]$, whilst with $[Ph_3PAuCl]$, the product is $[(Ar'N)_3TcAuPPh_3]$. The structural characteristics of $[(Ar'N)_3TcAuPPh_3]$ and $[(Ar'N)_3TcHgTc(NAr')_3]$ have been confirmed by the results of X-ray diffraction studies. In the former compound, the Tc-Au bond distance is 258.9(1) pm and the Tc-Au-P core is, as expected, linear. The Tc-Hg-Tc core of $[(Ar'N)_3TcHgTc(NAr')_3]$ is linear with Tc-Hg bond distances of 261.5(1) pm. Fenske-Hall molecular orbital calculations have been used to analyse the bonding in the model compound $Tc_2(NH)_6$ having either an ethane-like or bridged structure [34].

10. ^{99m}Tc labelling studies

This final section reports representative papers dealing with ^{99m}Tc labelling studies. A quantitative radio-HPLC method for the analysis of radiolabelled ^{99m}Tc complexes including proteins and antibodies has been developed by Mudduкrishna *et al.* The strategy is the re-oxidation to $[TcO_4]^-$ of reduced column-absorbed ^{99m}Tc species; the oxidizing agent in H_2O_2. Automation of the procedure has resulted in analysis times of $\approx$30 min [35].

After reduction of complex-bound ^{99}Tc by tin(II), complex formation with 2,3-dicarboxypropane-1,1-diphosphonic acid leads to the formation of two complexes which are characterized in their electronic spectra by absorptions at λ_{max} 410 nm (pH 3-7) and λ_{max} 515 nm (pH 5-9.6). The stoichiometries of these complexes have been determined by Job's method to be 2:1 and 2:3, and the oxidation states of the technetium in the complexes have been determined by potentiometric titration — technetium(III) or technetium(IV) is present depending upon the reducing conditions. The results are important within diagnostic nuclear medicine because they address the dependence of ^{99m}Tc radiopharmaceutical complexes on the sequence of reagent addition [36].

Hydroxamamide-based ligands may be useful in respect of designed ^{99m}Tc radiopharmaceutical complexes with chelating ligands. Three such ligands have been studied — benzohydroxamamide, 4-toluhydroxamamide and 4-pyridylhydroxamamide. Radiolabelling using the stannous tartrate method was successful and the resulting ^{99m}Tc-labelled complexes were tested for organ distribution, blood clearance and urinary excretion in mice [37]. A ^{99m}Tc-labelled complex containing the bis(oxime) ligand 2,9-bis(hydroxyimino)-4,7-diaza-5,6-dioxodecane has been prepared. Its protein binding, partition coefficient and tissue distribution have been studied, as have those of two related complexes, but the biodistribution is not exceptional [38]. New methods to synthesize derivatives of the ligand 4,8-diaza-3,3,9,9-tetramethylundeca-2,10-dione dioximes have been developed;

labelled technetium complexes of these ligands are of interest as commercial radiopharmaceuticals [39]. ^{99m}Tc-Labelled complexes containing mercaptacetyltriglycine and related ligands have been investigated. Both direct labelling and ligand exchanges reactions were monitored using radio-TLC separation. Compounds in which there is a strongly polar sulfonyl substituent exhibit lower protein binding than complexes with mercaptacetyltriglycine, and this characteristic makes the former compounds potentially useful as renal agents [40].

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