

## 5. Technetium

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### INTRODUCTION

This review covers the coordination chemistry of technetium reported in the literature in 1991. There has been an over-long period since the last report of technetium chemistry (1983 literature) in this series [1]; a report of medical chemistry appeared in 1987 [2]. A report on the 1990 literature will appear in the near future.

In this survey, complexes of technetium are arranged in sections according to the oxidation state of the technetium centre. For most oxidation states, there are sub-sections dealing with complexes arranged by donor atom. Complexes in the review may appear in more than one section

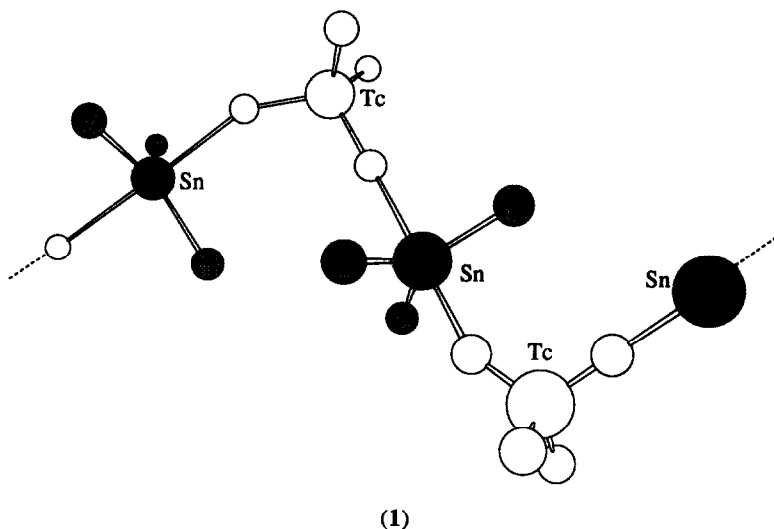
depending upon the ligands present. Medical applications are highlighted where appropriate but papers are not included where the medical uses of the compounds are the prime areas of interest rather than synthetic, structural, spectroscopic, kinetic or reactivity aspects of the complexes. Organometallic complexes have not been included here; a review of the organometallic chemistry of the group 7 metals for the year 1987 appeared in 1991 [3].

An acknowledgement is due to the Cambridge Crystallographic Data Centre for providing atomic coordinates for structures which have been redrawn for this review; hydrogen atoms have generally been omitted from these structural figures.

By way of a cautionary note,  $^{99}\text{Tc}$  is a weak  $\beta^-$  emitter ( $E = 0.292 \text{ MeV}$ ,  $t_{1/2} 2.12 \times 10^5 \text{ yr}$ ).

### 5.1 TECHNETIUM(VII)

The reaction of  $\text{Tc}_2\text{O}_7$  with tetramethyltin yields the polymeric complex  $\{\text{Me}_3\text{SnOTcO}_3\}_n$  (1), in addition to  $\text{MeTcO}_3$  and  $\{\text{Me}_2\text{TcO}_2\}_2$ . The crystal structure of (1) has been determined; unlike its rhenium analogue, (1) does not contain a crystallographic mirror plane [4].



When the salt  $[\text{Ph}_4\text{As}]_2[\{\text{TcN}(\text{O}_2)_2\}_2(\text{ox})]$  is recrystallised from acetone, crystals of  $[\text{Ph}_4\text{As}]_2[\{\text{TcN}(\text{O}_2)_2\}_2(\text{ox})].2\text{Me}_2\text{CO}$  are recovered. The structure of this complex has been elucidated by X-ray diffraction methods. The oxalate ligand bridges between the two technetium(VII) centres in the anion  $[\{\text{TcN}(\text{O}_2)_2\}_2(\text{ox})]^{2-}$  and exhibits a tetradentate, side-on mode of coordination. The distorted pentagonal-bipyramidal coordination sphere of each technetium atom is completed by a nitrido ligand (*trans* to one of the oxalate *O*-donor atoms) and two  $\eta^2$ -peroxo ligands. Pertinent distances are  $\text{Tc}\equiv\text{N} = 1.69(3)$  and  $1.61(4) \text{ \AA}$ ,  $\text{Tc}-\text{O}_{\text{peroxo}} = 1.86(3)$  to  $1.98(3) \text{ \AA}$ , and  $\text{Tc}-\text{O}_{\text{oxalate}} = 2.09(2)$  and  $2.11(2) \text{ \AA}$  (*cis* to the nitrido ligand) and  $2.47(2) \text{ \AA}$  and  $2.40(2) \text{ \AA}$

(*trans* to the nitrido group). In the infrared spectrum of the complex, the peroxo ligands are characterised by a  $\nu(\text{O-O})$  absorption at  $900\text{ cm}^{-1}$  [5].

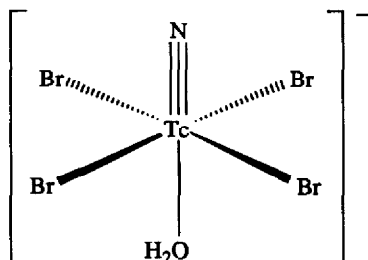
## 5.2 TECHNETIUM(VI)

### 5.2.1 Complexes with halide ligands

The reactions of  $[\text{Tc}(\text{N})\text{Cl}_4]^-$  and  $[\text{Tc}(\text{N})\text{Br}_4]^-$  with HBr and HCl, respectively, yield the mixed halide complex ions  $[\text{Tc}(\text{N})\text{Cl}_{4-x}\text{Br}_x]^-$  ( $x = 1-3$ ). These anions have been detected by ESR spectroscopy in concentrated solutions of HCl or HBr; equilibrium constants for their formation have been determined [6]. The crystal structure of  $[\text{Tc}(\text{N})\text{Cl}_5]^{2-}$ , isolated as the cesium salt, has been determined; the technetium atom is octahedrally sited, although there is a disordering of the chlorine and nitrogen atoms over all six sites. In a fixed model ( $\text{Tc} \equiv \text{N} = 1.6\text{ \AA}$ ), the metal atom is displaced  $0.401(3)\text{ \AA}$  from the  $\text{TcCl}_4$ -plane towards the nitrogen atom [7]. In the same paper, the preparation and characterisation of the complexes  $[\text{Et}_4\text{N}][\text{Tc}(\text{N})\text{X}_4(\text{H}_2\text{O})]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) have been reported (see Section 5.2.2) [7]. The orange anion  $[\text{Tc}(\text{N})\text{Cl}_4]^-$  is formed in thionyl chloride solution by the oxidation of  $[\text{Tc}(\text{N})\text{Cl}_2(\text{EPh}_3)_2]$ , ( $\text{E} = \text{P}$  or  $\text{As}$ ). An ESR study of the system has been carried out and technetium(VI) intermediates have been assigned as  $[\text{Tc}(\text{N})\text{Cl}_3(\text{EPh}_3)]$ . It is suggested that the geometry of this intermediate is distorted square-pyramidal with the nitrido ligand in the apical site [8]. The hydrolysis of  $[\text{Tc}(\text{N})\text{Cl}_5]^{2-}$  gives a brown precipitate referred to as nitridotechnetic(VI) acid. The reaction of  $\text{Cs}_2[\text{Tc}(\text{N})\text{Cl}_5]$  with sodium hydroxide is discussed in Section 5.2.2 [9].

### 5.2.2 Complexes with oxygen donor ligands

The salts  $[\text{Et}_4\text{N}][\text{Tc}(\text{N})\text{X}_4(\text{H}_2\text{O})]$ , ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), have been prepared and the crystal structure of the bromo complex has been determined. The identity of the cation is crucial to the isolation a particular species from solutions containing  $[\text{Tc}(\text{N})\text{X}_4(\text{H}_2\text{O})]^-$  and  $\text{X}^-$ . A small cation such as  $\text{Cs}^+$  results in the isolation of  $\text{Cs}_2[\text{Tc}(\text{N})\text{X}_5]$ , a large cation such as  $[\text{Bu}_4\text{N}]^+$  gives  $[\text{Bu}_4\text{N}][\text{Tc}(\text{N})\text{X}_4]$ , and a mid-sized cation such as  $[\text{Et}_4\text{N}]^+$  allows the isolation of the aqua-complexes  $[\text{Tc}(\text{N})\text{X}_4(\text{H}_2\text{O})]^-$  [7].



$$\text{Tc-Br} = 2.510(1), 2.518(1)\text{ \AA}$$

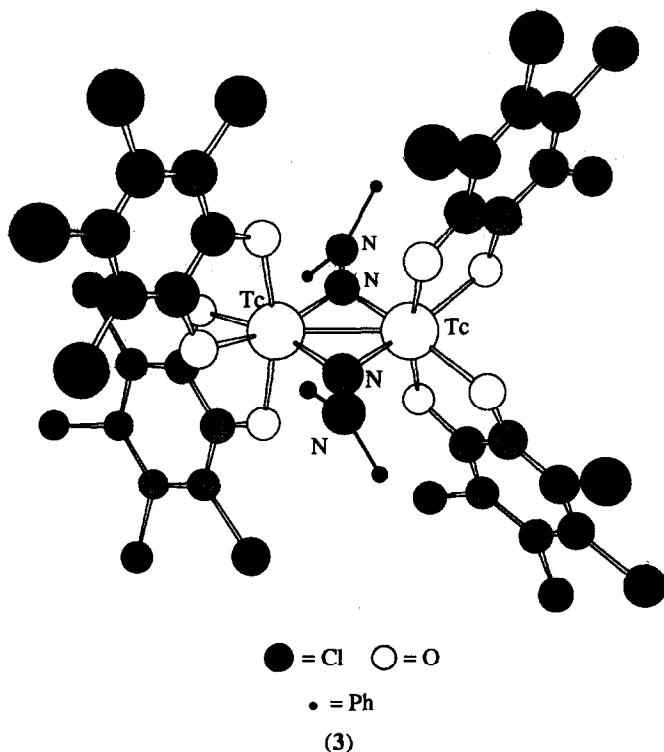
$$\text{Tc-N} = 1.599(9)\text{ \AA}$$

$$\text{Tc-O} = 2.443(7)\text{ \AA}$$

The reaction of  $\text{Cs}_2[\text{Tc}(\text{N})\text{Cl}_5]$  with  $\text{NaOH}$  followed by  $\text{Na}[\text{S}_2\text{CNET}_2] \cdot 3\text{H}_2\text{O}$  has been studied. Two yellow products are isolated; the first is  $[\text{Tc}(\text{N})(\text{S}_2\text{CNET}_2)_2]$  and the second is a dimeric technetium(VI) species,  $[[\text{Tc}(\text{N})(\text{S}_2\text{CNET}_2)_2(\mu\text{-O})_2]$  with a  $\text{Tc}_2(\mu\text{-O})_2$ -core [9]. The hydrolysis of  $\text{Cs}_2[\text{Tc}(\text{N})\text{Cl}_5]$  gives a brown precipitate known as nitridotechnetic(VI) acid. The treatment of this compound with aqueous cesium hydroxide leads to the formation of  $\text{Cs}_2[\text{Tc}_2(\text{N})_2(\text{O})_2(\text{OH})_4]$ . Spectroscopic characteristics for  $[\text{Tc}_2(\text{N})_2(\text{O})_2(\text{OH})_4]^{2-}$  include absorptions in the infrared spectrum at 1046 and  $734\text{ cm}^{-1}$  assigned to  $\nu(\text{Tc}\equiv\text{N})$  and  $\nu_{\text{asym}}(\text{Tc}-\text{O}-\text{Tc})$ , respectively. It is proposed that this anion contains a  $\{\text{N}=\text{Tc}(\mu\text{-O})_2\text{Tc}\equiv\text{N}\}$ -unit [9].

Three technetium-substituted polytungstates with the Keggin structure have been reported;  $[\text{PW}_{11}\text{Tc}(\text{N})\text{O}_{39}]^{4-}$  contains a technetium(VI) centre, (see also Section 5.3.1). The anionic complex  $[\text{PW}_{11}\text{Tc}(\text{N})\text{O}_{39}]^{4-}$  is produced in the reaction of  $[\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4-}$  with  $[\text{Tc}(\text{N})\text{Cl}_4]^-$  [10].

The mixed oxidation state technetium(VI)/technetium(V) dinuclear complex anion  $[\text{Tc}_2(\mu\text{-NNPh}_2)_2(\text{O}_2\text{C}_6\text{Cl}_4)_4]^-$ , (3), is formed in the reaction of *N,N*-diphenylhydrazine with  $[\text{Tc}(\text{O})(\text{O}_2\text{C}_6\text{Cl}_4)_2]^-$ , the structure of which is detailed in Section 5.3.1. The crystal structure of (3) has been determined. The dinuclear structure is supported by two unusual bridging hydrazido ligands (see Section 5.2.4). The Tc-Tc separation is  $2.612(2)\text{ \AA}$ . Two catecholato ligands are coordinated in a didentate manner to each technetium centre; Tc-O distances lie in the range  $1.966(8)$  to  $2.041(10)\text{ \AA}$  [11].



### 5.2.3 Complexes with sulfur donor ligands

The reaction of  $[\text{Tc}(\text{N})\text{Cl}_5]^{2-}$  with sodium hydroxide and  $[\text{S}_2\text{CNEt}_2]^-$  leads to the technetium(V) complex  $[\text{Tc}(\text{N})(\text{S}_2\text{CNEt}_2)_2]$  and the technetium(VI) dimer,  $[\{\text{Tc}(\text{N})(\text{S}_2\text{CNEt}_2)_2(\mu\text{-O})_2\}]$  which exhibits a  $\text{Tc}_2(\mu\text{-O})_2$ -core [9].

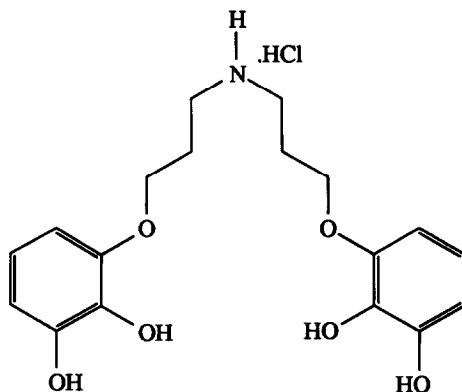
### 5.2.4 Complexes with nitrogen donor ligands

Technetium(VI) nitrido complexes have already been discussed in Sections 5.2.1, 5.2.2 and 5.2.3, and will not be mentioned here further. The mode of attachment of the hydrazido ligands in the mixed valence anion  $[\text{Tc}_2(\mu\text{-NNPh}_2)_2(\text{O}_2\text{C}_6\text{Cl}_4)_4]^-$ , (3), deserves further comment in this section. Anion (3) is formed when  $[\text{Tc}(\text{O})(\text{O}_2\text{C}_6\text{Cl}_4)_2]^-$  is treated with *N,N*-diphenylhydrazine. The results of a crystallographic study of (3) reveal a novel  $\eta^1$ -bridging mode for each *N,N*-diphenylhydrazido ligand; the Tc-N bond lengths are 1.935(12) and 1.937(9) Å [11].

## 5.3 TECHNETIUM(V)

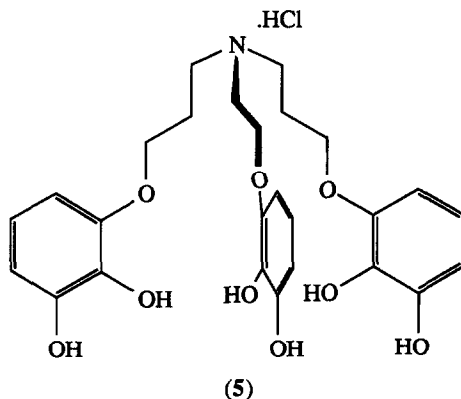
### 5.3.1 Complexes with oxygen donor ligands

The technetium(VI)-substituted polytungstate  $[\text{PW}_{11}\text{Tc}(\text{N})\text{O}_{39}]^{4-}$  is discussed in Section 5.2.2). Two related technetium(V) polytungstate anions have also been reported. These are  $[\text{PW}_{11}\text{Tc}(\text{O})\text{O}_{39}]^{4-}$  and  $[\text{SiW}_{11}\text{Tc}(\text{O})\text{O}_{39}]^{5-}$ , each of which incorporates a  $\{\text{Tc}=\text{O}\}^{3+}$ -unit into the Keggin-type structure. The anion  $[\text{PW}_{11}\text{Tc}(\text{O})\text{O}_{39}]^{4-}$  is formed by treating  $[\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4-}$  with  $[\text{Tc}(\text{O})\text{Cl}_4]^-$ . The tungstate  $[\text{SiW}_{11}\text{Tc}(\text{O})\text{O}_{39}]^{5-}$  is the product of the reaction of  $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$  with  $[\text{Tc}(\text{O})\text{L}_2]^-$  where  $\text{H}_2\text{L} = 1,2$ -ethanediol. The products have been characterised by mass spectrometry, their infrared and electronic spectroscopic characteristics, and by electrochemical studies [10].

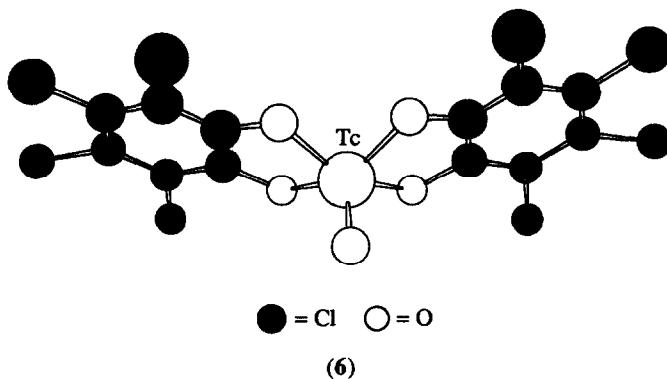


(4)

The metal-promoted degradation of the ligand  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  results in the formation of  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCO}_2\text{H}$ , L, which coordinates via one-O donor atom to the technetium(V) centre in the complex cation  $[\text{Tc}(\text{N})(\text{en})_2\text{L}]^{2+}$ . This complex is discussed further in the next section [12].



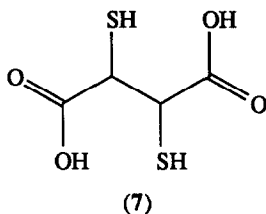
The di- and tricatechol ligands (4), DIPACE, and (5), TRIPACE, have been synthesised. Both ligands reduce  $^{99\text{m}}[\text{TcO}_4]^-$  to a lower valent state. Although the complexes formed have not been characterised, the uptake of  $^{99\text{m}}\text{Tc}$  in the form of *trans*- $\text{TcO}_2^+$  is discussed [13,14]. The technetium(V) complex  $[\text{Tc}(\text{O})\text{L}_2]^-$ , (6), in which  $\text{H}_2\text{L}$  is tetrachlorocatechol, has been prepared from  $[\text{Tc}(\text{O})\text{Cl}_4]^-$  and  $\text{H}_2\text{L}$  in anhydrous methanol. Anion (6) is characterised in its infrared spectrum by an absorption at  $969\text{ cm}^{-1}$  assigned to the  $\text{Tc}=\text{O}$  group. A crystallographic study of  $[\text{nBu}_4\text{N}][\text{(6)}]$  has been carried out and confirms a square-pyramidal environment for the technetium(V) centre in the anion (6). Important distances are  $\text{Tc}-\text{O}_{\text{oxo}} = 1.646(5)\text{ \AA}$ ,  $\text{Tc}-\text{O}_{\text{cat.}} = 1.945(4), 1.948(4), 1.959(4)$  and  $1.967(5)\text{ \AA}$ . The complex anion (6) reacts with *N,N*-diphenylhydrazine to yield the mixed technetium(VI)/technetium(V) dinuclear complex anion  $[\text{Tc}_2(\mu\text{-NNPh}_2)_2(\text{O}_2\text{C}_6\text{Cl}_4)_4]^-$ , (3). The structure of (3) was discussed in preceding sections of this review; two catecholato ligands are coordinated to each metal centre and  $\text{Tc}-\text{O}$  distances are in the range  $1.966(8)$  to  $2.041(10)\text{ \AA}$  [11].



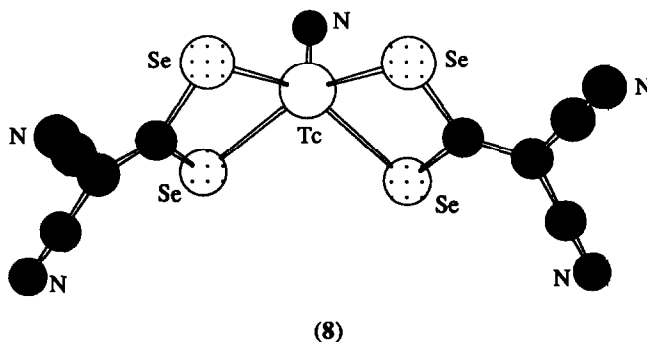
A range of technetium(V) complexes involving a {Tc=O} unit has been reported and the square-pyramidal geometry is dominant amongst these species [15-21, 24]. These complexes are discussed in sections (Sections 5.3.2 and 5.3.5) according to the basal ligands, which mostly exhibit mixed-donor atoms.

### 5.3.2 Complexes with sulfur and selenium donor ligands

A tumour-targeting radiopharmaceutical which is known as pentavalent  $^{99m}\text{Tc}$ -*meso*-dimercaptosuccinic acid has been studied in order to investigate its structure and chemical properties. The radiopharmaceutical is identical to the discrete complex  $[\text{}^{99}\text{Tc}(\text{O})(\text{DMSA})_2]^-$  where  $\text{H}_2\text{DMSA}$  is (7). In this complex anion, the technetium(V) centre is five-coordinate and the coordination sphere is made up of an oxo ligand and four S-donor atoms from two  $\text{DMSA}^{2-}$  ligands. The product mixtures contain three stereoisomers (*syn-endo*, *syn-exo*, and *anti*) which differ in the relative orientations of the carboxylate groups. All three isomers are components of the radiopharmaceutical formulation but it has not been determined if it is only one stereoisomer which is tumour-specific [18].

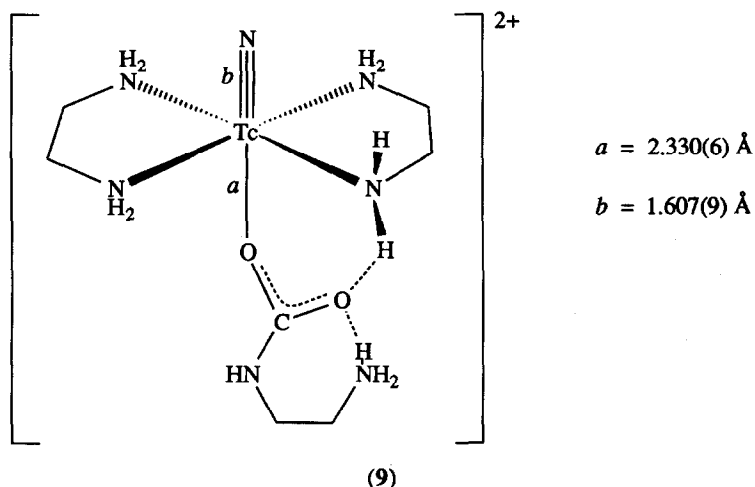


The reaction between  $[\text{}^n\text{Bu}_4\text{N}][\text{Tc}(\text{N})\text{Cl}_4]$ ,  $[\text{}^n\text{Bu}_4\text{N}]\text{Br}$  and  $\text{K}_2\text{L}$  ( $\text{H}_2\text{L}$  = 1,1-dicyanoethane-2,2-diselenol) leads to yellow crystals of  $[\text{}^n\text{Bu}_4\text{N}][\text{Tc}(\text{N})\text{L}_2]$ ,  $[\text{}^n\text{Bu}_4\text{N}](8)$ . The new complex has been characterised by infrared and UV-VIS spectroscopies, mass spectrometry, and X-ray diffraction methods. The anion (8) exhibits a five-coordinate technetium(V) centre with the nitrido group in the apical site; the  $\text{Tc}\equiv\text{N}$  bond is 1.61(1) Å in length [22].



### 5.3.3 Complexes with nitrogen donor ligands

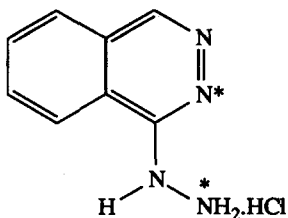
Nitrido, like oxo, complexes of technetium(V) are relatively well exemplified. The anion  $[\text{Tc}(\text{N})\text{L}_2]^-$ , (**8**), ( $\text{H}_2\text{L} = 1,1\text{-dicyanoethane-2,2-diselenol}$ ) [22], was described in the previous section. Oxidation of the technetium(V) complexes  $[\text{Tc}(\text{N})\text{Cl}_2(\text{EPh}_3)_2]$ , ( $\text{E} = \text{P}$  or  $\text{As}$ ) in thionyl chloride solution yields  $[\text{Tc}(\text{N})\text{Cl}_4]^-$  (see Section 5.2.1) [8]. The structure of  $[\text{Tc}(\text{N})\text{Cl}_2(\text{AsPh}_3)_2]$  has been elucidated and is described in the following Section [8]. The reaction of  $[\text{Tc}(\text{N})\text{Cl}_2(\text{PPh}_3)_2]$  with an excess of  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  in benzene/ethanol solution under aerobic conditions leads, surprisingly, to the dicationic complex (**9**). No reaction occurs under anhydrous, anaerobic conditions. Complex (**9**), isolated as the tetraphenylborate salt, has been characterised by elemental analysis, infrared, mass and  $^1\text{H}$  NMR spectroscopies, and magnetic susceptibility measurements. The unexpected nature of the ligands was confirmed by a single crystal X-ray diffraction study. The monodentate *O*-bonded  $\text{HN}_2\text{CNHCO}_2\text{H}$  ligand is oriented such that the non-coordinated oxygen atom is involved in hydrogen-bonded interactions to two amino groups. Although the mechanism of formation of (**9**) remains to be fully established, it has been suggested from the results of trial reactions that the en and  $\text{HN}_2\text{CNHCO}_2\text{H}$  ligands are produced by a metal-promoted degradation of the original  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  ligand [12]. Other nitrido-complexes of technetium(V) [23, 24] are described in Section 5.3.5.



A phenylimido ligand is found in the diamagnetic complex *trans*- $[\text{Tc}(\text{PPh}_3)_2(\text{NPh})\text{Cl}_3]$  which is produced by reacting  $\text{PhNHNHC}(\text{O})\text{Me}$  with  $[\text{NH}_4][\text{TcO}_4]$  in  $\text{MeOH}$  in the presence of  $\text{HCl}$ . The complex has been structurally characterised and this confirms an octahedral coordination sphere for the technetium(V) centre. The imido ligand is bound in a nearly linear fashion ( $\angle \text{Tc-N-C} = 171.8(4)^\circ$ ) and the  $\text{Tc-N}$  bond length of  $1.704(4) \text{ \AA}$  is indicative of triple bond character; this is corroborated by an absorption in the infrared spectrum at  $1090 \text{ cm}^{-1}$  [25].

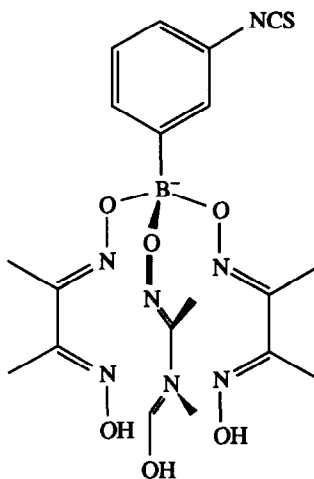


The unusual mode of attachment of the two *N,N*-diphenylhydrazido ligands in the mixed technetium(V)/technetium(VI) dimer  $[\text{Tc}_2(\mu\text{-NNPh}_2)_2(\text{O}_2\text{C}_6\text{Cl}_4)_4]^-$ , (3), was detailed in Sections 5.2.4 and 5.3.1 [11]. Hydralazine.HCl, ( $\text{H}_3\text{L.HCl}$ ), (10), reacts with  $[\text{Tc}(\text{O})\text{Cl}_4]^-$  in methanol at ambient conditions to give the technetium(V) complex  $[\text{TcLCl}_2(\text{PPh}_3)_2]$ . At reflux, the nitrido complex  $[\text{Tc}(\text{N})\text{Cl}_2(\text{PPh}_3)_2]$  is produced. The complex  $[\text{TcLCl}_2(\text{PPh}_3)_2]$  has been structurally characterised. Hydralazine undergoes triple deprotonation during the reaction and binds to the technetium atom in a didentate manner through the donor atoms indicated in structure (10). The two phosphine ligands are mutually *trans*. The structure of  $[\text{Tc}(\text{N})\text{Cl}_2(\text{PPh}_3)_2]$  has also been determined, and is compared with that of its arsine analogue in Section 5.3.4 [26].



\* = coordination site in triply deprotonated ligand

(10)



(11)

Neutral seven-coordinate BATO complexes (BATO = boronic acid adducts of technetium dioximes) find a use as myocardial and cerebral perfusion agents. The complexes are of the type  $^{99}\text{TcCl}\{(\text{dioxime})_3\text{BR}\}^-$  where R is a protein reactive substituent (*e.g.* 3-isothiocyatophenyl). The ligand  $[(\text{Hdmg})_3\text{BR}]^-$ , (11), provides a cavity in which the metal atom can reside; a ligand in which the dioxime is 1,2-cyclohexane dioxime has also been utilised. The complexes

$^{99}\text{TcCl}\{(\text{dioxime})_3\text{BR}\}$  have been prepared from  $^{99}\text{TcCl}(\text{dioxime})_3(\mu\text{-OH})\text{SnCl}_3$  [27]. The chloride ligand in each of the complexes  $^{99}\text{TcCl}\{(\text{dioxime})_3\text{BR}\}$  is axially coordinated and is labile with respect to substitution by other anions such as hydroxide under physiological conditions. The rate of *in vitro* exchange of hydroxide for chloride ion has been studied and it is proposed that an  $\text{S}_{\text{N}}1\text{-CB}$  mechanism operates via a transient six-coordinate neutral complex. The chloro and hydroxy derivatives exhibit different biodistributions [28].

### 5.3.4 Complexes with phosphorus and arsenic donor atoms

The diamagnetic complex *trans*- $[\text{Tc}(\text{PPh}_3)_2(\text{NPh})\text{Cl}_3]$  (see Section 5.3.3) has been prepared and structurally characterised. The Tc-P distances are 2.489(2) and 2.517(2) Å and the angle  $\angle\text{P-Tc-P} = 173.56(5)^\circ$  [25].

The crystal structures of two related complexes, (12), have been determined:  $[\text{Tc}(\text{N})\text{Cl}_2(\text{PPh}_3)_2]$  [26] and  $[\text{Tc}(\text{N})\text{Cl}_2(\text{AsPh}_3)_2]$  [8]. Bond parameters for the two complexes are compared in Table 1. In  $[\text{Tc}(\text{N})\text{Cl}_2(\text{AsPh}_3)_2]$ , the technetium and nitrogen atoms lie on a crystallographically imposed 2-fold axis.

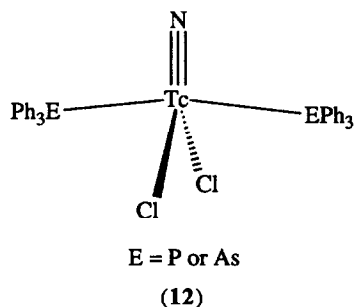
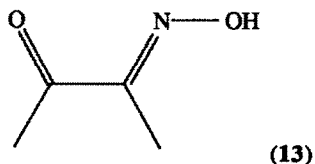


Table 1 Selected bond distances and angles for  $[\text{Tc}(\text{N})\text{Cl}_2(\text{EPh}_3)_2]$  (E = P or As).

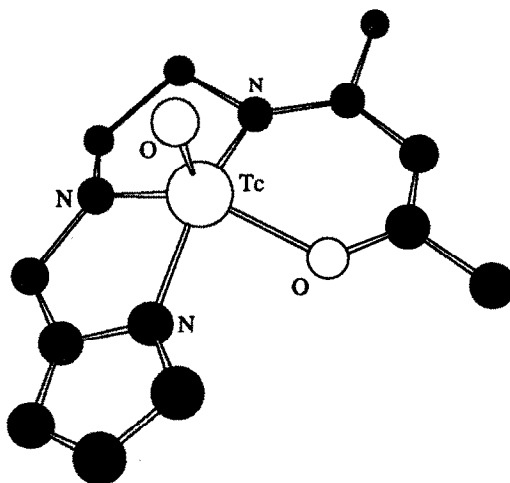
Parameter	E = P (ref. [26])	E = As (ref. [8])
Distances / Å		
Tc-N	1.602(8)	1.601(5)
Tc-E	2.464(3), 2.462(3)	2.5440(4)
Tc-Cl	2.377(2), 2.375(2)	2.373(1)
Angles / deg		
E-Tc-E	162.0(1)	161.56
E-Tc-N	99.1(1), 98.9(1)	99.22(1)
N-Tc-Cl	109.9(1), 109.8(1)	110.51(3)

### 5.3.5 Complexes with mixed donor-atom ligands

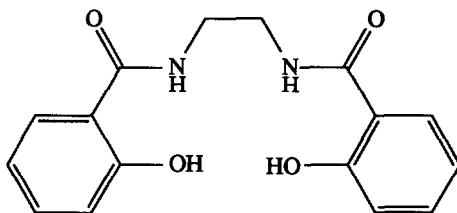
The structure of butane-2,3-dione monoxime, (13), HL, has been probed by using PPP(SCF)-CI calculations; ionisation potential, electron affinity, and charge distribution data have been determined. The complex cation  $[\text{Tc}(\text{O})\text{L}_2(\text{H}_2\text{O})]^+$  has been prepared and characterised by infrared and UV-VIS spectroscopy, electrophoresis, and HPLC. The complex is formed by the reduction of  $[\text{TcO}_4]^-$  with  $\text{NaBH}_4$  in the presence of (13) in alkaline conditions [15].



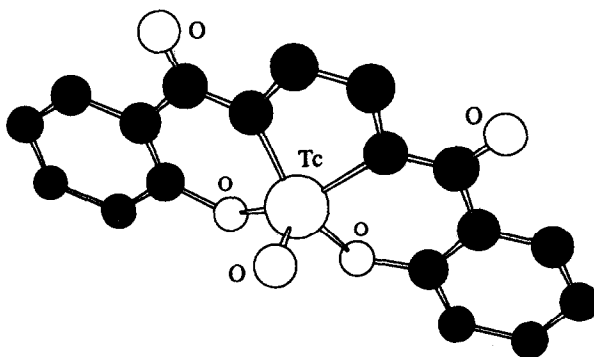
The compound  $N$ -[2(1*H*-pyrrolylmethyl)]- $N'$ -(2-oxo-4-pent-3-enyl)ethane-1,2-diamine,  $\text{L}'$ , has been synthesised and fully characterised. The reaction of this ligand with  $[\text{Bu}_4\text{N}][\text{Tc}(\text{O})\text{L}_2]$ , (where  $\text{H}_2\text{L} = 1,2$ -ethanediol), gives the red-orange technetium(V) complex  $[\text{Tc}(\text{O})\text{L}']$ , (14). The infrared spectrum of (14) exhibits an absorption at  $953\text{ cm}^{-1}$  which is characteristic of the  $\{\text{Tc}=\text{O}\}$  unit. The complex has also been characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass, and UV-VIS spectroscopies and also by a single crystal X-ray diffraction study. The technetium(V) centre exhibits a five-coordinate geometry with the oxo ligand in the apical site ( $\text{Tc}-\text{O} = 1.666(3)\text{ \AA}$ ). The  $N,N',N'',O$ -donor set of ligand  $\text{L}'$  completes the distorted square-pyramidal coordination sphere; the metal centre lies out of the ligand plane and the pyrrole moiety is displaced towards the oxo ligand. Bond distances involving the technetium(V) centre and the donor atoms of  $\text{L}'$  are  $\text{Tc}-\text{O} = 2.025(3)\text{ \AA}$ ,  $\text{Tc}-\text{N}_{\text{pyrrole}} = 1.993(4)\text{ \AA}$ ,  $\text{Tc}-\text{N} = 2.033(4)$  and  $1.897(4)\text{ \AA}$ . Complex (14) provides only the second example of a structural characterisation of a  $\text{Tc}-\text{N}_{\text{pyrrole}}$  interaction [16].



(14)



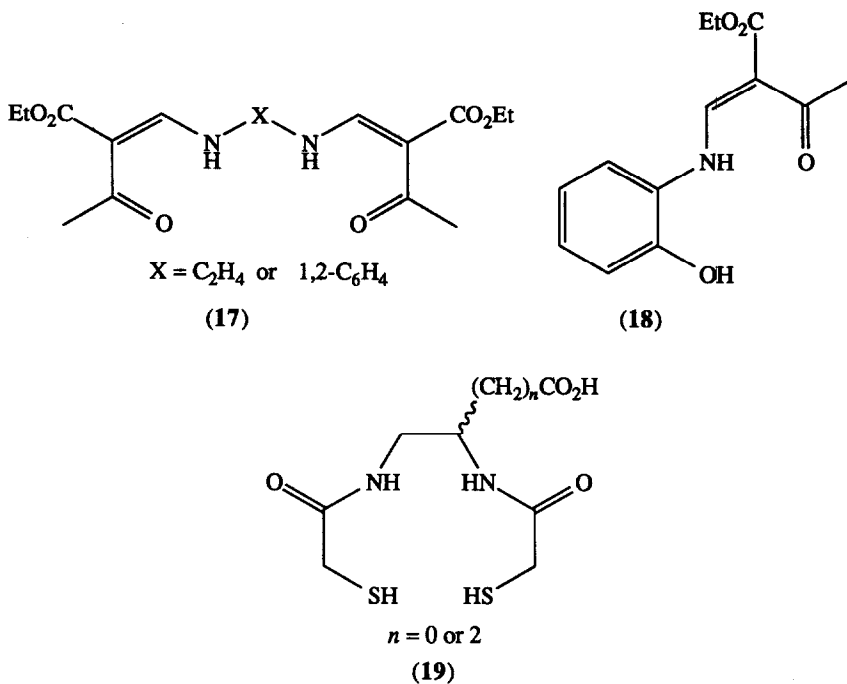
(15)



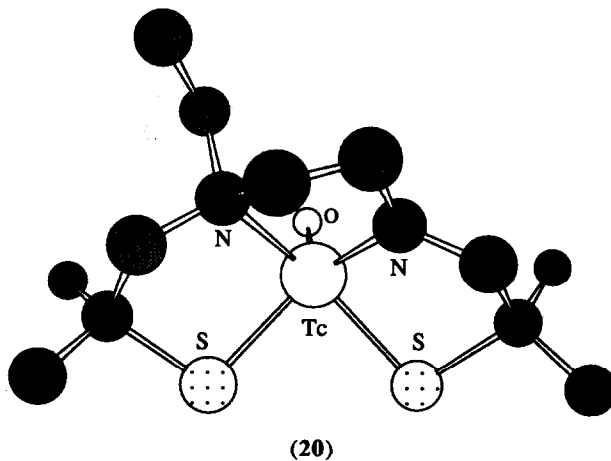
(16)

The reaction of  $H_4L$ , (15), with  $[^nBu_4N][Tc(O)Cl_4]$  gives the orange salt  $[^nBu_4N][Tc(O)L]$ ,  $[^nBu_4N][(16)]$ . The new complex has been characterised by infrared spectroscopy (KBr disc:  $\nu(Tc=O) = 965\text{ cm}^{-1}$ ) and by X-ray crystallography. Anion (16) possesses a square-pyramidal structure with the oxo ligand occupying the apical site. The metal atom lies  $0.65\text{ \AA}$  above the plane defined by the  $O,N,N',O'$ -donor set of  $L^{4-}$ . Bond distances to the technetium(V) centre are  $Tc-O_{oxo} = 1.648(3)\text{ \AA}$ ,  $Tc-O_L = 1.963(3)$  and  $1.956(3)\text{ \AA}$ , and  $Tc-N = 1.979(4)$  and  $1.975(4)\text{ \AA}$  [17].

The ligands  $H_2L$ , (17), and  $H_2L'$ , (18), possess electron withdrawing substituents. Ligands (17) react with the technetium(V) complex  $[Tc(N)Cl_2(PPh_3)_2]$  to yield the complexes  $[Tc(N)L]$  whilst the tridentate ligand (18) reacts with  $[Tc(N)Cl_2(PPh_3)_2]$  to give  $[Tc(N)L'(PPh_3)]$ . All the new complexes are air stable. In the infrared spectra of the complexes  $[Tc(N)L]$  and  $[Tc(N)L'(PPh_3)]$ , absorptions due to  $\nu(Tc\equiv N)$  have not been unequivocally assigned. The crystal structure of  $[Tc(N)L'(PPh_3)]$  has been determined. The technetium centre is in a distorted square-pyramidal environment with the nitrido ligand occupying the apical site. The  $O,N,O'$ -donor set of  $[L']^{3-}$  occupies three sites of the basal plane with the phosphine ligand completing the coordination sphere and displaced towards the technetium atom; important distances are  $Tc-N_{nitrido} = 1.608(5)\text{ \AA}$ ,  $Tc-N_L = 2.067(4)\text{ \AA}$ ,  $Tc-O = 2.027(4)$  and  $2.049(4)\text{ \AA}$ , and  $Tc-P = 2.398(2)\text{ \AA}$  [23].

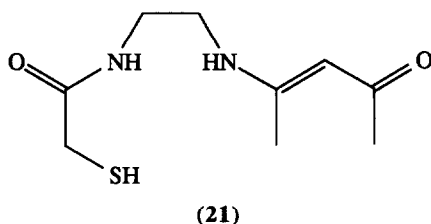


The complexes  $[\text{Tc}(\text{O})\text{L}]^-$  in which  $\text{H}_4\text{L} = (19)$  have been prepared and characterised. The  $S,N,N',S'$ -donor set of each deprotonated ligand forms the basal plane of a square-pyramidal complex. Two chelate ring epimers result on complex formation since the carboxylate group can be in a *syn* or *anti* orientation and the epimers can be separated by using HPLC. The salts  $[\text{Ph}_4\text{P}][\text{Tc}(\text{O})\text{L}]$  and  $[\text{Ph}_4\text{As}][\text{Tc}(\text{O})\text{L}]$  have been characterised by infrared, NMR and UV-VIS spectroscopies as well as by mass spectrometry [19].

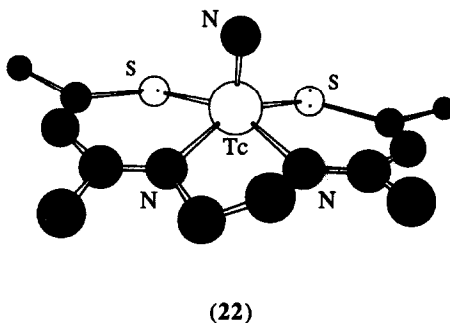


The reduction of aqueous  $[\text{NH}_4][^{99}\text{TcO}_4]$  by basic sodium dithionite in the presence of the appropriate diaminothiol,  $\text{H}_3\text{L}$ , gives the neutral technetium(V) complex *syn*- $[\text{syn-}^{99}\text{Tc}(\text{O})\text{L}]$ , (20). A single crystal X-ray diffraction study of this complex confirms the metal coordination geometry and the conformation of the *N*-substituted ligand. Pertinent bond distances are  $\text{Tc}=\text{O} = 1.681(2) \text{ \AA}$ ,  $\text{Tc}-\text{N} = 1.921(2)$  and  $2.224(2) \text{ \AA}$  and  $\text{Tc}-\text{S} = 1.265(1)$  and  $2.300(1) \text{ \AA}$  [20].

The reaction of ligand (21) with  $[\text{Bu}_4\text{N}][\text{Tc}(\text{O})\text{X}_4]$ , ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), leads to the formation of dark red crystals of the complex  $[\text{Tc}(\text{O})\text{L}]$ . This compound has been characterised by elemental analysis, infrared and  $^1\text{H}$  NMR spectroscopies, mass spectrometry, and single crystal X-ray analysis. The technetium centre in  $[\text{Tc}(\text{O})\text{L}]$  exhibits, as expected, a square-pyramidal geometry with the oxo-ligand in the apical site. The  $\text{Tc}=\text{O}$  bond distance is  $1.657(2) \text{ \AA}$  [21].

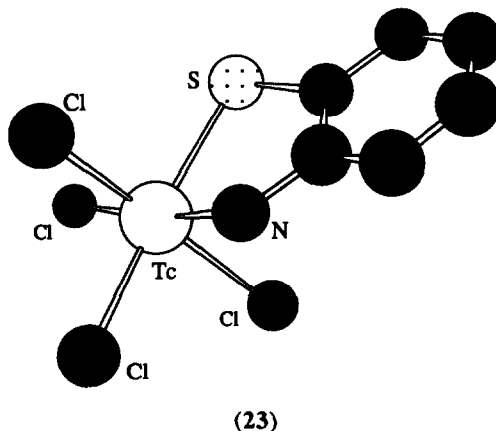


The technetium(V) nitrido-complex, (22), is formed as an orange solid by reacting  $[\text{NH}_4][\text{Tc}(\text{N})\text{Cl}_4]$  with thioacetylacetonylideneimine,  $\text{H}_2\text{L}$ . The crystal structure of (22) has been elucidated;  $\text{Tc}-\text{N}_{\text{nitrido}} = 1.621(8) \text{ \AA}$ ,  $\text{Tc}-\text{N}_{\text{L}} = 2.105(8)$  and  $2.119(8) \text{ \AA}$ , and  $\text{Tc}-\text{S} = 2.347(3)$  and  $2.354(3) \text{ \AA}$ . The infrared spectrum of complex (22) exhibits an absorption at  $1075 \text{ cm}^{-1}$  assigned to  $\nu(\text{Tc}=\text{N})$ . Thioacetylacetonylideneimine,  $\text{H}_2\text{L}$ , also reacts with  $[\text{Bu}_4\text{N}][\text{Tc}(\text{O})\text{Cl}_4]$  at room temperature to yield the green technetium(V) complex  $[\text{Tc}(\text{O})\text{LCl}]$ ; in methanol at reflux, the product is  $[\{\text{Tc}(\text{O})\text{L}\}_2\text{O}]$ . The oxo-complexes have been characterised by spectroscopic methods [24].



By treating  $[\text{Bu}_4\text{N}][\text{Tc}(\text{O})\text{L}_2]$ , ( $\text{H}_2\text{L} = 2\text{-aminobenzenethiol}$ ), with 12M hydrochloric acid, the blue technetium(V) complex  $[\text{Bu}_4\text{N}][\text{TcLCl}_4]$  is produced. The oxidation state of the metal centre is confirmed by a measured magnetic moment of  $2.86 \mu_B$ . The crystal structure of this salt reveals that the anion  $[\text{TcLCl}_4]^-$ , (23), contains an octahedrally coordinated technetium(V) centre; bond lengths around the metal atom are  $\text{Tc}-\text{N} = 2.145(4) \text{ \AA}$ ,  $\text{Tc}-\text{S} = 2.322(2) \text{ \AA}$ , and  $\text{Tc}-\text{Cl}_{\text{trans-N}} =$

2.322(2) Å, Tc-Cl<sub>trans-S</sub> = 2.390(2) Å, Tc-Cl<sub>cis</sub> = 2.361(2) and 2.324 (2) Å. The infrared spectrum of (23) exhibits an absorption at 3252 cm<sup>-1</sup> and this indicates that one NH proton is retained. The colour of a solution of [Bu<sub>4</sub>N][TcLCl<sub>4</sub>] depends upon the solvent; in solvents such as pyridine, the solution becomes deep orange and this is attributed to solvent coordination [29].



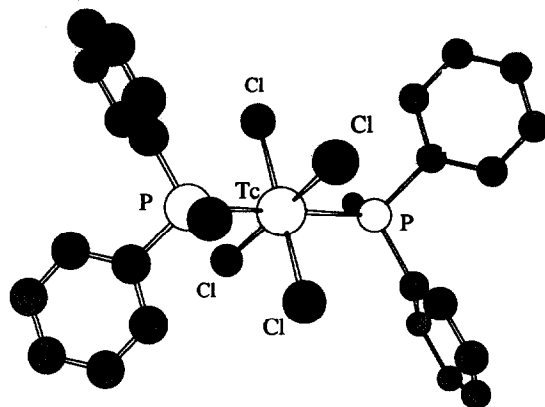
## 5.4 TECHNETIUM(IV)

### 5.4.1 Complexes with halide ligands

The technetium(IV) anions [TcCl<sub>n</sub>Br<sub>6-n</sub>]<sup>2-</sup> for  $n = 1$  to 5 have been separated by ion exchange chromatography on diethylaminoethyl-cellulose. Product characterisation shows that the reactions of [TcBr<sub>6</sub>]<sup>2-</sup> with HCl, or [TcCl<sub>6</sub>]<sup>2-</sup> with HBr, are stereospecific and this is attributed to the relative *trans*-effects of bromide and chloride ligands. Infrared and Raman spectra of ten complexes in the series [TcCl<sub>n</sub>Br<sub>6-n</sub>]<sup>2-</sup>, recorded at 80 K, have been completely assigned. The assignments are supported by the results of a normal coordinate analysis which is based on a general valence force field. The fact that the *trans*-influence of chloride is less than that of bromide ion, it is noted that in asymmetric axes Cl-Tc-Br, the Tc-Br bond is strengthened and the Tc-Cl bond is weakened with respect to corresponding bonds in the symmetric axes Br-Tc-Br and Cl-Tc-Cl [30].

In a study of the reaction of [NH<sub>4</sub>][TcO<sub>4</sub>] with triphenylphosphine in acidic acetone, the salts [PPh<sub>3</sub>H][TcCl<sub>6</sub>] and [Ph<sub>3</sub>PCMe<sub>2</sub>CH<sub>2</sub>COMe][TcCl<sub>5</sub>(PPh<sub>3</sub>)] have been isolated. When the reaction is carried out in dma in the presence of HCl, [NH<sub>2</sub>Me<sub>2</sub>][dmaH][TcCl<sub>6</sub>].Ph<sub>3</sub>PO is formed. On the other hand, in dmf, the product is a technetium(III) complex, (see Section 5.5.1). A octahedral geometry for the [TcCl<sub>6</sub>]<sup>2-</sup> anion has been confirmed; Tc-Cl distances lie in the range 2.324(2) to 2.379(2) Å [31]. The same authors have reported the syntheses and crystal structures of the technetium(IV) complexes *trans*-[TcCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub>], (24), *trans*-[TcCl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>], and [PEt<sub>3</sub>H][TcCl<sub>5</sub>(PEt<sub>3</sub>)]. Complex (24) is formed in the reaction of [NH<sub>4</sub>][TcO<sub>4</sub>] with PMePh<sub>2</sub> in

ethanolic HCl. An X-ray diffraction analysis confirms an octahedral geometry; pertinent bond lengths are  $\text{Tc-Cl} = 2.324(1)$  and  $2.320(1)$  Å and  $\text{Tc-P} = 2.556(1)$  Å. The complexes *trans*- $[\text{TcCl}_4(\text{PEt}_3)_2]$  and  $[\text{PEt}_3\text{H}][\text{TcCl}_5(\text{PEt}_3)]$  are products of the reaction of  $[\text{NH}_4][\text{TcO}_4]$  with  $\text{PEt}_3$  in  $\text{EtOH}/\text{HCl}$  under reflux. In the octahedral complex *trans*- $[\text{TcCl}_4(\text{PEt}_3)_2]$ , bond distances to the technetium centre are  $\text{Tc-Cl} = 2.334(1)$  and  $2.331(1)$  Å and  $\text{Tc-P} = 2.541(1)$  Å. In the crystal lattice of  $[\text{PEt}_3\text{H}][\text{TcCl}_5(\text{PEt}_3)]$ , there are two independent technetium centres per unit cell but the geometries of the independent anions are very similar [32].



(24)

#### 5.4.2 Complexes with oxygen donor ligands

Investigations into the coordination of tripod-like ligands to technetium(IV) centres have been reported. The iodide salt of the ligand  $[\text{Me}_3\text{NC}(\text{CH}_2\text{OH})_3]^+$ ,  $[\text{H}_3\text{L}]^+$ , reacts with  $[\text{Tc}(\text{OMe})_6]^{2-}$ , or  $[\text{TcBr}_6]^{2-}$  with KOMe, to yield the white crystalline complex  $[\text{TcL}_2] \cdot 2[\text{H}_3\text{L}]\text{I}$ . The complex has been characterised by UV-VIS, infrared, and  $^1\text{H}$  NMR spectroscopies, and the molecular structure has been determined. In the  $[\text{TcL}_2]$  molecule, the technetium(IV) centre is octahedrally coordinated within the  $\text{O}_6$ -donor set provided by two tripod-like ligands. The  $\text{Tc-O}$  distances fall in the range  $1.987(4)$  to  $2.005(4)$  Å [33].

### 5.5 TECHNETIUM(III)

#### 5.5.1 Complexes with halide and oxygen donor ligands

The technetium(III) complex *mer*- $[\text{TcCl}_3(\text{PPh}_3)_2(o\text{-dmf})]$ , (see also Section 5.4.1), has been prepared from  $[\text{NH}_4][\text{TcO}_4]$  and triphenylphosphine in dmf in the presence of HCl. The octahedral geometry of the complex has been confirmed crystallographically. The dmf ligand is *trans* to a

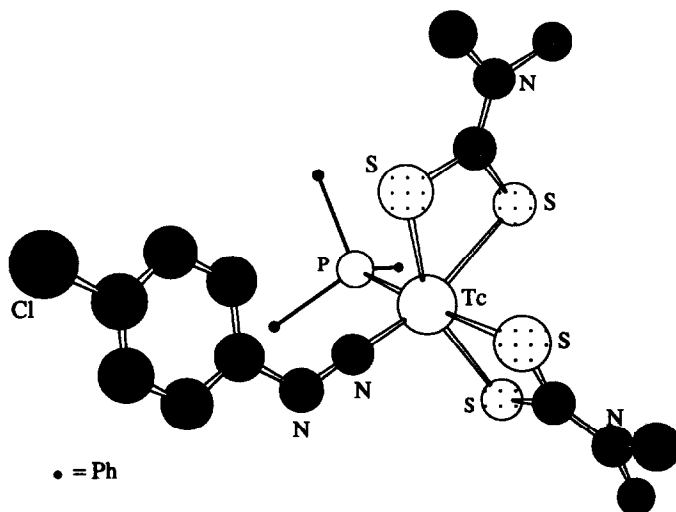


chloride ligand with  $\text{Tc-O} = 2.115(12) \text{ \AA}$  and  $\text{Tc-Cl}_{\text{trans}} = 2.339(5) \text{ \AA}$ . Each remaining  $\text{Tc-Cl}$  distance is  $2.342(3) \text{ \AA}$ , and the  $\text{Tc-P}$  bond lengths are  $2.499(5)$  and  $2.496(5) \text{ \AA}$  [31].

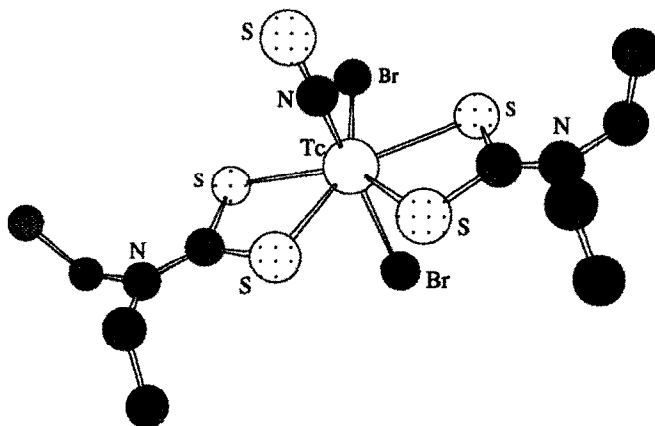
The complex *mer*- $[\text{TcCl}_3(\text{PMe}_3)_3]$  is discussed in Section 5.5.4.

### 5.5.2 Complexes with sulfur donor ligands

Thiocarbamate ligands features in several technetium(III) complexes. The complex  $[\text{Tc}(\text{CO})(\text{S}_2\text{NEt}_2)_3]$  has been prepared and characterised by infrared, and  $^1\text{H}$  and  $^{99}\text{Tc}$  NMR spectroscopies. A series of related technetium(I) complexes has also been reported (see Section 5.7) [34]. The crystal structure of the diazenido dithiocarbamato complex  $[\text{Tc}(\text{NNC}_6\text{H}_4\text{Cl})(\text{S}_2\text{CNMe}_2)_2(\text{PPh}_3)]$ , (**25**), has been determined [35]. The preparation and characterisation of the complex  $[\text{Tc}(\text{NS})(\text{S}_2\text{CNEt}_2)_2\text{Br}_2]$ , (**26**), have been reported. The complex (**26**) is formed in the reaction of  $[\text{Tc}(\text{N})(\text{S}_2\text{CNEt}_2)_2]$  with  $\text{SOBr}_2$ . In its infrared spectrum, the complex exhibits absorptions at  $1250 \text{ cm}^{-1}$  and  $1529 \text{ cm}^{-1}$  assigned to  $\nu(\text{N}\equiv\text{S})$  and  $\nu(\text{C}=\text{N})$ , respectively. The NS group is taken to be a three-electron donor (*i.e.* formally  $\text{NS}^+$ ) and thus the technetium centre is assigned as being in the +3 oxidation state. The magnetic properties of the previously reported and analogous chloro complex also support this assignment. A crystallographic study of complex (**26**) confirms the seven-coordinate technetium(III) centre; the geometry is a distorted pentagonal-bipyramid with the thionitrosyl group and one bromide ligand occupying the axial sites (see Section 5.5.3) [36].



(25)



(26)

### 5.5.3 Complexes with nitrogen donor ligands

The nitrosyl-containing technetium(III) complex  $[\text{Tc}(\text{NS})(\text{S}_2\text{CNEt}_2)_2\text{Br}_2]$ , (26), was described in the previous section. Bond parameters involving the  $\text{NS}^+$  group are  $\text{Tc}-\text{N} = 1.754(9) \text{ \AA}$ ,  $\text{N}=\text{S} = 1.504(9) \text{ \AA}$ , and  $\angle\text{Tc}-\text{N}-\text{S} = 177.27(7)^\circ$ . These data have been compared with the corresponding parameters for a range of related complexes [36].

In developing  $^{99\text{m}}\text{Tc}$  radiopharmaceuticals, it is important to be able to control the redox properties of the technetium centre. The electrochemical behaviour of members of the series of complexes  $\text{cis}(\text{X}), \text{trans}(\text{P})\text{-}[\text{Tc}^{\text{III/II}}\text{X}_2(\text{PR}_2\text{R}')_2\text{L}]^{+/0}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{PR}_2\text{R}' = \text{PMe}_2\text{Ph}$  or  $\text{PEt}_2\text{Ph}$ ;  $\text{L} = \text{bpy}$ , 4,4'- $\text{Me}_2\text{bpy}$  or phen) have been studied in 0.1 M  $[\text{Et}_4\text{N}][\text{ClO}_4]/\text{MeCN}$  solution. Each complex exhibits a diffusion controlled one electron  $\text{Tc}(\text{IV})/\text{Tc}(\text{III})$  redox couple in the range 1.044 to 0.956 V (*vs.* SCE) as well as a  $\text{Tc}(\text{III})/\text{Tc}(\text{II})$  couple in the range  $-0.049$  to  $-0.189$  V. Spectropotentiometric data have also been recorded and evaluated. An analysis of the ways in which the redox potentials are influenced by changing the technetium-bound ligands is presented [37].

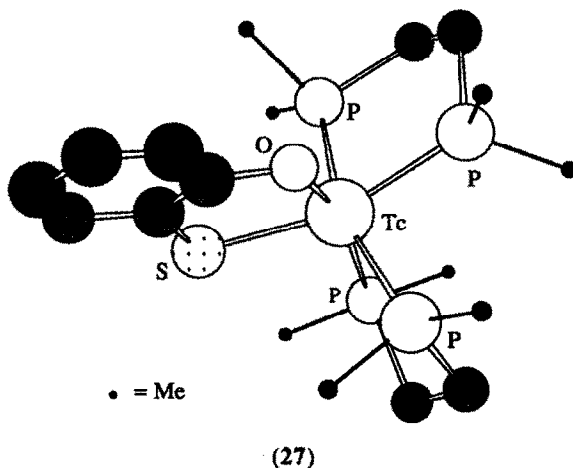
### 5.5.4 Complexes with phosphorus donor ligands

Some technetium(III) complexes incorporating phosphorus donor ligands have already been mentioned: *mer*- $[\text{TcCl}_3(\text{PPh}_3)_2(o\text{-dmf})]$  [31] and  $[\text{Tc}(\text{NNC}_6\text{H}_4\text{Cl})(\text{S}_2\text{CNMe}_2)_2(\text{PPh}_3)]$  [35].

A report has appeared of the first structurally characterised examples of technetium(III) complexes with  $\text{PMe}_3$  ligands. The reaction of  $[\text{Tc}(\text{S-tu})_6][\text{PF}_6]_3$  with  $\text{PMe}_3$  in methanol in a sealed tube at  $75^\circ\text{C}$  leads to the orange-yellow complex  $[\text{Tc}(\text{H})(\text{PMe}_3)_4(\eta^2\text{-N,S-HNC}(\text{NH}_2)\text{S})][\text{PF}_6]$ . This complex has been characterised by infrared and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{99}\text{Tc}$  NMR spectroscopies, mass spectrometry and X-ray crystallography. The hydride ligand was not located in the structural study although its presence as a terminally bound atom is consistent with the

observation of a multiplet in the  $^1\text{H}$  NMR spectrum at  $\delta -8.9$ . The technetium(III) environment, ignoring the Tc-H interaction, is that of a distorted octahedron; a significant gap in the coordination sphere occurs between the two phosphorus atoms that lie in the plane of the *N,S*-donor atoms and it is here that the hydride ligand is most sensibly placed. Technetium-phosphorus bond lengths lie in the range 2.323(4) to 2.416(5) Å. The reaction of  $[\text{Bu}_4\text{N}][\text{TcO}_4]$  with  $\text{PMe}_3$  in acetonitrile at reflux in a sealed tube gives the yellow-orange technetium(III) complex *mer*- $[\text{TcCl}_3(\text{PMe}_3)_3]$ , the structure of which has been elucidated. This complex co-crystallises with an equivalent of triphenyl isocyanourate. The technetium centre in *mer*- $[\text{TcCl}_3(\text{PMe}_3)_3]$  is octahedrally sited; bond distances are Tc-P = 2.387(1) and 2.4528(8) Å and Tc-Cl = 2.440(1), 2.352(1) and 2.370(1) Å [38].

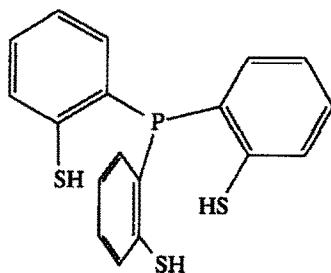
The reactions of *trans*- $[\text{TcCl}_2(\text{dmpe})_2]^+$  with  $\text{e}_{\text{aq}}^-$  (generated by pulse radiolysis) have been studied. The reduction with  $\text{e}_{\text{aq}}^-$  proceeds at a diffusion-controlled rate to yield technetium(II) complexes. In the presence of surfactants (SDS), the rate of reduction is dramatically slower [39]. The reaction of  $[\text{TcCl}_2(\text{dmpe})_2]\text{Cl}$  with 2-mercaptophenol, HL, in ethanol leads to the formation of the cation  $[\text{TcL}(\text{dmpe})_2]^+$ , (27), which has been isolated as the tetraphenylborate salt. The fact that reduction of the technetium from the +3 to +2 state does not accompany the ligand substitution is rather unexpected. The technetium(III) environment in the cation (27) is distorted octahedral with Tc-P bond lengths in the range 2.356(3) to 2.403(2) Å and Tc-O and Tc-S distances of 2.095(4) and 2.352(3) Å, respectively [40].



#### 5.5.5 Complexes with mixed donor-atom ligands

The complex cation  $[\text{TcL}(\text{dmpe})_2]^+$ , (27), in which HL = 2-mercaptophenol was described in the above section. This cation exhibits an *O,S*-chelating ligand [40]. The complexation of technetium(III) ions by  $[\text{edta}]^{4-}$  has been reported [41]. In the octahedral cation  $[\text{Tc}(\text{H})(\text{PMe}_3)_4(\eta^2\text{-}N,S\text{-HNC}(\text{NH}_2)\text{S})]^+$ , a deprotonated thiourea ligand is incorporated in a

chelating *N,S*-mode. The Tc-N and Tc-S distances are 2.190(13) and 2.543(4) Å, respectively. The complex is discussed further in Section 5.5.4 [38].



(28)

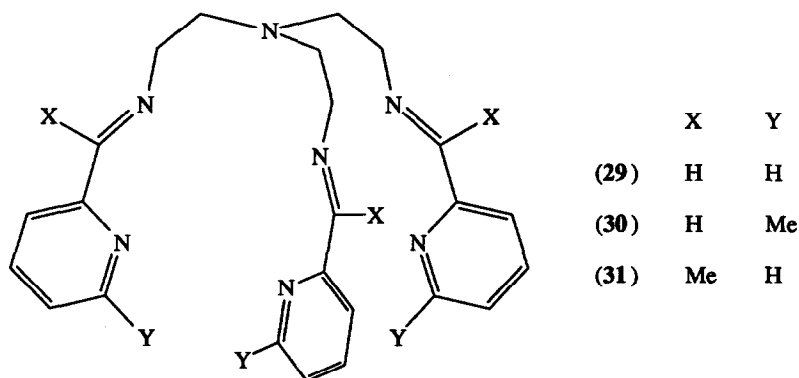
Tris(2-mercaptophenyl)phosphine, (28),  $H_3L$ , is a potential tetradentate ligand offering a *P,S,S',S''*-donor set to a metal centre. The reaction of ligand (28) with  $[NH_4][TcO_4]$ , sodium dithionite and MeNC produces the technetium(III) complex  $[TcL(CNMe)]$ . This complex has been characterised by mass, infrared,  $^1H$  NMR and UV-VIS spectroscopies. The analogous complex  $[TcL(CN^iPr)]$  has similarly been prepared and has been characterised by X-ray diffraction methods. The complex exhibits a trigonal-bipyramidal coordination geometry with the *P*-donor atom of the  $L^{3-}$  ligand occupying an axial site and the three *S*-donors arranged in the equatorial plane. A blue crystalline complex can be isolated from a solution of  $[TcL(CNMe)]$  in  $CHCl_3/MeOH$  in the presence of MeNC but its identity has not been unambiguously confirmed. For the analogous  $CN^iPr$  derivative however, the complex  $[TcL(CNMe)_2]$  is isolated. This complex has been structurally characterised and possesses an octahedral technetium(III) centre with the two isonitrile ligands mutually *cis* [42].

Complexation of technetium(III) ions by (2-aminophenyl)diphenylphosphine, HL, has been reported. Treatment of an ethanol suspension of  $[NH_4][TcO_4]$  with HL and heating the solution at reflux yields  $[TcL_3]$ . The magnetic moment of  $[TcL_3]$  is  $2.49 \mu_B$  (293 K), consistent with the +3 oxidation state; UV-VIS spectroscopic and molar conductivity data have also been recorded. A modification of preparative conditions allows the complexes  $[TcL_2(HL)]X$ , ( $X = CF_3CO_2$ ,  $TcO_4$ , or  $ClO_4$ ), to be prepared. The structure of  $[TcL_2(HL)][ClO_4]$ , which forms blue crystals, was determined by X-ray diffraction analysis. The cation  $[TcL_2(HL)]^+$  is octahedral with the ligands arranged in *mer*-configuration [43].

## 5.6 TECHNETIUM(II)

An investigation of the electrochemical behaviour of the complexes *cis*(*X*),*trans*(*P*)- $[Tc^{III/II}X_2(PR_2R')_2L]^{+/0}$  ( $X = Cl$  or  $Br$ ;  $PR_2R' = PMe_2Ph$  or  $PEt_2Ph$ ;  $L = bpy$ , 4,4'- $Me_2bpy$  or phen) was described in Section 5.5.3 [37].

The complexes  $[\text{Tc}(\mathbf{29})][\text{BPh}_4]_2$ ,  $[\text{Tc}(\mathbf{29})][\text{PF}_6]_2$ ,  $[\text{Tc}(\mathbf{30})][\text{BPh}_4]_2$  and  $[\text{Tc}(\mathbf{31})][\text{BPh}_4]_2$  were synthesised by template methods. The complexes were characterised by elemental analysis, UV-VIS and mass spectroscopies, conductivity measurements, cyclic voltammetry, and, for  $[\text{Tc}(\mathbf{29})][\text{PF}_6]_2$ , single crystal X-ray analysis. In the  $[\text{Tc}(\mathbf{29})]^{2+}$  cation, the ligand encapsulates the technetium(II) ion rendering the metal centre "pseudo seven-coordinate". This description is given because the apical nitrogen atom is 2.933(7) Å distant from the technetium(II) centre; the mean Tc-N<sub>py</sub> and Tc-N<sub>imino</sub> distances are 2.109 Å and 2.071 Å, respectively [44].

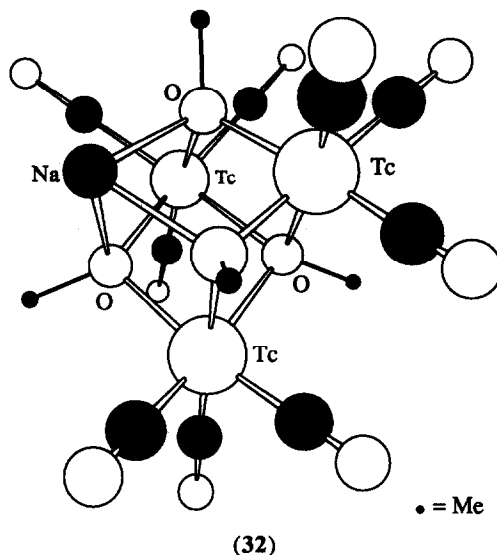


## 5.7 TECHNETIUM(I)

The cubane-type complex  $\text{Na}[\text{Tc}_3(\text{CO})_9(\text{OMe})_4]$  has been prepared and characterised. Being a source of the  $\{\text{Tc}(\text{CO})_3\}$ -fragment,  $\text{Na}[\text{Tc}_3(\text{CO})_9(\text{OMe})_4]$  is a convenient precursor to carbonyl complexes in the family  $\text{LTc}(\text{CO})_3$ . The complex  $\text{Na}[\text{Tc}_3(\text{CO})_9(\text{OMe})_4]$  is formed in the reaction of  $\text{Na}[\text{TcO}_4]$  with CO in methanol. The crystal structure of  $\text{Na}[\text{Tc}_3(\text{CO})_9(\text{OMe})_4]$ , (**32**), has been determined and the cubane framework has thus been confirmed. The Tc-O distances are in the range 2.140(4) to 2.201(3) Å [45].

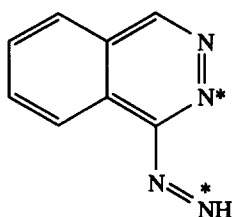
A series of dithiocarbamate technetium(I) and related complexes has been synthesised. These compounds include  $\text{Tc}(\text{CO})_4(\text{S}_2\text{NEt}_2)$ ,  $\text{Tc}(\text{CO})_2(\text{PPh}_3)_2(\text{S}_2\text{NEt}_2)$ ,  $\text{Tc}(\text{CO})_2(\text{PPh}_3)_2(\text{S}_2\text{OEt})$  and  $\text{Tc}(\text{CO})_2(\text{PPh}_3)_2(\text{S}_2\text{P}(\text{PMe}_2)_2)$  and they have been characterised by infrared and  $^1\text{H}$  and  $^{99}\text{Tc}$  NMR spectroscopies [34].

When  $[\text{Tc}(\text{N})\text{Cl}_2(\text{PMe}_2\text{Ph})_3]$  is treated with  $\text{S}_2\text{Cl}_2$  in  $\text{CH}_2\text{Cl}_2$  solution, a red powder is formed; brown crystals of *mer*- $[\text{Tc}(\text{NS})\text{Cl}_2(\text{PMe}_2\text{Ph})_3]$  are isolated after recrystallisation. This complex is diamagnetic, consistent with an assignment of a +1 oxidation state to the metal atom. The compound *mer*- $[\text{Tc}(\text{NS})\text{Cl}_2(\text{PMe}_2\text{Ph})_3]$  has been characterised by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{99}\text{Tc}$  NMR spectroscopies and mass spectrometry and its crystal structure has been determined. The geometry around the technetium(II) centre is slightly distorted octahedral; the thionitrosyl ligand is bound in a linear manner ( $\angle\text{Tc-N-S} = 178.8(2)^\circ$  and  $\text{N}\equiv\text{S} = 1.548(4)$  Å) [46].



The reaction of  $[\text{Tc}(\text{dmpe})_3]^+$  with  $\text{Cl}_2^-$  (generated by pulse radiolysis) has been studied; see also Section 5.5.4 [39].

Oxidation of ligand (10) gives (33), HL, and this binds in its neutral form to technetium(I) in the complex  $[\text{Tc}(\text{HL})_3]^+$ . This cation is formed in the reaction of  $[\text{TcO}_4]^-$  with (10) and is isolated as the air stable tetraphenylborate salt. The complex  $[\text{Tc}(\text{HL})_3][\text{BPh}_4]$  has been characterised by mass and  $^{99}\text{Tc}$  NMR spectroscopies. It is proposed that coordination of HL is through the two nitrogen donor atoms indicated in structure (33) and that the six-coordinate technetium(I) centre probably adopts a distorted trigonal prismatic geometry rather than an octahedral one [47].



\* = coordination site

(33)

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