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CRYSTAL STRUCTURES OF TECHNETIUM COMPOUNDS

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CONTENTS

A. INTRODUCTION

The development of technetium chemistry has been hindered by the fact that technetium is not a naturally occurring element. There is therefore no backlog of chemical observations for Tc (as for example there is for the adjacent elements Mo, Ru, and Re) upon which modern chemical studies can be based. It has only been recently that macroscopic amounts of the relatively stable isotope ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ y) have become available for

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chemical investigation. In this unusual historical situation, single crystal X-ray structural analysis has been extensively used to definitively characterize technetium complexes and thus rapidly construct a firm foundation for the further development of synthetic and mechanistic technetium chemistry. During the last few years sufficient structural studies have been reported so that this foundation is beginning to take shape, and thus the authors feel that a review of technetium crystal structures will be useful and will focus attention on those areas that still require elucidation. Previous reviews of technetium chemistry [1–18], some of which are quite exhaustive, are more general in nature and do not focus on particular subjects.

One of the reasons for the increased interest in technetium chemistry during the last few years is the widespread use of radiopharmaceuticals labelled with ^{99m}Tc. Figure 1 shows that studies on technetium, as reported in Chemical Abstracts, expanded exponentially from 1950 to 1977 reflecting both fundamental research interest and the growing requirements of nuclear medicine. Technetium-99m is in fact the main radionuclide used in diagnostic nuclear medicine. The pre-eminence of this isotope is due (i) to its favorable nuclear properties ($\gamma = 140$ KeV, $t_{1/2} = 6$ h) which allow images of high resolution to be obtained with a low radiation dose to the patient, (ii) its ready availability via commercial Mo-99/Tc-99m generators, and (iii) the ability of technetium to combine chemically with a variety of ligands to produce radiopharmaceuticals of high organ specificity [18,19]. However, Fig. 2 shows that the number of studies reported on new ^{99m}Tc radiopharmaceuticals has decreased from 1977 to 1980. This fact evidences a "stall"

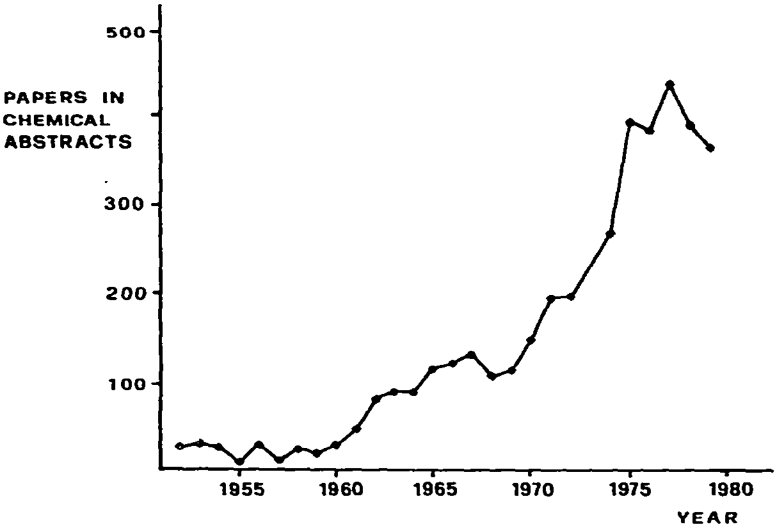

Fig. 1. Number of technetium studies reported in Chemical Abstracts as a function of year.

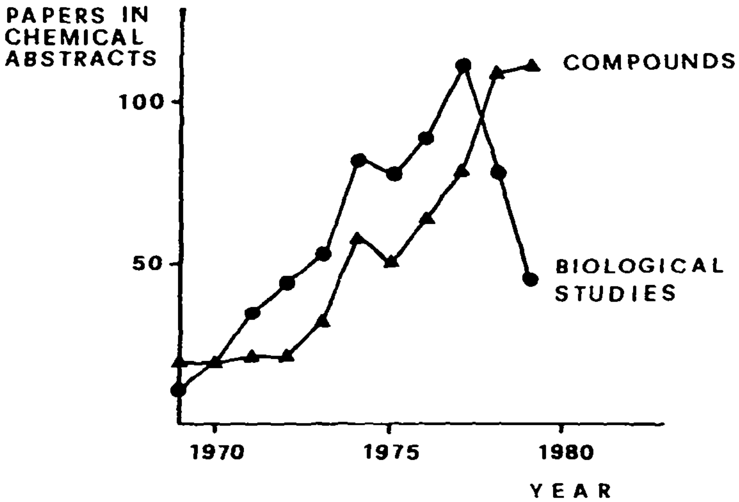

Fig. 2. Number of technetium studies reported in Chemical Abstracts; triangles represent chemical studies while circles represent biological studies.

position in radiopharmaceutical research that will only be alleviated by further development of technetium chemistry. Fortunately, studies on the coordination chemistry of technetium are expanding, and both interesting and potentially useful results are being obtained.

B. REMARKS

This review covers structural studies on technetium compounds and encompasses all collected molecular structures through the year 1980. It is meant to provide a summary of the important data for each independent molecule studied via X-ray single crystal diffraction, but it is not meant as a substitute for the original references. The relevant data have been collected and displayed in a fashion amenable for use by non-crystallographers. It was felt that it would be desirable to visualize the molecular structures rather than to merely rely on interpretation of numerical results, and thus a perspective view of each structure is presented. In accordance with this general goal, papers dealing with powder X-ray patterns have been only briefly mentioned. In none of the following views of molecular structures are the hydrogen atoms indicated, even if they were located in the original analysis. In most cases these atoms are fixed by geometry and it was felt that addition of hydrogen atoms would obscure the views. Moreover, for clarity, a universal size code for atoms is adopted and labels for carbon atoms are omitted. Plotting of the perspective view drawings was accomplished by use of the PLUTO program [20].

C. OXIDES, TECHNETATE, AND PERTECHNETATE COMPOUNDS

Only two oxides of technetium have been well characterized: Tc_2O_7 and TcO_2. Tc_2O_7 is one of the few known transition metal oxides having a molecular structure in the solid state. Ditechnetium heptoxide crystallizes in the orthorhombic system, contains isolated centrosymmetric molecules with a linear central Tc–O–Tc bridge, and contains Tc(VII) in a tetragonal coordination environment (Fig. 3). The Tc–O bond lengths are: 1.84 (bridge), 1.66. 1.68, and 1.71 Å. The structure is more closely related to those of CrO_3, RuO_4, and OsO_4 than to that of Re_2O_7 [21]. In fact the last consists of strongly distorted ReO_6 octahedra and fairly regular ReO_4 tetrahedra.

The crystal structure of TcO_2 has been calculated [22] assuming the metal position to be equivalent to that of molybdenum in MoO_2, an assumption which seems to be justified by the close similarity of the lattice dimensions and the identical space groups of the two structures. The TcO_2 structure is of a deformed 'rutile (TiO_2) type' (Fig. 4); the TcO_6 octahedra are essentially joined in the same way as are the TiO_6 octahedra in TiO_2, but the technetium atoms within the strings are drawn near to each other to form doublets, leading to distortion of the TcO_6 octahedra. TcO_2 has also been prepared by thermal decomposition of NH_4TcO_4 at 950°C in a flow of nitrogen [23]; this material, by its X-ray powder pattern, has the same distorted rutile structure.

The X-ray powder pattern of the technetium metal obtained when TcO_2 is gradually reduced by a stream of H_2 (or CO_2/CO) indicates a hexagonal close packed structure for the technetium atoms. The cell constants reported by Muller et al. [23] and Lam et al. [24] are in good agreement. On the contrary, the considerably smaller cell dimensions [25] reported by Mooney

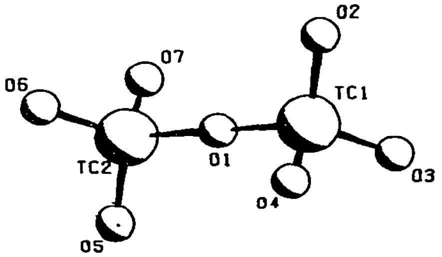

Fig. 3. Tc_2O_7.

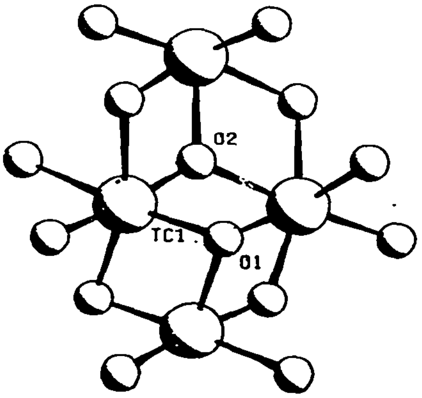

Fig. 4. A portion of the TcO_2 polymeric structure.

represent, with some degree of confidence, a virtually oxygen-free technetium metal. There is some evidence that technetium metal can hold small amounts of oxygen in the lattice.

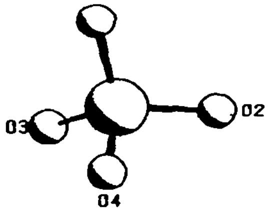

Fig. 5. $[TcO_4]^-$.

Muller et al. [23] also report a list of ternary oxides of technetium, in particular technetium-containing spinels and rare earth technetium pyrochlores, characterized only by X-ray powder patterns. Using rare earth pyrochlores as an indicator of relative sizes of tetravalent ions, an ionic radius of 0.67 Å was assigned to Tc(IV) (d^3 electron configuration).

X-ray diffraction analysis of tetramethylammonium technetate(VI) was performed by the Debye–Scherrer method [26]. In an attempt to solve the structure in the cubic space group $F\bar{4}3m$, it was assumed that the TcO_4^{2-} tetrahedra are not fixed in position but rather are rotating, similar to the anions in the high temperature modification of Li_2SO_4 [27] and $NaClO_4$ [28].

In addition to crystal data obtained for many pertechnetates [29,30], an accurate X-ray structure determination was performed on $KTcO_4$ [31] (Fig. 5). This 'scheelite type' structure represents the first precise determination of the Tc(VII)–O bond length (1.711 or 1.724 Å if corrected for vibrational oscillation of the tetrahedra). In this paper a correlation is shown to exist between bond lengths and oxidation number for the complete series of stable tetrahedral d^0 transition metals. Using the definition of Shannon and Prewitt [32], an 'effective ionic radius' of 0.35 Å can be derived for tetrahedral Tc(VII).

Lock has recently [33] reported on the structure of NH_4TcO_4 at 295, 208, and 141 K.

D. HALIDE AND OXYHALIDE COMPOUNDS

Among the known halogen and oxyhalogen compounds of technetium, listed in Table 1, complete X-ray structural determinations have been performed only for $(TcCl_4)_n$ [34] and $(TcOF_4)_3$ [35], while cell parameters have been determined for two modifications (cubic at room temperature and orthorhombic at reduced temperatures) of TcF_6 [36] and TcF_5 [37].

TABLE 1

Halogen and oxyhalogen technetium compounds

Oxidation state	Fluorine	Chlorine	Bromine
VII	TcO_3F	TcO_3Cl	—
VI	TcF_6 $TcOF_4$	$TcCl_6$	—
V	TcF_5	$TcOCl_3$	$TcOBr_3$
IV	—	$TcCl_4$	—

The structure of $TcCl_4$ represents a new structure-type for AB_4 compounds and consists of chain polymers of composition $(TcCl_4)_n$ (Fig. 6). The repeating unit of the chain, having the composition Tc_2Cl_8, comprises two parallel, approximately planar $TcCl_4$ groups. The two unshared *cis*-chlorine atoms form an edge of the distorted $TcCl_6$ units. The differences in length among the three pairs of chemically distinct Tc–Cl bonds (2.24, 2.38, and 2.49 Å, the shortest for the non-bridging chlorine atoms) have been tentatively explained in terms of varying degrees of π-bonding.

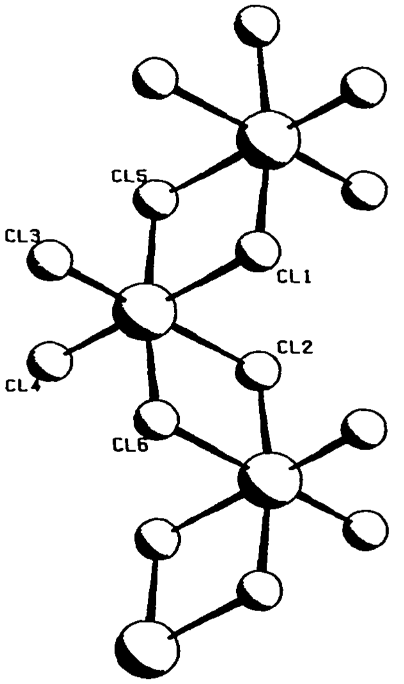

Fig. 6. A portion of the $TcCl_4$ polymeric structure.

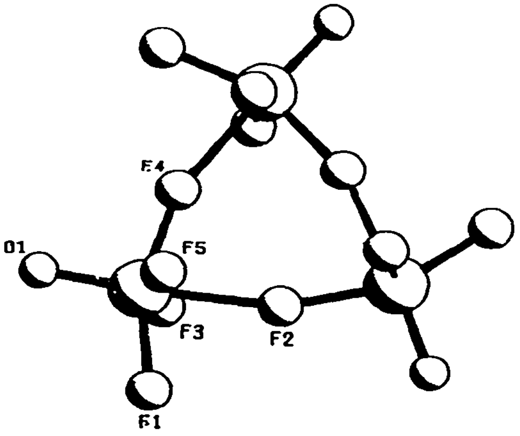

Fig. 7. The $(TcOF_4)_3$ trimer.

In $(TcOF_4)_3$ the octahedrally coordinated units are linked into trimers by *cis*-bridging fluorine atoms, an arrangement similar to that observed in molybdenum and rhenium oxotetrafluorides [38,39] (Fig. 7). The distortion in the coordination geometry corresponds to a 0.36 Å displacement of the technetium atom from the centre of the octahedron towards the oxygen atom. This distortion reflects the large steric requirements of the oxo ligand. The mean values for the distances are: Tc–O 1.66, Tc–F (terminal) 1.81, and Tc–F (bridge) 1.89 and 2.26 Å. These last represent the only Tc–F bond lengths measured to date.

E. POLYHALIDE AND POLYPSEUDOHALIDE COMPLEXES

Crystal data have been reported for the halo-, cyano-, and isothiocyanatotechnetate compounds reported in Table 2.

A structural study was carried out on potassium hexachlorotechnetate(IV) (Fig. 8) and the isomorphous $K_2Tc(OH)Cl_5$ [54]. A value of 1.36 Å was obtained for the octahedral covalent radius of technetate(IV), assuming a value of 2.35 Å for Tc(IV)–Cl in the regular octahedron and 0.99 Å for the Cl covalent radius. In a more recent paper [55] on the structure of $(NH_4)_2TcCl_6$ the Tc(IV)–Cl distance in the regular octahedron was determined to be 2.353 Å, a value significantly less than the value of 2.46 Å predicted from ionic radii [33]. Crystals of hexachlorotechnetic acid nonahydrate, $H_2TcCl_6 \cdot 9\ H_2O$, are composed of $TcCl_6^{2-}$ distorted octahedra with an average Tc–Cl distance of 2.33 Å and an average Cl–Cl separation of 3.44 Å. Within the crystal lattice only one chlorine atom is in contact with a Cl atom of a neighboring octahedron [65].

TABLE 2

Polyhalide and pseudopolyhalide complexes of technetium

Oxidation state	Complexes of known structure
V	$NaTcF_6$ [40], $KTcF_6$ [40], $[Ph_3PNPPh_3]TcOCl_4$ [62], $[(CH_3)_4N]Tc(NCS)_6$ [48]
IV	K_2TcF_6 [41], Rb_2TcF_6 [40], $(NH_4)_2TcF_6$ [41,42], Rb_2TcCl_6 [43,45], Cs_2TcCl_6 [45], $(NH_4)_2TcCl_6$ [45,46,55], K_2TcBr_6 [43–45], Rb_2TcBr_6 [43,47], Cs_2TcBr_6 [47], $(NH_4)_3TcBr_6$ [45,49], K_2TcI_6 [44,48], Rb_2TcI_6 [43,48], Cs_2TcI_6 [48], $(NH_4)_2TcI_6$ [48]
III	$[(n\text{-}C_4H_9)_4N]_3Tc(NCS)_6$ [67]
III, II	$[(n\text{-}C_4H_9)_4N]_2Tc_2Cl_8$
I	$K_5Tc(CN)_6$ [52]

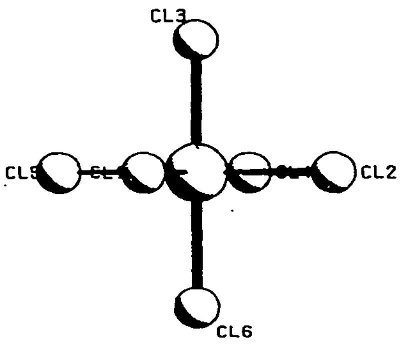

Fig. 8. $[TcCl_6]^{2-}$.

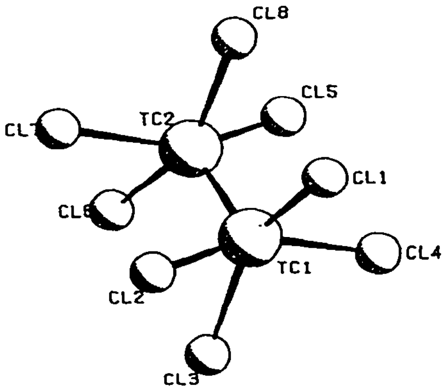

Fig. 9. $[Tc_2Cl_8]^{3-}$.

The structure of the trinegative octachloroditechnetate ion in $(NH_4)_3[Tc_2Cl_8] \cdot H_2O$ was determined by Bratton and Cotton [56]. The anion has the same non-bridged, eclipsed Cl_4M-MCl_4 structure (idealized D_{4h} symmetry) as do the $[Re_2Cl_8]^{2-}$ [57,58] and $[Mo_2Cl_8]^{4-}$ [59] ions (Fig. 9). The short Tc–Tc distance (2.13 Å) is indicative of a metal–metal bond ('quadruple bond'), while the mean Tc–Cl distance (2.36 Å) falls in the normal range [55]. Subsequent X-ray characterization of $[K_3Tc_2Cl_8] \cdot nH_2O$ [60] has conclusively identified the $[Tc_2Cl_8]^{3-}$ anion and determined more accurately the Tc–Tc distance (2.117 Å). A preliminary communication on this structure has come from Koz'min and Novitskaya [61]. The discrepancy indexes of the three structural variants of $K_8[H_3O][Tc_2Cl_8]_3 \cdot 3\,H_2O$ [66] are too high to allow an accurate description of these species. In general the $[Tc_2Cl_8]^{3-}$ geometry confirms those features emphasized by Cotton and Shive [60].

The dinegative octachloroditechnetate(III) anion [51] has also been isolated and it resembles the analogous rhenium complex in magnetic spectroscopic properties and preliminary structural data [53,58].

The identity and complete structure of $[n\text{-}C_4H_9N]_3[Tc(NCS)_6]$ have been determined unequivocally [67]. In hexakis(isothiocyanato)technetate(III) (Fig. 10) the technetium atom is situated on a crystallographic threefold rotation axis and its coordination environment is that of a nearly perfect octahedron, with Tc–N bond lengths of 2.04 and 2.05 Å and N–Tc–N angles ranging from 88.0 to 92.1°. This complex was originally misformulated [50].

The reduction of TcO_4^- by H_3PO_2 in aqueous HCl yields a dark green solution from which light olive crystals of $[(Ph_3P)_2N][TcOCl_4]$ [62] can be isolated. The square pyramidal tetrachlorooxotechnetate(V) anion (Fig. 11) is somewhat distorted and possesses only approximate C_{2v} symmetry with Cl–Tc–Cl angles of 139.2 and 153.7°. Contrariwise, the analogous $[ReOCl_4]^-$

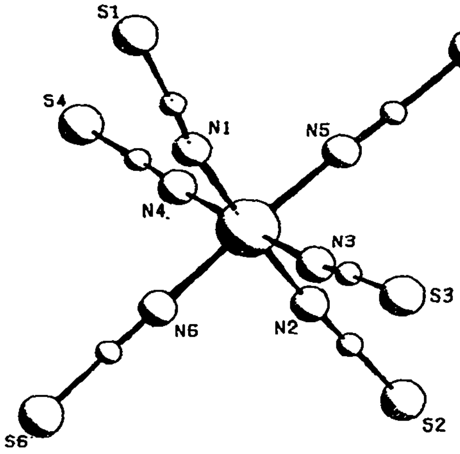

Fig. 10. $[Tc(NCS)_6]^{3-}$.

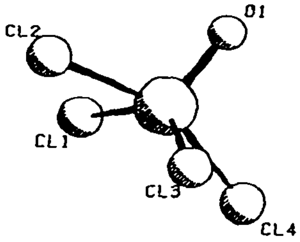

Fig. 11. $[TcOCl_4]^-$.

anion possesses C_{4v} symmetry [63] and the related $[MoOCl_4]^-$ [64] anion possesses a crystallographic C_{3v} site symmetry. The structure of $[TcOCl_4]^-$ is parental to the structures of several technetium(V) complexes containing the TcO^{3+} core that will be discussed in later sections [84–87]. In $[TcOCl_4]^-$ the strong *trans* influence of the oxo ligand is manifested by the absence of a *trans* ligand in the solid state, and the large steric requirement of the oxo ligand is manifested by bending of the chlorine atoms away from the $Tc=O$ moiety. This latter effect causes the Tc atom to lie 0.66 Å above the S_4-ruffled "square base" of four chlorine atoms. The Tc–O bond length is rather short at 1.61 Å.

F. COMPLEXES

(i) Complexes containing π-acceptor ligands

As expected, π-acceptor ligands stabilize technetium in low oxidation states, the resulting complexes being primarily six-coordinate with a more or less distorted octahedral coordination geometry. However, in certain cases higher coordination numbers and higher oxidation states are observed [67,72,94]. Because of the interest in technetium complexes with π-acceptor ligands as potential radiopharmaceuticals, the crystal structures of several such complexes have been determined recently; these are listed in Table 3.

A study of the oxidative addition of molecular chlorine to six-coordinate $[Tc(diars)_2Cl_2]^+$ to yield eight-coordinate $[Tc(diars)_2Cl_4]^+$ [68] led to structural determinations of $[Tc(diars)_2Cl_2]Cl$, $[Tc(diars)_2Cl_2]ClO_4$, and

TABLE 3

Complexes of technetium with π-acceptor ligands

Oxidation state	Complexes [a]
V	$[TcCl_4(diars)_2]PF_6$ [68]
IV	$[PPh_3R'][TcCl_5PPh_3]$ [69]
III	$[TcCl_2(diars)_2]ClO_4$ [70], $[TcCl_2(diars)_2]Cl$ [70], *mer*-$TcCl_3(PMe_2Ph)_3$ [71], $TcCl_3(CO)(PMe_2Ph)_3$ [72], $TcCl(acac)_2PPh_3$ [73,74]
II	$TcCl_2(P(OEt)_2Ph)_4$ [76]
I	$[Tc(CO)_2(P(OEt)_2Ph)_4]\ ClO_4$ [77], $TPP[Tc(CO)_3]_2$ [78]
0	$Tc_2(CO)_{10}$ [79,80]

[a] Abbreviations: R′ = (1-dimethyl-3-oxo)butyl; diars = *o*-phenylenebis(dimethylarsine); acac = acetylacetonate; and TPP = *meso*-tetraphenylporphine.

$[Tc(diars)_2Cl_4]PF_6$ (diars = *o*-$C_6H_4(As(CH_3)_2)_2$). The structures of the salts $[Tc(diars)_2Cl_2]X$ (X = Cl or ClO_4), reported by Elder et al. [70], show the Tc to be six-coordinate in a *trans*-octahedral coordination geometry; the two chlorine ligands are situated *trans* to one another, and the four As atoms, from the two nearly coplanar diars ligands, form the basal plane of the octahedron (Fig. 12).

In $[Tc(diars)_2Cl_4]PF_6$ the Tc is eight-coordinate in a D_{2d} dodecahedral coordination geometry; the four chlorine ligands form one compressed tetrahedron, while the four As atoms form a second elongated tetrahedron [68] (Fig. 13).

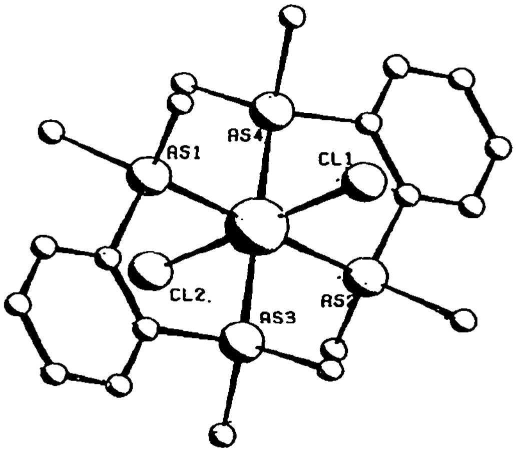

Fig. 12. *tr*-$[Tc(diars)_2Cl_2]^+$.

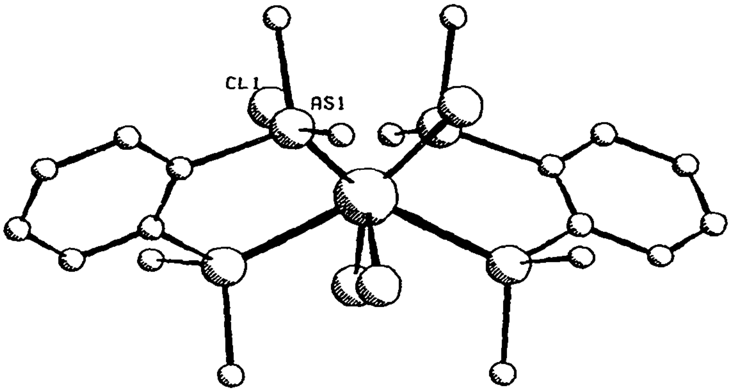

Fig. 13. $[Tc(diars)_2Cl_4]^+$

$[Tc(diars)_2Cl_2]Cl$ belongs to the space group $P2_1/c$, while $[Tc(diars)_2Cl_2]ClO_4$ belongs to the space group $C2$. The structural data for these complexes are generally in good agreement; the Tc–As and As–C distances, as well as the geometry of the diars ligands, are quite similar for both salts. However, the Tc–Cl distances show significant differences, caused apparently by the different distortions from ideal symmetry in each structure. In the chloride salt, with $\bar{1}$ site symmetry, the unique Tc–Cl distance is 2.329 Å and this value agrees well with the average value of 2.318 Å found for the perchlorate salt. But in this latter structure the two crystallographically independent Tc–Cl distances differ by 0.060 Å. This may arise from intramolecular forces elongating Tc–Cl(1) (2.348 Å) and intermolecular forces compressing Tc–Cl(2) (2.288 Å). $[Tc(diars)_2Cl_4]PF_6$ belongs to the orthorhombic space group *Fddd* [68]. The metal–ligand bond lengths in this eight-coordinate structure are longer than are the comparable bond lengths in the six-coordinate structures (Tc–As, 2.58 versus 2.51 Å; Tc–Cl, 2.44 versus 2.32 Å), reflecting the influence of the increased coordination number. The remarkable chemical stability of the eight-coordinate complex results at least in part from the presence of the diars ligands which are known to promote high coordination numbers.

The anionic complex $[Tc(PPh_3)Cl_5]^-$ has been recently synthesized [69] by reduction of pertechnetate with PPh_3 in hydrochloric acid. Within the usual octahedral geometry (Fig. 14), the Tc–Cl bond lengths (av. 2.34 Å) are in the normal range while the Tc–P bond length (2.57 Å) is very long.

Mer-$Tc(PMe_2Ph)_3Cl_3$ [71] is comprised of two independent molecules in the asymmetric unit of a large monoclinic unit cell. The coordination around technetium is that of a distorted octahedron and the two groups of ligands are arranged in *meridional* positions (Fig. 15). In this configuration the

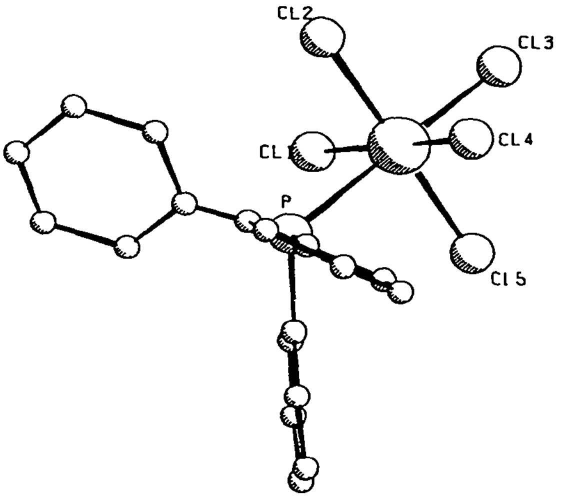

Fig. 14. $[Tc(PPh_3)Cl_5]^-$.

phosphine ligands undergo the least amount of steric hindrance. However, distortion of angles between *cis* ligands suggests mutual repulsion of the bulky phosphine ligands. Such distortions are common in transition metal complexes of phosphine ligands and have been ascribed to the contraction of the metal–phosphorus bond. The *trans* influence of the phosphine ligands has been noted [71]: the Tc–Cl bond length *trans* to P is 2.43 Å while those *trans* to Cl are both 2.33 Å.

The seven-coordinate complex $TcCl_3(CO)(PMe_2Ph)_3$ was studied in detail

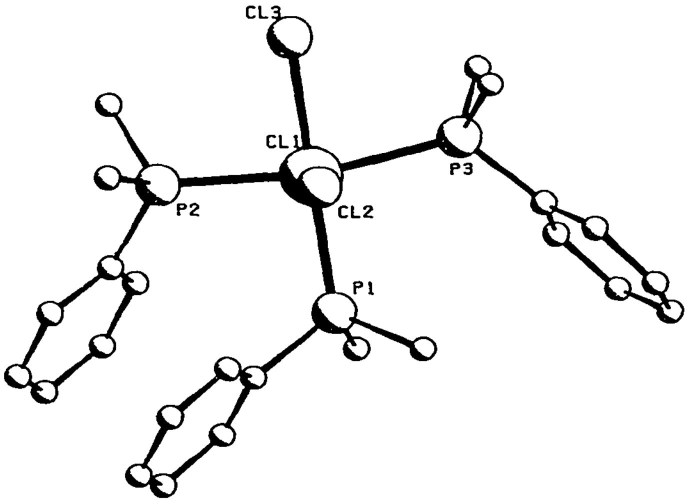

Fig. 15. *mer*-$Tc(PMe_2Ph)_3Cl_3$.

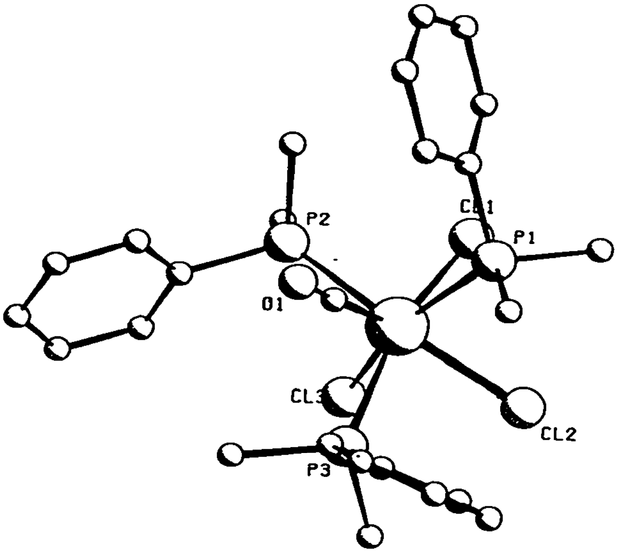

Fig. 16. $TcCl_3(CO)(PMe_2Ph)_3$.

by Bandoli et al. [72]. The coordination polyhedron (Fig. 16) is best described as a distorted, capped octahedron.

The technetium atom is bonded to three phosphine ligands (capped face), three chlorine ligands (uncapped face), and to a carbonyl group which occupies the unique capping position. The Tc–P distances average 2.44 Å,

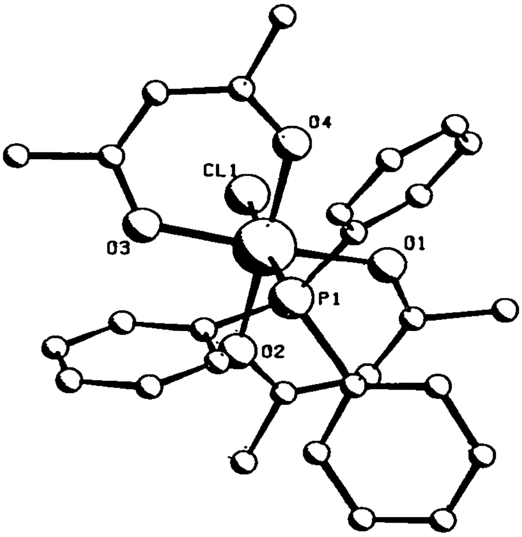

Fig. 17. *tr*-$Tc(acac)_2(PPh_3)Cl$.

the Tc–Cl distances average 2.48 Å and all three are equivalent. The Tc–CO distance is 1.86 Å. The C_{3v} symmetry of this structure was compared by the authors [72] to other symmetries possible for seven-coordinate complexes in terms of repulsion theory and the angular overlap model.

$TcCl(acac)_2PPh_3$ [73,74] is a member of a series of recently prepared acetylacetonate complexes of technetium which includes $[PPh_4][TcX_4(acac)]$, $TcBr_3(acac)PPh_3$, $TcX_2(acac)(PPh_3)_2$, $TcX(acac)_2PPh_3$, and $Tc(acac)_3$ (X = Cl or Br) [75]. $TcCl(acac)_2PPh_3$ (Fig. 17) crystallizes in two forms, and both modifications have been elucidated by X-ray analysis [73,74]. The first crystalline form contains two independent molecules per asymmetric unit. Both molecules are monomeric with a tetragonally distorted octahedral coordination geometry. The four oxygen atoms of the acac ligands comprise the basal plane (Tc–O, 2.01 Å) while the chlorine and phosphine ligands occupy apical positions (Tc–Cl, 2.42 Å; Tc–P, 2.46 Å). The acetylacetonate ligands are, as is usual, coordinated to the metal center in the enolate form through both oxygen atoms. Chemically equivalent bond lengths and angles within the acac ligands differ by less than two standard deviations, except for one C–O bond length. This longest C–O distance is associated with a short adjacent C–C bond. The angles at C and O are greater than 120°, reflecting the strain imposed by the small O–Tc–O angle and the requirement that the acac ring be planar in order to maximize electron delocalization. The second crystalline form consists of well separated monomeric units,

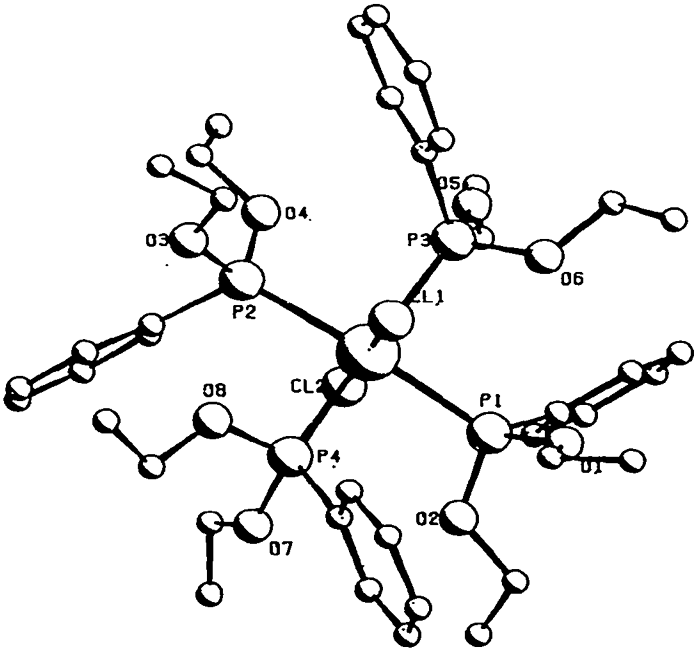

Fig. 18. *tr*-$Tc(PPh(OEt)_2)_4Cl_2$.

there being no substantial differences between structural parameters for the two forms. That the two triclinic modifications are not merely the same crystalline form in different settings is supported by the observations that (i) the IR spectra of the two forms in the 700–800 cm^{-1} region are different, and (ii) the Tc–Tc separation is different in the two forms (7.39 and 7.68 Å).

Dichlorotetrakis(diethylphenylphosphonite)technetium(II) [76] crystallizes in a monoclinic cell, the molecular symmetry being that of a coordination polyhedron $\bar{4}\,2\,m$, a subgroup of $4/mmm(D_{4h})$. The coordination geometry is that of a distorted octahedron, with four phosphorus atoms in the equatorial plane and two chlorine atoms in the apical positions (Fig. 18). The distortion results largely from the packing requirements of the bulky ligands. The observed Tc–P distances (2.41 Å) are short when compared with those of the *trans* phosphine ligands in *mer*-$TcCl_3(PMe_2Ph)_3$, but the Tc–Cl distances within the comparable linear Cl–Tc–Cl fragments of the two complexes are similar (2.41 Å).

Another interesting mixed phosphonite-carbonyl complex, $[Tc(CO)_2(P(OEt)_2Ph)_4]ClO_4$ has been structurally characterized by Mazzi and co-workers [77]. The structure consists of discrete monomeric *cis*-$[Tc(CO)_2(P(OEt)_2Ph)_4]^+$ cations (Fig. 19) and perchlorate anions. The tech-

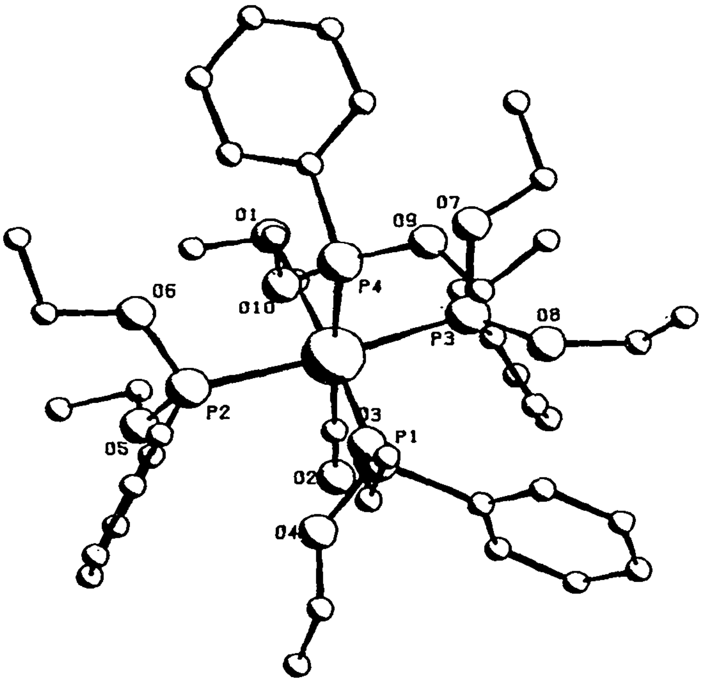

Fig. 19. *cis*-$[Tc(CO)_2(PPh(OEt)_2)_4]^+$.

netium(I) coordination geometry is that of a distorted octahedron; the two *trans*-situated phosphorus atoms, P2 and P3, are bent away from P1 within the plane containing Tc, P1, P2, P3, and C, thus reducing the P2–Tc–P3 angle to 170.4°. The Tc–P bonds *trans* to CO are longer than those *trans* to P (2.44 versus av. 2.39 Å) consistent with the greater *trans* influence of the carbonyl ligand relative to the phosphonite ligands.

Tsutsui et al. [78] have synthesized a series of technetium and rhenium mesotetraphenylporphyrin(TPP) complexes starting from $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$. Monometallic and bimetallic complexes (both homo- and heteronuclear) porphyrin complexes were obtained. In the bimetallic complexes the porphyrin acts as a bridging bis(tridentate) ligand, while in the analogous monometallic complexes it acts as a simple tridentate ligand. Each metal ion is bonded to three carbonyl groups and three adjacent pyrrole nitrogen atoms, and is therefore not within the plane of the porphyrin ring. The homodinuclear complexes $TPP[Tc(CO)_3]_2$ (Fig. 20) and $TPP[Re(CO)_3]_2$ are isostructural. The better defined Tc structure consists of centrosymmetric complexes having two metal ions bonded to a highly distorted porphyrin macrocycle. One Tc atom is 1.42 Å above, and one is an equal distance below, the plane of the four pyrrole nitrogen atoms. The metal ions are not positioned directly over the center of the macrocycle but are offset. Thus there are three types of Tc–N distances; the distance from Tc to the non-bonded nitrogen atom is 3.21 Å, the distance from Tc to the bridging nitrogen atoms (N2 and N4) is 2.39 Å (average), and the distance from Tc to the non-bridging nitrogen atoms (N1 and N3) is 2.16 Å.

The crystal structure determination of ditechnetium decacarbonyl [79–80],

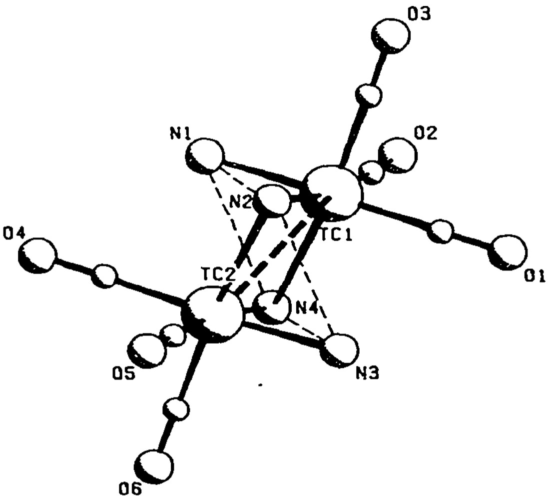

Fig. 20. $TPP[Tc(CO)_3]_2$.

in conjunction with comparable data for the $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ analogues, has generated several theoretical studies of this important molecule. The monoclinic unit cell contains a dimeric molecule located on a crystallographic twofold axis that is perpendicular to the Tc–Tc bond. The molecules possess D_{4d} symmetry, the octahedral coordination about each technetium center being such that the two sets of four equatorial carbonyl ligands are in a staggered configuration (Fig. 21). The Tc–Tc bond distance, 3.036 Å is 0.11 Å greater than the Mn–Mn distance in $Mn_2(CO)_{10}$, and, surprisingly, is 0.02 Å greater than the Re–Re distance in $Re_2(CO)_{10}$ [81,82]. It is noteworthy that this Tc–Tc distance is much larger than the Tc–Tc distance (2.13 Å) in $Tc_2Cl_8^{3-}$ which contains a multiple bond between the two metal atoms [56]. The equatorial and apical carbonyl ligands in $Tc_2(CO)_{10}$ are significantly different. For the equatorial carbonyl groups the average Tc–C distance is 2.00 Å and the average C–O distance is 1.12 Å; for the apical carbonyl groups the Tc–C distance is 1.90 Å and the C–O distance is 1.20 Å. Thus the equatorial Tc–C distances are 0.1 Å (average) longer than the apical Tc–C distance, and the equatorial C–O bonds are 0.085 Å (average) shorter than the apical C–O bond. The same phenomenon is observed in $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ [82], and $HMn(CO)_5$ [83], and is readily explained by the strong π-acid character of coordinated CO. In octahedral complexes of the form $XMn(CO_5)$, where X is a poorer π-acid than CO (here X is $Tc(CO)_5$, $Mn(CO)_5$, $Re(CO)_5$, or H), the CO *trans* to X accepts greater π-electron density from M than do the CO groups *cis* to X. This excess π-electron density on the *trans* (apical) CO group weakens the C–O bond and strengthens the Tc–C bond.

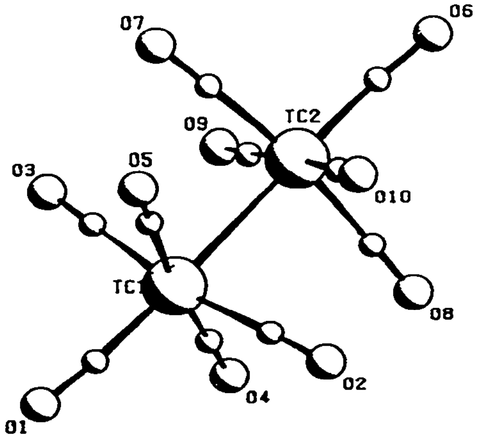

Fig. 21. $Tc_2(CO)_{10}$.

(ii) Complexes containing the Tc = O group

Reduction of pertechnetate in aqueous media is very likely to lead to complexes containing the Tc = O group. Since these are exactly the synthetic conditions that are used to generate ^{99m}Tc radiopharmaceuticals, it is important to understand the physical and chemical properties associated with the Tc = O moiety. It is to be expected that the structural chemistry of complexes containing the Tc = O linkage will be dominated by the strong *trans* influence and great steric requirement of the oxo ligand. These expectations are fulfilled in all the technetium(V) structures containing the TcO^{3+} core that have been reported to date, including the parental structure of $TcOCl_4^-$ which was discussed earlier (Fig. 11).

DePamphilis et al. [84] synthesized the $[TcO(SCH_2COS)_2]^-$ anion by adding an aqueous solution of pertechnetate to an aqueous solution of technical grade thioglycolic acid that had been adjusted to pH 7.5. The technical grade $HSCH_2COOH$ was contaminated with $HSCH_2COSH$ which preferentially coordinated to the technetium center. Addition of $[(n\text{-}C_4H_9)_4N]Br$ to the reaction mixture caused precipitation of yellow-brown $[(n\text{-}C_4H_9)_4N][TcO(SCH_2COS)_2]$ powder which upon recrystallization yielded crystals belonging to the monoclinic space group *Cm*. The coordination environment around the technetium(V) center is that of an approximate square pyramid with the oxo oxygen atom at the apex and the four sulfur atoms forming the basal plane (Fig. 22). The deviation from ideal square pyramidal geometry involves a slight difference in the length of the Tc–S1 and Tc–S2 bonds (2.336 and 2.303 Å). The technetium atom is 0.791 Å above the basal plane and the Tc–O line (1.672 Å) is perpendicular to the least-squares plane formed by the four sulfur atoms. The authors noted

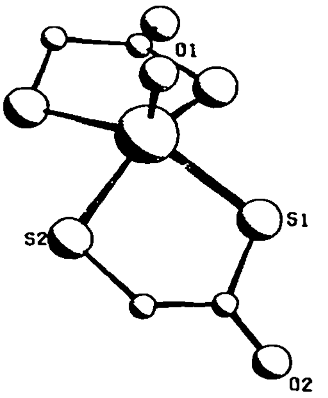

Fig. 22. $[TcO(SCH_2COS)_2]^-$.

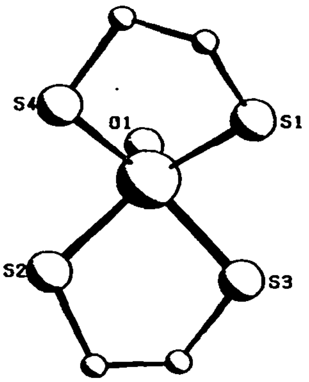

Fig. 23. $[TcO(SCH_2CH_2S)_2]^-$.

several similarities between the "$TcOS_4$ core" and the isoelectronic "$MoOS_4$ core" of $MoO((n\text{-}C_3H_7)_2dtc)_2$.

In a companion paper Smith et al. [85] investigated the complexation of technetium by dithiols and structurally characterized the anionic $[TcO(SCH_2CH_2S)_2]^-$ complex. This material was synthesized by reducing pertechnetate with $NaBH_4$ in the presence of 1,2-ethanedithiol, followed by precipitation with Ph_4AsCl. The same complex may be prepared by substitution of 1,2-ethanedithiol onto $[TcOCl_4]^-$ [86]. The structure of the $[TcO(SCH_2CH_2S)_2]^-$ anion is very similar to that of $[TcO(SCH_2COS)_2]^-$ anion (Figs. 22 and 23). Again, the oxo oxygen atom forms the apex of an approximate square pyramid, the technetium atom being 0.761 Å above the mean plane of the four sulfur atoms. The average Tc–S distance is 2.30 Å, and the Tc–O distance is 1.64 Å.

In contrast to the above five-coordinate complexes formed from TcO^{3+} core and two bidentate ligands, Thomas et al. [87] prepared a six-coordinate complex from the TcO^{3+} core by using a tripodal, tridentate ligand. Dichloro(hydrotris(1-pyrazolyl)borato)oxotechnetium(V) may be synthesized by reduction of pertechnetate in 3 M HCl containing the $[HBPz_3]^-$ ligand, or by substitution of $[HBPz_3]^-$ onto $[TcOCl_4]^-$ [88]. The crystal structure consists of discrete $TcOCl_2(HBPz_3)$ molecules with technetium in a distorted octahedral coordination environment. The six ligating atoms are the oxo oxygen atom, two chlorine atoms, and the three nitrogen atoms of the tripodal $HBPz_3^-$ ligand which occupy one face of the coordination octahedron (Fig. 24). The Tc–N bond that is *trans* to the oxo functionality is ca. 0.2 Å longer than are the other Tc–N bonds which are *trans* to the chlorine ligands (2.26 versus 2.09 Å). The Tc–O distance of 1.656 Å is normal for a doubly bonded oxo ligand. The oxo group dominates the structural description of $TcOCl_2(HBPz_3)$ in that it not only induces a large

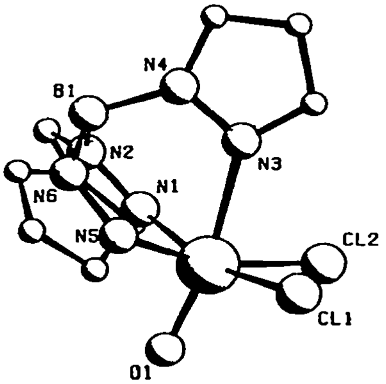

Fig. 24. $Tc(HBPz_3)Cl_2O$.

structural *trans* effect, but also the large steric requirement of this group causes the *cis* ligands to bend away from the Tc = O linkage and toward the *trans* pyrazolyl ring. The effect of this bending of the equatorial ligands away from the oxo group is readily observed in the inter-ring angles of the $[HBPz_3]^-$ ligand.

The TcO^{3+} core may also be incorporated into a seven-coordinated technetium(V) complex by using the hexadentate EDTA ligand [89]. Reaction of H_4EDTA with $[TcOCl_4]^-$ in anhydrous dimethylsulfoxide yields the $[Tc(O)EDTA]^-$ anion in nearly quantitative yield. Structural analysis of the anhydrous barium salt, $Ba[Tc(O)EDTA]_2$ shows that it consists of discrete, monomeric anions that are bridged by coordination to barium cations. Each barium atom is eight-coördinate, with an approximately dodecahedral coordination geometry, being ligated by each of the eight carboxylates within the unit cell. In this arrangement every carboxylate group bridges a Tc center to a Ba center. Each technetium atom is seven-coordinate with a coordination geometry that can best be described as a distorted pentagonal bipyramid; two carboxylate oxygen atoms of the EDTA occupy the axial sites, while the equatorial sites are occupied by the two nitrogen atoms, the oxo oxygen atom, and the other two carboxylate oxygen atoms of the hexadentate EDTA ligand (Fig. 25). The midpoint of the two nitrogen atoms is approximately *trans* to the oxo oxygen atom, and correspondingly the Tc–N bond length is rather long (2.350 Å). The doubly bonded Tc–O distance within the TcO^{3+} core is normal at 1.657 Å, while the singly bonded Tc–O distances associated with the carboxylate groups are rather long (2.16 and 2.03 Å) reflecting both the seven-coordination about Tc and the fact that the carboxylates bridge Tc to Ba.

$[TcO_2(py)_4]^+$, a technetium(V) complex containing the linear TcO_2^+ core

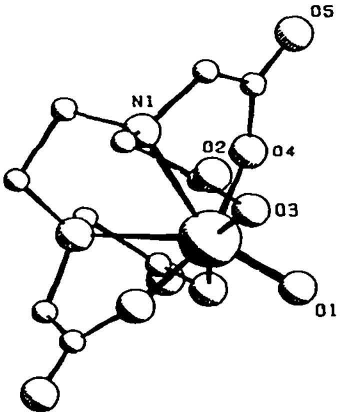

Fig. 25. $[TcO(EDTA)]^-$.

(py = pyridine), has been briefly examined by Kuznetzov et al. [90]. They report that orange-red crystals of $[TcO_2(py)_4]Cl \cdot n\ H_2O$ are not stable and become dark in a few days, and thus accurate structural data could not be obtained. However, limited X-ray and IR data established that this technetium complex is isostructural with the more stable rhenium analogue $[ReO_2(py)_4]Cl \cdot 2\ H_2O$ [91,92]. Thus it is inferred that the coordination geometry about technetium is that of a distorted octahedron, the four pyridine nitrogen atoms forming a basal plane and the *trans*-situated oxo oxygen atoms occupying apical sites; the chloride counterion and waters of crystallization are not coordinated to the metal. No bond lengths or bond angles were reported.

(iii) Other complexes

The first X-ray structural determination of a technetium complex containing a ligand which forms the basis of a clinically useful ^{99m}Tc radiopharmaceutical was accomplished by Libson et al. [93]. They reported on the synthesis and structure of $\{[Li(H_2O)_3][Tc(OH)(MDP)] \cdot \frac{1}{3}\ H_2O\}_n$ where MDP represents methylenediphosphonate, $[O_3PCH_2PO_3]^{4-}$, a ligand which is used in the preparation of efficacious ^{99m}Tc skeletal imaging agents and ^{99m}Tc myocardial infarct imaging agents. The structure of this material consists of infinite polymeric chains. Each MDP ligand bridges two symmetry related technetium atoms and each technetium atom is bound to two symmetry related MDP ligands (Fig. 26); the MDP/Tc ratio within the polymer is therefore 1 : 1. The polymeric repeat unit is completed by an oxygen atom (presumably in the form of an hydroxyl ion) that bridges two symmetry related technetium atoms, and by a hydrated lithium cation which neutralizes the charge associated with each repeat unit. In addition, there is a single oxygen atom (presumably in the form of a distorted water molecule) on the threefold axis of the space group ($R\bar{3}$). The postulated protonation states of the bridging and non-coordinated oxygen atoms are chemically reasonable and consistent with an assumed Tc(IV) oxidation state, but are not definitively established by the X-ray data. Other possible formulations include $\{[Li(H_2O)_3][Tc^{IV}(O)MDP] \cdot \frac{1}{3}\ H_2O\}_n$ and $\{[Li(H_2O)_3][Tc^{V}(O)MDP] \cdot \frac{1}{3}\ H_2O\}_n$. Each technetium center has approximately octahedral coordination geometry, the two bridging oxygen atoms occupying *cis* coordination sites. The bridging oxygen to technetium bond distance (1.94 Å average) is generally in line with observed Tc–O single bond lengths (1.98–2.09 Å), Tc = O double bond lengths being considerably shorter (1.61–1.71 Å). Bond lengths and bond angles within the MDP ligand are generally as expected from structural studies on the free ligand.

The structure of another technetium complex of relevance to nuclear medicine was reported by Deutsch et al. [94]. Following a general procedure for the synthesis of ^{99m}Tc radiopharmaceuticals, pertechnetate was reduced by $SnCl_2$ in the presence of dimethylglyoxime (dmg); on standing in air this reaction mixture yielded crystals of the binuclear technetium–tin complex

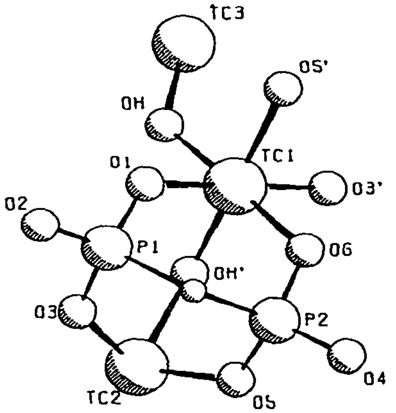

Fig. 26. A portion of the $[Tc(OH)(MDP)]_n^-$ polymeric structure.

$[Tc(dmg)_3(SnCl_3)(OH)] \cdot 3\ H_2O$. In this material the Tc and Sn atoms are joined by three bridges, the separation between the metal centers being 3.47 Å. One bridge is comprised of a single oxygen atom, while the other two bridges consist of two-atom N–O linkages from different dmg ligands. The Sn atom is octahedrally coordinated; three sites are occupied by chloride ligands in a *fac* configuration, the fourth position is filled by the bridging oxygen atom, and the last two sites contain oxime oxygen atoms from two dmg ligands that are also bonded to Tc. The technetium atom is seven-coordinate in what may be described as a capped trigonal prismatic arrangement (Fig. 27); six imino nitrogen atoms from the free dmg ligands, and the bridging oxygen atom, comprise the coordination sphere. The formal oxidation states of the tin and technetium cannot be definitively assigned from the X-ray data. However, on the basis of observed Sn–Cl bond lengths the tin is undoubtedly present as Sn(IV), and on the basis of magnetic measurements the technetium is most likely present as Tc(V). The structure of $[Tc(dmg)_3(SnCl_3)(OH)] \cdot 3\ H_2O$ exhibits several novel aspects: the close association between Tc and Sn, the unusual coordination number and environment of Tc, the unusual mode of coordination of the dmg ligands (which does not involve any intraligand hydrogen bonding), and the oxygen atom bridge between Tc and Sn. The authors speculate that this oxygen atom bridge may be formed during the inner sphere reduction of technetium by Sn(II). Such an inner sphere reduction process would involve coordina-

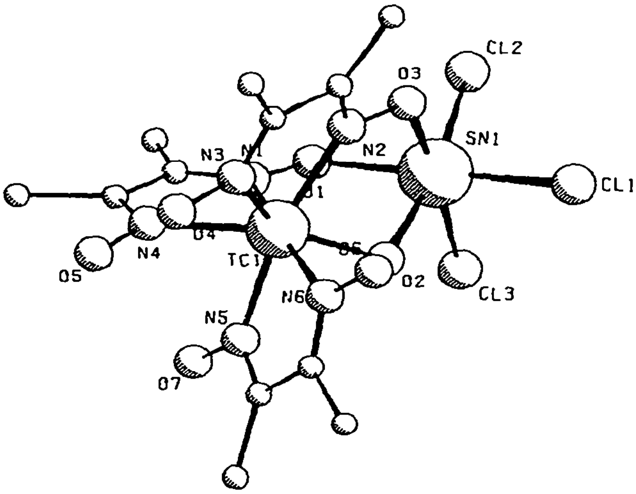

Fig. 27. $Tc(dmg)_3(SnCl_3)(OH)$.

tion of one of the oxygen atoms of pertechnetate to $SnCl_3^-$ (the form of tin(II) in aqueous HCl media) prior to a two electron transfer from Sn(II) to Tc; this electron transfer would maintain the Sn–O–Tc linkage and create the relatively stable $Cl_3Sn(IV)$–O–Tc bridge moiety. Such a process could account for the close association between Tc and Sn observed in many ^{99m}Tc radiopharmaceuticals prepared by the stannous ion reduction of pertechnetate. Taken together, the pair of structures $\{[Li(H_2O)_3][Tc(OH)MDP]\cdot\frac{1}{3}\ H_2O\}_n$ and $[Tc(dmg)_3(SnCl_3)(OH)]\cdot 3\ H_2O$ emphasize that the oxo group of TcO^{3+} (and presumably also TcO_2^+) cores are potential ligands for other metal centers. Thus, by coordination to a second metal center, monodentate oxo ligands can be converted into bidentate oxygen atom bridges as in the Tc–O–Tc and Tc–O–Sn linkages of the structures just cited.

Cotton and co-workers have continued their theoretical and structural studies of dimeric complexes derived from $Tc_2Cl_8^{3-}$ (Fig. 9). Crystals of the Tc^{III}–Tc^{III} dimer $Tc_2Cl_2(OCCMe_3)_4$ (Fig. 28) were prepared by dissolving the Tc^{II}–Tc^{III} salt $(NH_4)_3Tc_2Cl_8$ in molten pivalic acid [95]. The structure consists of discrete molecules of crystallographic 4/m symmetry. Within each molecule four carboxylate ligands bridge two technetium atoms that also contain axially coordinated Cl ions. There is a quadruple Tc–Tc bond of length 2.192 Å. This Tc^{III}–Tc^{III} distance is at least 0.07 Å longer than that in $Tc_2Cl_8^{2-}$ since the metal–metal distance in this latter Tc^{III}–Tc^{III} compound is likely to be even shorter than in the Tc^{II}–Tc^{III} dimer $Tc_2Cl_8^{2-}$ where it is 2.117 Å. The authors noted that in $Re_2Cl_2(O_2CCMe_3)_4$ the Re^{III}–Re^{III} distance (2.236 Å) is within the range observed for $Re_2Cl_8^{2-}$ in

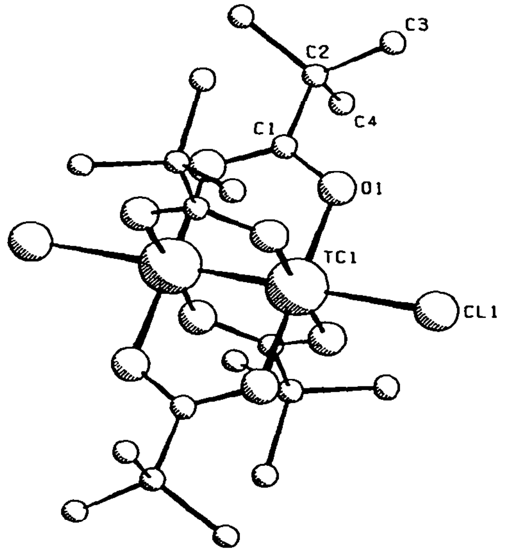

Fig. 28. $Tc_2Cl_2(OOCCMe_3)_4$.

various compounds (2.222–2.241 Å). From this they concluded that the long Tc–Tc bond of $Tc_2Cl_2(O_2CCMe_3)_4$ is directly related to the fact that it also contains remarkably short axial Tc–Cl bonds (2.408 Å).

The reaction of 2-hydroxypyridine (α-pyridone) with $Tc_2Cl_8^{3-}$ yields the Tc^{II}–Tc^{III} dimer $[Tc_2(OC_5H_4N)_4]Cl$ [96] in which the Tc–Tc bond is maintained. The structure of this material consists of infinite chains of $[Tc_2(OC_5H_4N)_4]^+$ units (Fig. 29) symmetrically linked by bridging chloride ions. The space group $I4/m$ was assigned by treating each ligand as being subject to a twofold orientational disorder. In this disordered model the point symmetry of an individual cation cannot be assigned. The very short Tc–Tc distance (2.095 Å) in this dimer was viewed as being related to the rather long Tc–Cl axial bonds (2.678 Å); the long Tc–Tc and short Tc–Cl bonds of $Tc_2Cl_2(O_2CCMe_3)_4$ provide an obvious counterpoint.

An interesting complex of technetium(IV) with salicylaldehyde(sal), $[Ph_4P][TcCl_4(sal)]$, has been recently characterized (Fig. 30) [97]. The salicylaldehydate ligand is bidentate and, as expected, the two chemically inequivalent oxygen atoms are at different distances from the Tc center (1.98 and 2.04 Å).

In a systematic effort to prepare ammine complexes of low valent technetium, Armstrong and Taube [98] isolated crystals of *trans*-$[Tc(NH_3)_4(H_2O)(NO)]Cl_2$. In their report [98] they present some results of a single crystal X-ray diffraction analysis conducted by J.L. Hoard of Cornell

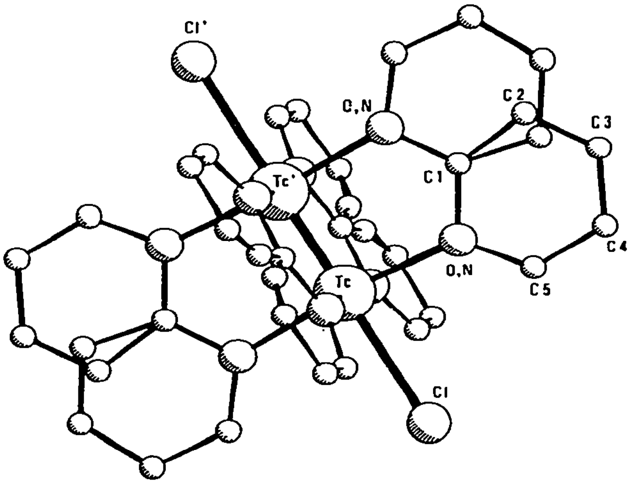

Fig. 29. $[Tc_2(OC_5H_4N)_4]Cl$.

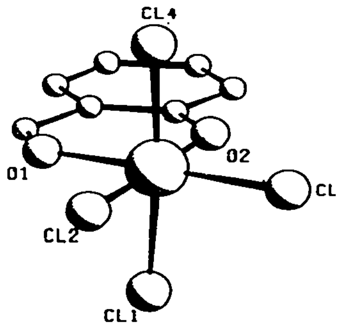

Fig. 30. $[TcCl_4(sal)]^-$.

University. Bond distances (Å): N–O, 1.203; Tc–NO, 1.716; Tc–NH_3(average), 2.163; and Tc–OH_2, 2.168. Bond angle: Tc–N–O, 178.7°.

The unusual technetium(VII) complex K_2TcH_9 has been prepared by reaction of pertechnetate with potassium metal in anhydrous ethylenediamine–ethanol mixtures [99]. Powder patterns show that this material is isostructural with the rhenium analog K_2ReH_9 which has been characterized by neutron diffraction [100]. It is therefore inferred that the technetium atoms are at the centers of trigonal prisms of H atoms, with three additional H atoms beyond the centers of the prism faces.

G. MISCELLANEOUS

Some alloys containing technetium and one other element (Si, Al, N, or B) have been studied by X-ray techniques. Whitmann and Nowotny [101] examined "technetium disilicide" by powder diffraction and found it to be $TcSi_{1.75}$, the smallest cell containing Tc_4Si_7. This structure was compared to other so called "M–Si_2" compounds. $TcAl_6$ was investigated by Wilkinson [102]. The Tc–Al bond length is well defined at 2.60 Å, but the Al–Al distances range from 2.56 to 2.98 Å. When technetium metal is heated in ammonia at 700–1100°C, powder diffraction analysis [103] shows the formation of a new phase of composition $TcN_{0.76}$ (NaCl type structure). Three well characterized technetium–boron alloys have been prepared by heating boron and technetium under high pressure for extended periods: Tc_3B, orthorhombic lattice, space group D_{2h}^{17}–$Cmcm$; Tc_7B_3, hexagonal symmetry, two molecules per unit cell, space group C_{6v}^4–$P6_3$mc; TcB_2, hexagonal symmetry, two molecules per unit cell, space group D_{6h}^4–P_6/mmc.

H. CONCLUSIONS

(i) General

As expected from its central position among the *d*-block metals, technetium exhibits a wide variety of oxidation states, coordination numbers, and coordination geometries [16]. For example, even just within the Tc(V) oxidation state, complexes of coordination numbers 5, 6, 7, and 8 have been structurally characterized. This variable coordination environment is dramatically illustrated by a series of increasingly complicated compounds constructed about the TcO^{3+} core. (1) Five coordinate $[TcOCl_4]^-$ (Fig. 11) is the simplest complex of this series, containing only four monodentate ligands [62]. This complex has coordination sites characterized by three different labilities: the oxo oxygen atom is very inert to substitution; the four chlorine atoms are susceptible to substitution and may be replaced by a variety of ligands to yield new complexes containing the TcO^{3+} core; the site *trans* to the oxo oxygen atom is very labile, and while in the solid state no ligand occupies this site, it is presumed that in solution ligands can loosely coordinate at this position. (2) The five-coordinate $[Tc(O)(dithiolato)_2]^-$ complexes (Figs. 22 and 23) are generated from $[TcOCl_4]^-$ by replacing the four monodentate chloride ligands by two chelating dithiolato ligands [84–86]. (3) The six-coordinate $TcOCl_2(HBPz_3)$ complex (Fig. 24) is generated by replacing two of the chloride ligands of $[TcOCl_4]^-$ by the tripodal, tridentate ligand $[HBPz_3]^-$. The tripodal configuration of this ligand forces one of the pyrazole rings into a position where it coordinates to the site *trans* to the oxygen atom [87]. (4) The seven-coordinate $[Tc(O)EDTA]^-$ complex (Fig. 25) is generated by replacing all four chloride ligands of $[TcOCl_4]^-$ by the six coordinating atoms of EDTA [89]. This increase in coordination number from five to seven is formally accomplished by adding the two nitrogen atoms of EDTA to the previously vacant coordination site *trans* to the oxo oxygen atom. The two nitrogen atoms are held in this very labile "*trans*" site by coordination of the four carboxylate arms of EDTA to the less labile "*cis*" sites and the resulting hexadenticity. (5) The seven-coordinate environment can become even more complicated when the oxo oxygen atom of the TcO^{3+} core acts as a ligand to a second metal center. This is the situation observed in $[Tc(dmg)_3(SnCl_3)(OH)] \cdot 3\ H_2O$ (Fig. 27) wherein the seven-coordinate technetium(V) center is bridged to tin via a Tc–O–Sn linkage [94]. This flexible coordination environment of the TcO^{3+} core is not surprising when the electronic configuration of technetium(V) is considered.

The strong ligand field of the oxo ligand destabilizes the d_{yz} and d_{xz} orbitals sufficiently so that the two d electrons of technetium(V) are paired in the d_{xy} orbital (all the above TcO^{3+} complexes are diamagnetic). Thus the TcO^{3+} core has a "closed shell" electronic configuration and does not lose or gain ligand field stabilization energy as a function of the coordination environment. In this situation the d^2 TcO^{3+} core behaves as a d^0 metal and can readily adapt to that coordination geometry dictated by the particular properties (denticity, number of chelate rings, etc.) of a given ligand.

The oxo group dominates the chemistry of high valent technetium complexes, especially those produced by the reduction of pertechnetate in aqueous media (all of the above TcO^{3+} complexes can be synthesized by this route). In terms of structural chemistry this domination is manifested in three ways. (1) The oxo ligand induces a large structural *trans* effect (STE, or *trans* influence) which in some of the TcO^{3+} examples noted above leads to five-coordinate complexes [62,84,85]. In $TcOCl_2(HBPz_3)$ the STE is 0.17 Å [87] and in $(TcOF_4)_3$ [39] it is 0.37 Å. (2) The oxo group has a large steric requirement, primarily because of the short Tc = O distance (ca. 1.65 Å). In the five-coordinate TcO^{3+} complexes this is manifested in the four ancillary ligand atoms bending away from the oxo group, causing the Tc center to be situated significantly (0.65–0.80 Å) above the plane of the four ancillary ligand atoms [62,84,85]. In six-coordinate $TcOCl_2(HBPz_3)$ this is manifested most dramatically by the equatorial pyrazolyl rings bending away from the oxo ligand and towards the *trans* pyrazolyl ring; this leads to the largest tris(pyrazolyl)borate inter-ring angle yet observed (139°) [87]. (3) The oxo group can function as a ligand to a second metal center, thus generating oxygen atom bridged structures such as illustrated in Figs. 26 and 27 [93,94]. Bridge formation converts a doubly bonded, monodentate, oxo ligand to a bridging, bis(monodentate) ligand, and thus the Tc–O bond lengthens considerably (from ca. 1.65 to 2.03 Å).

The technetium(V) complex $[TcO_2(py)_4]^+$ contains the *trans*-TcO_2^+ core rather than the TcO^{3+} core [90]. Other very recent examples of complexes containing the *trans*-TcO_2^+ core are also known (e.g. $[TcO_2(cyclam)]^+$ [104] and $[TcO_2(diars)_2]^+$ [105]). These structures raise the question as to what factors determine whether the technetium(V) center is more stable with one or two oxo ligands. From the limited data available it appears that the major factor is neutralization of the high formal charge on technetium(V). If the ancillary ligands donate significant negative charge to the technetium center, then only one oxo group is required and the TcO^{3+} core is favored; this is the case with all the TcO^{3+} complexes with negatively charged ligands (chloride, dithiolates, EDTA, etc.) discussed above. However, if the ancillary ligands do not donate significant negative charge (e.g. neutral ligands such as pyridine or diars), or if they remove negative charge by efficient π-backbonding (e.g. cyanide [106]), then two oxo groups are required and the TcO_2^+ core is favored.

(ii) Bond lengths

Bond lengths are probably the most useful form of structural data and accordingly Tables 4–6 list Tc–X bond lengths for the limited number of technetium compounds that have been structurally characterized. As expected, Tc–X bond lengths are a function of the technetium oxidation state, the technetium coordination number, and the nature of the *trans*-situated group. For certain X atoms the Tc–X distance is also a function of the ability of the technetium center to donate π-electron density, and the nature of the non-technetium substituents bonded to X. Given these variables, the assignment of a "normal" or "average" Tc–X bond length has doubtful validity. However, in those cases where the range of observed Tc–X bond lengths is reasonably narrow the authors have specified an "average" Tc–X length in the expectation that these "average" values may be useful in deciding when newly reported Tc–X distances are significantly aberrant.

Tc–Cl

Table 4 lists the available Tc–Cl bond-length data. There are 12 Tc–Cl entries wherein (i) the Tc oxidation state is mixed II/III, III, IV, or V, (ii) the coordination number of Tc is six, and (iii) the *trans*-situated atom is either chloride, singly bonded oxygen, or singly bonded nitrogen. These 12 values range from 2.32 to 2.36 Å and thus for the stated conditions it is reasonable to assign an "average" Tc–Cl bond length of 2.34 Å. Changing the technetium coordination from six causes the Tc–Cl bond length to vary in a predictable manner: in five-coordinate $[TcOCl_4]^-$ the Tc–Cl decreases slightly to 2.31 Å while in eight-coordinate $[TcCl_4(diars)_2]^+$ it increases significantly to 2.44 Å. From these comparisons it would seem as though the technetium coordination number is more important than the technetium oxidation state in determining the Tc–Cl distance. If chlorine is *trans* to a phosphorus atom in a six-coordinate Tc(II) or Tc(III) complex, the Tc–Cl distance increases significantly due to the structural *trans* effect induced by P; for the four examples of Table 4 the range is 2.41–2.45 Å and the average is 2.43 Å. If the chlorine is *trans* to P in a seven-coordinate complex, the Tc–Cl distance further increases to 2.48 Å (one example).

Tc–P

To a first approximation Tc–Cl bond distances are only dependent upon the technetium oxidation state, the technetium coordination number, and the nature of the *trans*-situated group. However, because of extensive π-back-

TABLE 4

Collection of Tc–Cl and Tc–P bond lengths (Å)

Compound [a]	Coordination number	Oxidation state	Tc–Cl	Tc–P	Ref.
$[TcCl_4]_n$	6	IV	2.24; 2.38; 2.49		34
$K_2[TcCl_6]$	6	IV	2.35		54
$K_2[Tc(OH)Cl_5]$	6	IV	2.33		54
$(NH_4)_2[TcCl_6]$	6	IV	2.35		55
$H_2TcCl_6 \cdot 9\ H_2O$	6	IV	2.33		65
$(NH_4)_3[Tc_2Cl_8] \cdot 2\ H_2O$	5	II, III	2.36		56
$K_3[Tc_2Cl_8] \cdot nH_2O$	5	II, III	2.36		60
$(Ph_3PNPh_3)[TcOCl_4]$	5	V	2.31		62
$[TcCl_4(diars)_2]PF_6$	8	V	2.44		68
$[TcCl_5(PPh_3)]PPh_3R'$	6	IV	2.34	2.57	69
trans-$[TcCl_2(diars)_2]Cl$	6	III	2.33		70
trans-$[TcCl_2(diars)_2]ClO_4$	6	III	2.32		70
mer-$TcCl_3(PMe_2Ph)_3$	6	III	2.33; 2.45	2.42; 2.47	71
$[TcCl_3(PMe_2Ph)_3(CO)] \cdot EtOH$	7	III	2.48	2.44	72
trans-$TcCl(PPh_3)(acac)_2$ (α-form)	6	III	2.42	2.46	73
trans-$TcCl(PPh_3)(acac)_2$ (β-form)	6	III	2.42	2.44	74
$TcCl_2(P(OEt)_2Ph)_4$	6	II	2.41	2.41	76
cis-$[Tc(CO)_2(P(OEt)_2Ph)_4]ClO_4$	6	II		2.42	77
$Tc(HBPz_3)Cl_2O$	6	V	2.33		88
$Tc_2(O_2CCMe_3)_4Cl_2$	6	III	2.41		95
$Tc_2(\alpha\text{-pyr})_4Cl_n$	6	II, III	2.68		96
$[TcCl_4(sal)]PPh_4$	6	IV	2.33		97

[a] Abbreviations: R′=(1-dimethyl-3-oxo)butyl; diars=*o*-phenylenebis(dimethylarsine); acac=acetylacetonate; HBPz=hydrotris(1-pyrazolyl)borate; α-pyr=2-oxopyridinate; sal=salicylaldehydate; Me=CH_3; Et=C_2H_5; and Ph=C_6H_5.

bonding from low valent technetium to phosphorus, Tc–P bond lengths are *also* sensitive to the formal charge on the technetium center and the π-acid character of the phosphorus ligand. These additional variables complicate the situation to the extent that there are not sufficient systematic data available to explain the observed differences in Tc–P bond lengths (Table 4). For tertiary phosphine complexes of Tc(II) and Tc(III), both six- and seven-coordinate, the range of five observed Tc–P bond lengths is 2.42–2.47 Å and thus it is reasonable to assign an "average" Tc–P bond length of 2.45 Å for these conditions. When the phosphorus-containing ligand is a phosphonite rather than a phosphine, the Tc–P length is somewhat shorter (2.41 Å) due to the increased π-acidic character of the phosphonite ligand. In *mer*-$TcCl_3(PMe_2Ph)_3$ [71] longer Tc–P bonds are observed when the phosphine is *trans* to Cl, and shorter Tc–P bonds are observed when the phosphine is *trans* to P.

Tc = O

From the data of Table 5 there appear to be two categories of Tc = O bond lengths. The first occurs when there are multiple Tc = O bonds around a Tc(VII) center, the range of three observed values being 1.68–1.71 Å (av. 1.70 Å). The second category occurs when there is a single Tc = O linkage associated with a Tc(V) center, and here the range of five observed values is 1.61–1.67 Å (av. 1.65 Å). The difference between the two average values can be understood on the basis that a single oxo ligand is less effective at neutralizing the charge of a metal center than are several oxo ligands, and therefore will be drawn more closely to the technetium. Within the series of five-coordinate TcO^{3+} complexes, the Tc = O bond length increases with increasing ability of the ancillary ligands to donate negative charge, again in line with simple electrostatic considerations. The long (1.84 Å) Tc = O bond in Tc_2O_7 is unique in that this oxygen atom bridges the Tc centers and therefore this "Tc = O bond" has some single-bond character.

Tc–O

Table 5 lists five Tc–O entries wherein (i) the technetium oxidation state is III or V, (ii) the coordination number of technetium is six or seven, and (iii) the *trans*-situated atom is singly bonded oxygen or nitrogen. These five values range from 2.01 to 2.03 Å and thus for these conditions it is reasonable to assign an "average" Tc–O bond length of 2.02 Å. In *tr*-$[Tc(NH_3)_4(H_2O)(NO)]^{2+}$ the *trans* influence of the NO group causes the Tc–O bond to lengthen to 2.17 Å, while in $[TcCl_4(sal)]^-$ the two different Tc–O bond lengths (1.98 and 2.04 Å) arise from the properties of this specific ligand.

TABLE 5

Collection of Tc=O, Tc-O, Tc-N, and Tc-S bond lengths (Å)

Compound [a]	Coordination number	Oxidation state	Tc=O	Tc-O	Tc-N	Tc-S	Ref.
Tc_2O_7	4	VII	1.68; 1.84				21
$KTcO_4$	4	VII	1.71				31
NH_4TcO_4	4	VII	1.70				33
$(TcOF_4)_3$	6	VI	1.66				35
$(Ph_3PNPPh_3)[TcOCl_4]$	5	V	1.61				62
$[n\text{-}C_4H_9N]_3[Tc(NCS)_6]$	6	III			2.04		67
trans-$[TcCl(PPh_3)(acac)_2]$ (α-form)	6	III		2.01			73
trans-$[TcCl(PPh_3)(acac)_2]$ (β-form)	6	III		2.01			74
$TPP[Tc(CO)_3]_2$ [b]	6	I			2.16; 2.39		78
$(Bu_4N)[TcO(SCH_2C(O)S)_2]$	5	V	1.67			2.32	84
$(Ph_4As)[TcO(SCH_2CH_2S)_2]$	5	V	1.64			2.30	85
$Tc(HBPz_3)Cl_2O$	6	V	1.66		2.09; 2.26		88
$Ba[Tc(O)EDTA]_2$ [c]	7	V	1.66	2.03; 2.16	2.35		89
$\{[Li(H_2O)_3][Tc(OH)(MDP)]\cdot \frac{1}{3}H_2O\}_n$ [d]	6	?		2.01			92
$TcCl_2(O_2CCMe_3)_4$	6	III		2.03			95
$[Tc(dmg)_3(SnCl_3)(OH)]\cdot 3\ H_2O$ [e]	7	V		2.03	2.09		94
trans-$[Tc(NH_3)_4(H_2O)NO]Cl_2$	6	II		2.17	2.16; 1.72		98
$[TcCl_4(sal)]PPh_4$	6	IV		2.04; 1.98			97

[a] For abbreviations see Table 4.

[b] TPP = *meso*-tetraphenylporphine.

[c] EDTA = ethylenediaminetetraacetate(4−).

[d] MDP = methylenediphosphonate(4−).

[e] dmg = dimethylglyoximate.

Tc–N

There are three comparable Tc–N bond distances in Table 5 (Tc(III) or Tc(V), six- or seven-coordinate technetium, *trans* to a singly bonded nitrogen atom) which range from 2.04 to 2.09 Å and average 2.07 Å. The long Tc–NH_3 distance in *tr*-$[Tc(NH_3)_4(H_2O)(NO)]^{2+}$ (2.16 Å) is not included in this list because of the known *cis* effect of the NO group; the Tc–NO bond length is, of course, very short at 1.72 Å. When the Tc–N bond is *trans* to an oxo group it lengthens to 2.26 Å in six-coordination and to 2.35 Å in seven-coordination.

Other

Table 6 lists some other Tc–X bond lengths of interest. The structural *trans* effect of the oxo ligand is manifested in the Tc–F bond lengths of $(TcOF_4)_3$. The effect of increasing the technetium coordination number from six to eight is obvious in the Tc–As bond lengths of $[Tc(diars)_2Cl_2]^+$ and $[Tc(diars)_2Cl_4]^+$. The difference between Tc–CO bond lengths in $Tc_2(CO)_{10}$ has previously been discussed in terms of π-backbonding. The Tc–Tc single bond in $Tc_2(CO)_{10}$ is much longer (3.04 Å) than the Tc–Tc quadruple bonds in the other dimeric structures (2.09–2.19 Å). The variation in Tc–Tc quadruple bond lengths has previously been discussed in terms of the sigma bonding framework of the Cl–Tc–Tc–Cl axis.

(iii) Summary

The crystal structures of technetium complexes that have been reported to date do indeed form a solid foundation for the continuing development of technetium chemistry. However, many more such structures will have to be determined in order to convert this foundation into a complete framework. Specifically needed are structures of systematic series of technetium compounds wherein variables (Tc oxidation state, Tc coordination number, etc.) are carefully controlled so that the effects of these variables on structural parameters may be determined. For example, structural data on the pair of complexes *tr*-$[Tc^{III}(diars)_2Cl_2]^+$ and *tr*-$[Tc^{II}(diars)_2Cl_2]$ would directly determine the effect of central metal charge on the primarily ionic Tc–Cl bond and on the more covalent Tc–P bond. Also required are structural characterizations of technetium complexes containing various "oxo cores" such as TcO^{3+}, TcO_2^+, and $Tc_2O_3^{4+}$ in order to determine what factors determine the relative stabilities of these related moieties. But most importantly, more structures must be determined of technetium complexes containing ligands of relevance to nuclear medicine. To data only two such structures are in hand, $[Tc(O)EDTA]^-$ and $\{[Li(H_2O)_3][Tc(OH)\cdot(MDP)]\cdot\frac{1}{3}\ H_2O\}_n$. The development of new and more efficacious ^{99m}Tc radiopharmaceuticals will

TABLE 6

Other well-determined distances (Å)

Compound [a]	Coordination number	Oxidation state	Tc–F	Tc–As	Tc–CO	Tc–Tc	Ref.
$(TcOF_4)_3$	6	VI	1.81; 1.89; 2.26				35
$(NH_4)_3[Tc_2Cl_8]\cdot 2\ H_2O$	6	II, III				2.13	56
$K_3[Tc_2Cl_8]\cdot n\ H_2O$	6	II, III				2.12	60
trans-$[TcCl_2(diars)_2]Cl$	6	III		2.51			70
trans-$[TcCl_2(diars)_2]ClO_4$	6	III		2.51			70
$[TcCl_4(diars)_2]PF_6$	8	V		2.58			68
$TcCl_3(CO)(PMe_2Ph)_3$	7	III			1.86		72
cis-$[Tc(CO)_2(P(OEt)_2Ph)_4]ClO_4$	6	II			1.90		77
$TPP[Tc(CO)_3]_2$	6	I			1.90		78
$Tc_2(CO)_{10}$	6	0			1.90; 2.00	3.04	80
$Tc_2Cl_2(O_2CCMe_3)_4$	6	III				2.19	95
$[Tc_2(\alpha\text{-pyr})_4Cl]_n$	6	II, III				2.09	96

[a] For abbreviations see Table 5.

depend to a large extent on the structural characterization of those technetium complexes already being used in the clinic.

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