Coordination Chemistry Reviews, 77 (1987) 275–324
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ANALYSES OF STRUCTURAL DATA OF TECHNETIUM COMPOUNDS

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(Received 9 June 1986)

CONTENTS

ABBREVIATIONS

$(acac)_2en$	*N*,*N*′-ethylenebis(acetylacetone iminate)
AcO	acetate
n-Bu_4N	*n*-tetrabutylammonium
$C_5H_9NO_2S$	D-penicillamine dianion deprotonated at S and O

$C_5H_{10}NO_2S$	D-penicillamine anion deprotonated at S
Cyclam	1,4,8,11-tetracyclotetradecane
diars	*O*-phenylenebis(dimethylarsine)
dmg	dimethylglyoxime
DMPE	bis(1,2-dimethylphosphino)ethane
dpa	*N*,*N*′-diphenylacetamidinate
DPPE	bis(1,2-diphenylphosphino)ethane
dtt	*N*,*N*′-di-*p*-tolyltriazenide
EDTA	ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate
ema	*N*,*N*′-ethylene-bis(2-mercaptoacetamide)
en	ethylenediamine
Et_4N	tetraethylammonium
Et_2NCS_2	*N*,*N*-diethyldithiocarbamate
$HBPz_3$	hydrotris(1-pyrazolyl)borate
hx	hexagonal
im	imidazole
L_{ax}	axial ligand
L_C	capped ligand
L_{cf}	capped face ligand
L_{eq}	equatorial ligand
L_{uf}	uncapped face ligand
m	monoclinic
MDP	methylenediphosphonate
Me_3CCO_2	pivalate
Meim	methylimidazole
Me_4N	tetramethylammonium
MeOX	2-methyl-8-quinolinate
MP	mesoporphyrin IX dimethyl-esterate
meso-$SCH(CO_2Me)$-$CH(CO_2Me)S$	1,2-di(carbomethoxy)ethane-1,2-dithiolate
Npy	4-nitropyridine
NTA	nitrilotriacetate
OC_5H_4N	2-oxo-pyridinate
or	orthorhombic
pd	pentane-2,4-dione
Ph_4As	tetraphenylarsonium
Ph_4P	tetraphenylphosphonium
$Ph_3PC(Me)_2CH_2COMe$	(1,1-dimethyl-3-oxobutyl)triphenylphosphonium
$(PH_3P)_2N$	bis(triphenylphosphin)iminium
phsal	*N*-phenylsalicylideneiminate
PMe_2Ph	dimethylphenylphosphine
pnao · 3H	[3,3′-(1,3-propanediyldiimino)bis(3-methyl-2-butanone oximato)(3 −)]

$P(OEt)_2Ph$	diethylphenylphosphonite
PPh_3	triphenylphosphine
py	pyridine
sal	salicylaldehyde
salbd	*N*,*N*′-butane-1,4-diylbis(salicylide-iminate)
$(sal)_2en$	*N*-*N*′-ethylenebis(salicylideneiminate)
salpd	*N*,*N*′-propane-1,3-diylbis(salicylideiminate)
tg	tetragonal
TPP	*meso*-tetraphenylporphyrine
tr	triclinic
trg	trigonal.

A. INTRODUCTION

The chemistry of technetium remains an active research area, with emphasis on the production of new compounds for use in diagnostic nuclear medicine [1]. All isotopes of technetium are unstable toward β decay or electron capture, and traces exist in nature only as fragments from the spontaneous fission of uranium. Isotopes available from commercial sources include ^{95m}Tc (60 d half-life), ^{99m}Tc (6 h) and ^{99}Tc (2.12×10^5 y). Most chemical studies utilize the relatively long-lived ^{99}Tc, which is available in sufficient quantities. Furthermore, since this isotope emits essentially only a 292 keV β-ray, mg quantities can be handled with negligible radiation exposure. The short-lived radionuclide ^{99m}Tc, with a 6 h half-life, a single γ emission of 140 keV and convenient availability as a ^{99}Mo/^{99m}Tc generator, is used extensively in routine clinical diagnostic imaging procedures.

The solvated technetium compounds have been the subject of numerous publications [2–12]. During the last few years abundant structural studies have been reported. However, with the exception of the review by Bandolli et al. [12], which compiles crystal structures of technetium compounds published through the year 1980, earlier reviews of technetium compounds are more general in nature. We review the basic crystal and structural data available through the year 1985 and we have classified the technetium compounds from a coordination chemistry point of view. The coordination numbers found in inorganic and organic complexes of technetium range from 4 to 8, with number 6 occurring most frequently.

B. STRUCTURAL DATA FOR TECHNETIUM COMPOUNDS WITH COORDINATION NUMBER FOUR

(i) Mononuclear compounds

Four-coordinate compounds have two possible geometries—tetrahedral and square planar, although intermediate and distorted structures are known

TABLE 1

Crystal data of the pertechnetates

Compound	Crystal class [a]	Space group	Z	a[Å] b[Å] c[Å]	$\alpha(°)$ $\beta(°)$ $\gamma(°)$	D (gcm^{-3})	V (Å^3)	Axial ratio c/a	Ionic radii of cation	Ref.
$CsTcO_4$	or	*Pnma*		5.718 5.918 14.304				2.501	181	80
NH_4TcO_4	tg	$I4_1/a$		5.790 – 13.310				2.298	175	80
NH_4TcO_4	tg	$I4_1/a$	4	5.775(2) [b] – 13.252		2.72	442.0	2.295	175	15
				5.769(2) [c] – 13.090(5)			437	2.269	175	15
				5.741(5) [d] – 13.121(7)			433	2.285	175	15
$KTcO_4$	tg	$I4_1/a$	4	5.654 – 13.030				2.304	152	80
$KTcO_4$ [e]	tg	$I4_1/a$	4	5.630(2) – 12.867(4)		3.24	407.8	2.285	152	14
$NaTcO_4$	tg	$I4_1/a$	4	5.339(1) – 11.869(5)		3.4(2)		2.223	116	81

$AgTcO_4$	tg	$I4_1/a$	4	5.319(1)		5.1(2)		2.232	108	81
				–						
				11.875(5)						
$Y(TcO_4)_3 \cdot 4H_2O$	tr		2	7.393	75.65	3.040	704.93	1.598	104	82
				8.615	96.43					
				11.819	104.56					
$Mg(TcO_4)_2$	hx		6	9.93		3.26	1070.81	1.263	86	83
				–						
				12.54						
$Mg(TcO_4)_2 \cdot 4H_2O$	tr		1	7.44	108.01	2.54	276.49	0.868	86	83
				7.03	93.32					
				6.46	120.41					
$H_0(TcO_4)_3 \cdot 4H_2O$	tr		2	7.157	73.62	3.354	722.68	1.715		84
				8.787	95.32					
				12.278	102.55					
$Er(TcO_4)_3 \cdot 4H_2O$	tr		2	7.251	73.13	3.398	715.44	1.666		85
				8.759	96.07					
				12.083	102.81					
$Tm(TcO_4)_3 \cdot 4H_2O$	tr		2	7.249	73.94	3.413	714.19	1.661		86
				8.777	96.38					
				12.038	103.71					
$Lu(TcO_4)_3 \cdot 4H_2O$	tr		2	7.193	73.99	3.510	698.83	1.660		82
				8.686	96.43					
				11.943	102.62					

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[a] hx, hexagonal; or, orthorhombic; tg, tetragonal; tr, trigonal; [b] At 295 K, Tc–O = 1.702(2) Å, O–Tc–O = 109.1(1) and 110.2(1)°; [c] At 208 K, Tc–O = 1.709(2) Å, O–Tc–O = 109.1(1) and 110.3(1)°; [d] At 141 K, Tc–O = 1.711(1) Å, O–Tc–O = 109.2(1) and 110.0(1)°; [e] Tc–O = 1.711(3) Å, O–Tc–O = 109.0(2) and 110.5(2)°.

[13]. Of these two common geometries only the tetrahedral structure is found in the chemistry of technetium coordination compounds. Crystal data of the pertechnetates are presented in Table 1. Figure 1 depicts a representative example, the crystal structure of $KTcO_4$ [14]. The simple tetrahedral technetium(VII) oxo-anion, $[TcO_4]^-$, consists of one Tc atom coordinated to four O atoms with Tc–O bond lengths of 1.711(3) Å, or 1.724 Å if corrected for vibrational oscillation of the tetrahedral and O–Tc–O angles of 109.0(2) and 110.5(2)° respectively.

Faggiani et al. [15] studied the crystal structure of NH_4TcO_4 at 295, 208 and 141 K. The Tc–O bond distances as well as O–Tc–O bond angles of NH_4TcO_4 (Table 1) are similar to those found in $KTcO_4$. These authors report that despite the changes in cell parameters (Table 1) the variation in structure as a function of temperature is only minor. There is very little effect on the cell volume, which increases gradually over the temperature range 129–295 K, while the axial ratio c/a decreases with a minimum phase transition. However, at temperatures over 210 K the c/a value increases as well.

Some general trends emerge from the crystal data presented in Table 1. The value of the axial ratio c/a decreases when the ionic radii (r_{ion}) of the

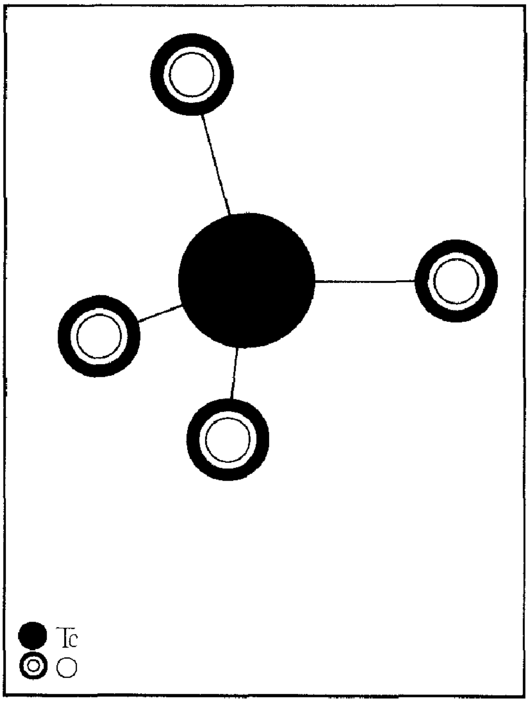

Fig. 1. A view of the technetium(VII) environment in $(TcO_4)^-$ [14].

cation are reduced in the following order: Cs^+ (c/a 2.501, r_{ion} 1.81 Å) < NH_4^+ (2.295, 1.75 Å) < K^+ (2.285, 1.52 Å) < Na^+ (2.223, 1.16 Å) < Y^{3+} (1.598, 1.04 Å) < Mg^{2+} (1.263, (0.868), 0.86 Å). In the lanthanide series the monotonic decrease of Ho < Er < Tm < Lu (Table 1), in both the unit cell volume as well as the axial ratio c/a, is due to the lanthanide contraction.

Muller et al. [16] studied ternary and quaternary oxides of technetium by X-ray analyses and reported the following values: Mg_2TcO_4 ($a = 8.498(3)$ Å); Co_2TcO_4 ($a = 8.450(3)$ Å); Mn_2TcO_4 ($a = 8.682(3)$ Å); $NiZnTcO_4$ ($a = 8.462(3)$ Å); $NiMnTcO_4$ ($a = 8.557(3)$ Å); $CoMnTcO_4$ ($a = 8.563(3)$ Å); $NiCdTcO_4$ ($a = 8.786(3)$ Å). Using rare earth pyrochlorides as an indicator of the relative size of the tetravalent ions, an ionic radius of 0.67 Å was assigned to Tc(IV). $(Me_4N)_2TcO_4$ crystallizes in antifluorite as a cubic face-centered lattice with $a = 11.20$ Å in the space group F-23 or F-43m with four molecules per unit cell [17,23].

(ii) Binuclear compounds

The crystal structure of ditechnetium(VII) heptaoxide, Tc_2O_7, was determined by Krebs [18]. The compound crystallizes in the orthorhombic system in space group *Pbca* with four molecules per unit cell and with unit cell dimensions of $a = 13.756(7)$, $b = 7.439(4)$ and $c = 5.617(3)$ Å. The compound contains isolated centrosymmetric Tc_2O_7 molecules with a linear central Tc–O–Tc bridge angle of 180.0° (Fig. 2). Four oxygen atoms are coordinated to each technetium(VII) atom, forming a tetragonal coordinate environment, with Tc–O bridge distances of 1.658(5), 1.684(5), 1.706(5) and

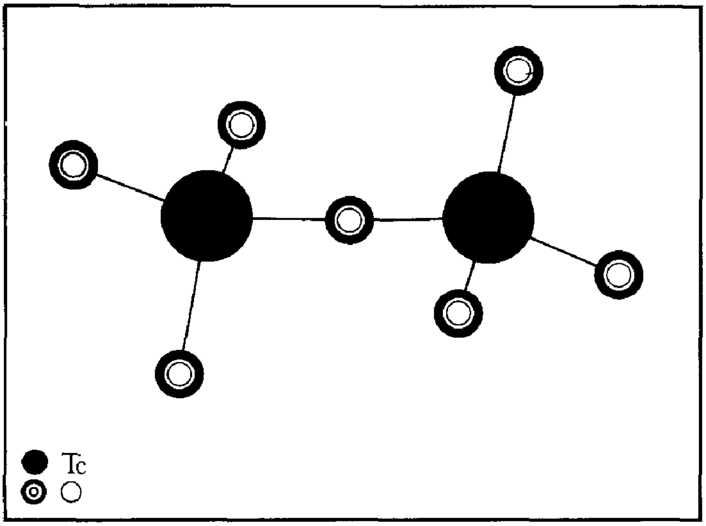

Fig. 2. A schematic view of the molecular structure of Tc_2O_7 [18].

1.840(1)Å, respectively. Although the Tc–O distances in this binuclear compound cover a rather large range (1.658–1.840 Å) the sum of all interatomic distances in the TcO_4 chromophore (6.88 Å) compares well with those found in mononuclear compounds (6.83 Å average). The O–Tc–O bond angles, which are in the range of 107.8(2) to 110.9(2)° in the dimer, are also comparable to those found in the monomers.

Unit cell dimensions in the lanthanide series: $Sm_2Tc_2O_7$ (a = 10.352(4) Å); $Dy_2Tc_2O_7$ (a = 10.245(4) Å) and $Er_2Tc_2O_7$ (a = 10.194(4) Å) are decreased due to lanthanide contraction [16].

C. STRUCTURAL DATA FOR TECHNETIUM COMPOUNDS WITH COORDINATION NUMBER FIVE

(i) Mononuclear compounds

Although five-coordinate compounds are less common than those with coordination number four or six, there has recently been considerable interest in the former and the number of known compounds of this type has increased rapidly. Furlani [19] has suggested the following classification for the stereochemical arrangements of five-coordinate compounds: regular trigonal bipyramid, slightly distorted trigonal bipyramid, highly distorted structures (trigonal bipyramidal or square pyramidal), regular square pyramid and distorted square pyramid. Distorted square pyramid is "distorted" in the sense that the metal atom lies above the plane of the four basal ligands, an arrangement found in all technetium compounds listed in Table 2. The structures are tabulated in order of increasing number of different ligands. Figure 3 depicts the crystal structure of $[TcO(S_2CH_2COS)_2]^-$ as a representative example of this class of complexes [20]. The technetium(V) atom is coordinated by four sulfur atoms in a basal plane (Tc–S = 2.303(3) Å (2 ×) and 2.336(3) Å (2 ×)) and by an oxygen (Tc–O = 1.672(8) Å) in an apical position. In this distorted square-pyramidal geometry the technetium atom lies 0.791 Å above the basal plane, and the Tc–O ligand is perpendicular to the least-squares plane formed by the four sulfur atoms [20]. As in most complexes of this type, the metal atom is positioned above the basal plane towards the apex ligand resulting in a strong apical bond and weaker basal bonds. Likewise, good ligand donors, such as "free" oxygen and nitrogen, usually seek the apical positions. The bond lengths shown in Table 2 support this suggestion. There is an obvious correlation between bond lengths and movement of the metal atom: out-of plane technetium–ligand distances increase upon displacement of the technetium (V) atom from the basal plane towards the apical ligand. There are some exceptions, but they could reflect the presence of increased numbers of different ligands.

TABLE 2

Structural data for mononuclear technetium compounds with a square pyramidal geometry

Compound	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α[°] β[°]	M–L$_{eq}$ L^a (Å)^b	M–L$_{ap}$ M-out-of-plane L^a (Å)^b	L$_{eq}$–M–L$_{eq}$ *cis* *trans* L$_{eq}$–M–L$_{ap}$ (degrees)	Ref.
[$(Ph_3P)_2N$][Tc(V)OCl_4]	*Pna*2_1	4	$TcCl_4O$	21.618(5) 16.870(5) 9.658(3)		Cl 2.304(2.13)^b	O 1.610(4) 0.66	85.1–85.8(1) 139.2, 153.7(1) 103.0–111.5(2)	21
(Ph_4As)[Tc(VI)Cl_4N]	*P*4/*n*	2	$TcCl_4N$	12.707(2) – 7.793(1)		Cl 2.3220(9)	N 1.581(5) 0.54	86.95(1) 153.33(6) 103.34(3)	78
[Tc(V)O(pnao · 3H)]	*Pc*	2	TcN_4O	6.950(4) 11.187(3) 11.060(4)	104.13(5)	N 2.001(3.92)	O 1.679(3) 0.678(1)	77.0–92.7(2) 139.0, 141.0(1) 108.6–110.5(1)	22
(Bu_4N[Tc(V)O($SCH_2COS)_2$]	*Cm*	2	TcS_4O	10.451(5) 14.855(8) 9.927(7)	90.0 114.88(5)	S 2.319(3.17)	O 1.672(8) 0.791	81.2–85.1(1) 140.1(1) 109.7, 110.2(3)	20,87
(Ph_4As[Tc(V)O($SCH_2CH_2S)_2$]	*Pbca*	8	TcS_4O	19.669(3) 18.745(4) 15.122(3)		S 2.300(4.13)	O 1.64(1) 0.761(2)	82.4–84.8(1) 138.5, 144.4(4) 106.3–111.3(4)	88
(Et_4N)[Tc(V)O{*meso*-SCH-(CO_2Me)CH(CO_2Me)S}$_2$]	*P*2_1/*c*	4	TcS_4O	12.722(3) 13.820(4) 18.313(5)	107.13(4)	S 2.316(4.9)	O 1.672(6) 0.78	80.1–85.5(1) 135.8, 143.8(1) 108.6–113.0(2)	89
[Tc(V)N($S_2CNEt_2)_2$]	*P*2_1/*c*	4	TcS_4N	14.823(1) 9.159(1) 12.865(1)	107.98(1)	S 2.401(2.9)	N 1.604(6) 0.745(1)	73.0–96.9(1) 143.1, 144.6(1) 107.0–108.9(2)	90
(Ph_4As)[Tc(V)O($SCH_2CH_2O_2$]	*Pbca*	8	TcO_3S_2	15.039(2) 18.510(3) 19.196(3)		S 2.290(2.9) O 1.949(4.14)	O 1.662(5) 0.720(1)	79.8–86.09(7) 138.1, 141.8(1) 108.7–112.0(2)	91
[Tc(V)O(phsal)Cl]	*P*2_1/*a*	4	TcO_3NCl	13.423(6) 12.570(5) 7.769(3)	106.53(5)	O 1.948(5)(2×) N 2.055(6) Cl 2.302(3)	O 1.634(7) 0.67	78.7–88.5(3) 136.8, 145.9(2) 106.3–111.9(3)	24
[Tc(V)O(ema)]	*P*2_1/*c*	4	TcN_2S_2O	10.203(2) 13.449(2) 16.140(4)	110.37(1)	N – S –	O 1.679(5) 0.771(5)		23
[$AsPh_4$][Tc(VI)NBr_4]	*P*4/*n*	2	$TcBr_4N$	12.875(2) – 7.992(1)		Br 2.4816(2)(4×)	N 1.596(6) –	87.08(1) 153.91(4) 103.04(2)	92

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[a] Chemical identity of the coordinated atom; [b] Mean value of chemically equivalent bond lengths. The first number in parentheses is the standard deviation, the second number is the maximum deviation from the mean.

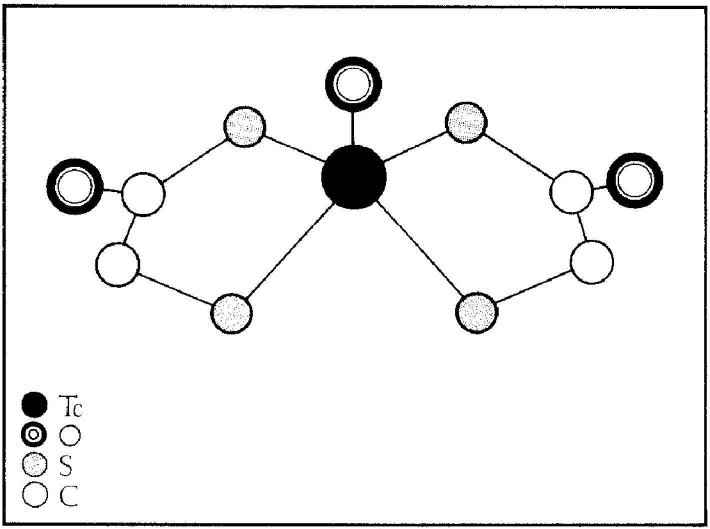

Fig. 3. A schematic view of the technetium(V) environment in [TcO(SCH$_2$COS)$_2$]$^-$ [20].

The data in Table 2 reveal that there is no example of five equivalent ligands and only two examples with five unidentate ligands, e.g. TcCl$_4$X$^-$ (X = O or N). The (TcCl$_4$O)$^-$ ion possesses C_{2v} symmetry with *trans* Cl$_{eq}$–Tc–Cl$_{eq}$ angles of 139.2(1) and 153.7(1)° and with two distinct different Tc–Cl$_{eq}$ bond distances. While the trans Cl$_{eq}$–Tc–Cl$_{eq}$ angles vary by at least 14.5°, which is the largest variation found among the technetium(V) compounds collected in Table 2, the *cis* Cl$_{eq}$–Tc–Cl$_{eq}$ angles vary only by 0.7°, which is the smallest variation observed. Furthermore, the Cl$_{eq}$–Tc–Cl$_{ap}$ angles from 103.0 to 111.5(2)° (the largest variation among these complexes, Table 2), indicates distortion of the oxo-tetrachlorotechnetium(V) anion from absolute C_{4v} symmetry. In the case of TcOCl$_4^-$, where there is no significant interionic contact [21], it appears that crystal-packing forces are responsible for the distortion.

There are two examples of tetradentate ligands, Tc(V)O(pnao · 3H) [22] and Tc(V)O(ema) [23]. In both compounds the chelating ligands are in the basal plane and the oxygen ligand is in the apex, in a nearly square-pyramidal environment about the technetium(V) atom.

A distorted square pyramidal geometry is observed in Tc(V)O(phsal)Cl [24]. The structure consists of the tridentate (phsal) ligand coordinated through two oxygen atoms and a nitrogen atom in the equatorial positions, a chlorine ligand in the remaining equatorial position and an oxo ligand in the axial position. This is the only example of a tridentate ligand in this series. In all other compounds (Table 2) basal planes are built up by two bidentate ligands and an O–ligand in the apex; in TcN(S$_2$CNEt$_2$)$_2$ the N ligand is in the apex. It is of interest to note that the central atom is always in an oxidation state of five. The one exception is $(Ph_4As)TcCl_4N$, where Tc is in an oxidation state of six (Table 2). As suggested by Wood [25], it is possible to enumerate a few factors that seem to predict formation of five-coordinate species. Among them, the size of the central atom is of importance. The larger radii of the second row elements, in their higher oxidation states, apparently prefer a lower coordination number. The data presented in Tables 1 and 2 generally follow this pattern. Another significant feature is that the apical position in a distorted square-pyramidal geometry, such as in $[Tc(VI)Cl_4N]^-$ and $[Tc(V)N(S_2CNEt_2)_2]$, is occupied by multiple technetium–nitrogen bonds (1.581(5) and 1.604(6) Å). In the remaining compounds (Table 2) the multiple technetium–oxygen bonds range from 1.610 to 1.679 Å with a mean of 1.65 Å.

Most of the five-coordinate compounds contain five-membered rings. Exceptions are the tetra- and tridentate ligands, which do also form five- and also six-membered chelate ring systems. As can be seen from the data in Table 2, the coordinated atoms residing in the basal plane are: chlorine, with Tc–Cl bonds from 2.291 to 2.317 Å (2.30 Å mean); oxygen, Tc–O = 1.930–1.963 Å (1.95 Å mean); nitrogen, Tc–N = 1.908–2.093 Å (2.02 Å mean); and sulfur, Tc–S = 2.283–2.405 Å (2.33 Å mean).

The average $Tc–O_{eq}$ bond length of 1.95 Å in five-coordinate technetium(V) compounds is, as expected, longer than the average Tc(VIII)–O length of 1.70 Å as observed in four-coordinate compounds (Section B (i)). Furthermore, the sum of all interatomic distances around the central atom increases with the combined values of van der Waals radii of the coordinated atoms, e.g. $TcN_4O < TcO_3NCl < TcO_3S_2 < TcCl_4O < TcS_4O < TcS_4N$ (values of van der Waals radii include [26]: O, 1.50; N, 1.55; Cl, 1.70–1.90; and S, 1.80 Å).

(ii) Binuclear compounds

Structural data for binuclear five-coordinate technetium compounds are presented in Table 3. The structures are listed in order of increased Tc–Tc′ bond distances. A representative example, the octachloroditechnetate(III) ion $(Tc_2Cl_8)^{2-}$, is depicted in Fig. 4 [27]. Four chlorine atoms and one technetium atom form the square-pyramidal coordination sphere of each Tc atom. There are two crystallographically independent anions with Tc–Tc′ bond distances of 2.151(1) Å (Tc(1)–Tc(1)′) and 2.133(3) Å (Tc(2)–Tc(2)′). It is of interest to note that while the Tc(1)–Tc(1)′ bond is 0.018 Å longer than the Tc(2)–Tc(2)′ bond, the mean value of the Tc–Cl bond length in the former is 0.018 Å shorter than in the latter. Such data are indicative of the presence of two distortion isomers of technetium(III) in $(n\text{-}Bu_4N)_2(Tc_2Cl_8)$ [28]. The observed difference suggests that the $(Tc_2Cl_8)^{2-}$ anion resides on a

TABLE 3

Structural data for binuclear technetium compounds with $TcCl_4Tc'$ chromophores [a]

Compound	Crystal class [b]	Space group	Z	α(°) β(°) δ(°)	Tc–Cl (Å [a]	Tc–Tc′ (Å)	Cl–Tc–Cl *cis*, *trans* Tc′–Tc–Cl (°)	Ref.
$K_3[Tc_2Cl_8]\cdot 2H_2O$	tg	$P3_121$ ($P3_221$)	3	12.80(5) 12.80(5) 8.30(4)	2.3	2.10	–	93
$Cs_3[Tc_2Cl_8]\cdot 2H_2O$	tg	$P3_121$ ($P3_221$)	3 3	12.90(5) 12.90(5) 8.70(5)				93
$Y[Tc_2Cl_8]\cdot 9H_2O$		$P42_12$	4	11.712(2) – 7.661(2)	2.363(2,4)	2.105(1)	86.48(7,7); 151.32(7,27) 104.34(6,14)	55
$K_3[Tc_2Cl_8]\cdot mH_2O$		$P3_121$	3	12.838(3) 12.838(3) 8.187(3)	2.364(3,15)	2.117(2)	86.2(1,29); 150.5(1,5) 104.8(8,30)	94
$(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$	tg	$P3_221$	3	13.04(2) – 8.40(1)	2.36(2,3)	2.13(1)	86.1(6,17) 105.1(6,15)	95,96
$K_8[Tc_2Cl_8]_3(H_3O)(H_2O)_3$	trg	$P3_121$	1	12.80(6) – 8.30(4)	2.37(3,14)	2.144(17)	104.4(1.8)	97
$(n\text{-}Bu_4N)_2[Tc_2Cl_8]$	m	$P2_1/c$	2	10.922 15.384 16.439				98
$(n\text{-}Bu_4N)_2[Tc_2Cl_8]$ [c]		$P2_1/c$	4	10.915(1) 15.382(3) 16.409(2)	2.320(4,8) 2.338(9,15)	2.151(1) 2.133(3)	86.7(3,4); 152.38(6,9) 103.8(4,7) 87.1; 153.7(1,2) 103.1(6,9)	27

[a] Mean value of chemically equivalent bond lengths. The first number in parentheses is the standard deviation, the second number is the maximum deviation from the mean. [b] m, monoclinic; tg, tetragonal; trg, trigonal. [c] $\beta = 122.37(1)°$; there are two crystallographically independent anions.

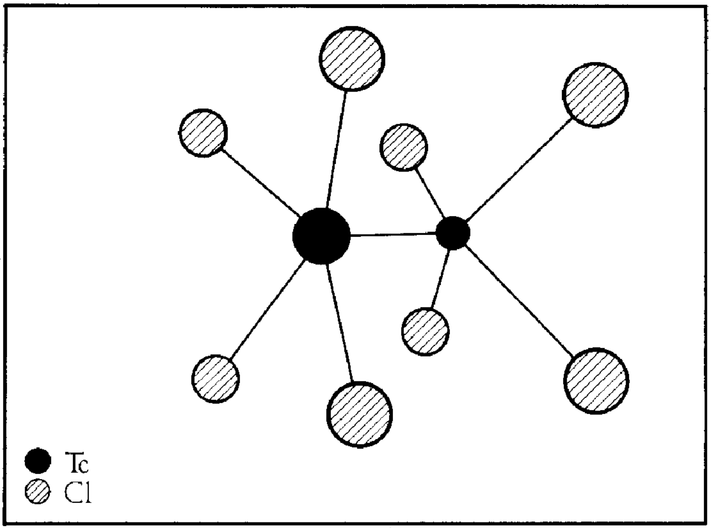

Fig. 4. A schematic view of the structure of $(Tc_2Cl_8)^{2-}$ [27].

center of inversion, and thus only half of it is crystallographically independent, whereas the entire cation is part of an asymmetric unit [27]. The Tc–Tc bond length in $[Tc_2Cl_8]^{2-}$ (2.142(4) Å mean) is 0.023 Å longer than that in $[Tc_2Cl_8]^{3-}$ (2.119 Å mean) (Table 3), reflecting the differences in technetium oxidation states (+ 3 and + 2.5 respectively). The matter has been discussed in detail by Cotton et al. [27]. Other differences also exist between the $(Tc_2Cl_8)^{2-}$ and $(Tc_2Cl_8)^{3-}$ ions. For instance, the average values of Tc–Cl distances are 2.33 Å and 2.36 Å respectively and the sum of all interatomic distances in $TcCl_4Tc'$ is almost constant, e.g. 11.45 Å in $(Tl_2Cl_8)^{2-}$ and 11.56 Å in $(Tc_2Cl_8)^{3-}$. The mean values of the *cis*- and *trans*-Cl–Tc–Cl angles in $(Tc_2Cl_8)^{2-}$ are 86.9 and 153.0°, which is about 0.7 and 2.0° larger than the 86.2 and 151.0° angles observed in $(Tc_2Cl_8)^{3-}$ (Table 3). On the other hand, the mean value of the Tc′–Tc–Cl angles in $(Tc{-}Cl_8)^{2-}$ (103.4°) is about 0.7° smaller than the 104.7° angle observed in $(Tc_2Cl_8)^{3-}$ (Table 3).

There is an obvious correlation between the oxidation state of the technetium atom and the Tc–Cl bond distances in five-coordinate compounds. The mean value of Tc–Cl bond lengths increases with decreased oxidation states of technetium, e.g. 2.30 Å (Tc(V)) < 2.33 Å (Tc (III)) < 2.36 Å (Tc (2.5)) (Tables 2 and 3). Insufficient data are available for analogous technetium compounds in order to allow for conclusion regarding the general nature of this tendency.

Finally, we note the lack of influence of the cation on the unit cell parameters. In the case of mononuclear pertechnetates, the value of the axial ratio c/a increases with larger ionic radii of the cation. No such correlation exists for binuclear compounds (Table 3) suggesting that other factors, such as strong interaction between the two technetium atoms and between the binuclear units, determine the unit parameters.

D. STRUCTURAL DATA FOR TECHNETIUM COMPOUNDS WITH COORDINATION NUMBER SIX

Crystal data for six-coordinate technetium compounds are presented in Table 4. It is obvious that the hexahalogeno-compounds of quadrivalent technetium have been more completely studied than the corresponding penta- or hexavalent-technetium compounds. The lattice constants of the hexahalogeno-complexes of quadrivalent technetium increase with increasing ionic radius of the alkali metal cation or substituted halogen, e.g. hexafluoro- < hexachloro- < hexabromo- < hexaiodo-compounds. X-ray diffraction patterns of TcF_6 (Table 4) indicate that the unit cell dimensions change with temperature; at lower temperatures a phase transition to a lower symmetry occurs [29]. In the series of the ternary oxides (Table 4), the axial ratio c/a of the orthorhombic unit cell increases with lower oxidation states of technetium. e.g. 5.655 (β-$Li_4Tc(IV)O_5$) < 5.760 (β-$Li_3Tc(V)O_5$) < 5.940 ($Li_2Tc(IV)O_3$). Ternary oxides with the hexagonal unit cell configuration do not follow this pattern, e.g. (2.80 ($Li_5Tc(VII)O_6$) and 2.81 ($Li_6Tc(VI)O_6$).

(i) Mononuclear compounds

Six is by far the most common coordination number of technetium compounds. Structural data for mononuclear six-coordinate technetium compounds are presented in Table 5. The structure are tabulated in order of increasing number of different ligands. Regular or nearly perfect octahedral symmetry around the technetium atom exists in $(NH_4)_2TcCl_6$ [30], K_2TcCl_6 [31], $(NH_4)_2TcBr_6$ [32], and $(n\text{-}Bu_4N)_3[Tc(NCS)_6]$ [33]. The crystal structure of $[Tc(NCS)_6]^{3-}$ is presented as a typical example (Fig. 5). In all four compounds the octahedral arrangement about the central technetium atom consists of six equivalent atoms. In spite of the presence of two different types of ligands, the technetium atom in *trans*-$[TcCl_2\{P(OEt)_2Ph\}_4]$, has an octahedral configuration with almost equal bond lengths in equatorial and axial positions (Table 5) [34].

There are three principal distortions of the octahedron. First of all tetragonal elongation or contraction along a single C_4 axis, which results in D_{4h} symmetry. A typical example of a mononuclear six-coordinate technetium compound with such a symmetry is α-*trans*-$[Tc(pd)_2(PPh_3)Cl]$ (Fig.

TABLE 4

Crystal data for technetium compounds with coordination number six

Compounds	Crystal class	Space group	Z	a(Å) b(Å) c(Å)	Ref.
$K_2Tc(VII)H_9$	hx			9.64 — 5.56	99
$Tc(VI)F_6$	c		2	6.16(3) [b]	29
$Tc(VI)F_6$			4	9.55(2) [c] 8.74(2) 5.02(2)	29
$NaTc(V)F_6$	c			5.77 [d]	100,101
$KTc(V)(F)_6$	c			4.97 [e]	100,101
$RbTc(V)F_6$	c			5.09 [f]	100
$CsTc(V)F_6$	c			5.25 [g]	100
$K_2Tc(IV)F_6$	tr	$C\bar{3}$		5.807 — 4.645	102,103
$Rb_2Tc(IV)F_6$	tr	$C\bar{3}m$		5.986 4.798	103
$(NH_4)_2Tc(IV)F_6$	hx			5.98 4.79	104
$Tc(V)F_5$	or			7.75 17.01 5.76	105
$Tc(VI)OF_4$	m		16	18.83 [h] 5.49 14.43	105
$K_2Tc(IV)Cl_6$		$Fm3m$		9.89	106
$K_2Tc(IV)Cl_6$	c	$Fm3m$	4	9.83(1) [i]	31
$K_2Tc(IV)Cl_6$	c			9.82(1)	107
$K_2Tc(IV)Cl_6$	c			9.825(2)	103
$K_2Tc(IV)Cl_6$	c			9.811(1)	108
$Rb_2Tc(IV)Cl_6$	c			9.965(2)	103
$Rb_2Tc(IV)Cl_6$	c			9.949(1)	108
$Cs_2Tc(IV)Cl_6$	c			10.237(4)	108
$(NH_4)_2Tc(IV)Cl_6$	c			9.936(1)	108
$(NH_4)_2Tc(IV)Cl_6$	c	$Fm3m$ [d]		9.92	109
$(NH_4)_2Tc(IV)Cl_6$	c	$Fm3m$	4	9.9072(8) [i]	30
$(PH_4As)_2Tc(IV)Cl_6$	tr	$P\bar{1}$	1	10.111(4) [i,j] 12.165(3) 10.263(5)	110
$K_2Tc(IV)Br_6$	c	$Fm3m$	4	10.37(2)	107
$K_2Tc(IV)Br_6$	c	$Fm3m$		10.354(1)	108
$K_2Tc(IV)Br_6$	c			10.371(2)	103
$Rb_2Tc(IV)Br_6$	c			10.460(2)	103

TABLE 4 (continued)

Crystal data for technetium compounds with coordination number six

Compounds	Crystal class	Space group	Z	a(Å) b(Å) c(Å)	Ref.
$Rb_2Tc(IV)Br_6$	c			10.461(2)	111
$Cs_2Tc(IV)Br_6$	c			10.650(3)	111
$(NH_4)_2Tc(IV)Br_6$	c	$Fm3m$	3	10.417(1) [i]	108,32
$K_2Tc(IV)I_6$	or			11.22(3) 8.00(3) 7.84(3)	107
$K_2Tc(IV)I_6$	or			11.24(2) 7.96(2) 7.85(2)	112
$Rb_2Tc(IV)I_6$	c			11.301(2)	103
$Rb_2Tc(IV)I_6$	c			11.410(2)	112
$(NH_4)_2Tc(IV)I_6$	or			11.24(2) 8.02(2) 7.92(2)	112
$Cs_2Tc(V)(O)Cl_5$	c			10.199(1)	113
$Cs_2Tc(V)(O)Br_5$	c			10.672(3)	113
$K_2Tc(IV)(OH)Cl_5$	c	$Fm3m$	4	9.829(7)	31
$K_2Tc(IV)(OH)Cl_5$	c			9.851(2)	113
$Rb_2Tc(IV)(OH)Cl_5$	c			9.964(2)	113
$Cs_2Tc(IV)(OH)Cl_5$	c			10.315(2)	113
$Cs_2Tc(IV)(OH)Br_5$	c			10.715(3)	113
$K_5Tc(1)(CN)_6$	c		4	11.890(2)	43
$Li_6Tc(VI)O_6$	hx			5.05(1) — 14.20(2)	114
$Li_5Tc(VII)O_6$	hx			5.04(1) — 14.10(2)	114
β-$Li_4Tc(VI)O_5$	or			5.055(2) [k] 8.755(2) 28.59(2)	114
$\beta Li_3Tc(V)O_5$	or			5.038(2) [k] 8.726(2) 29.02(2)	114
$Li_2Tc(IV)O_3$	or			4.988(2) [l] 8.639(2) 29.63(2)	114

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[a] c, cubic; hx, hexagonal; m, monoclinic; or, orthorhombic, tr, trigonal; [b] at 283 K; [c] at 253 K; [d] $\alpha = 55.8°$; [e] $\alpha = 97.0°$; [f] $\alpha = 95.5°$; [g] $\alpha = 96.2°$; [h] $\beta = 114.0°$; [i] structural data are given in Table 5; [j] $\alpha = 93.86(3)$; $\beta = 114.51(4)°$ and $\gamma = 99.08(3)°$; [k] $\beta = 99.8°$; [l] $\beta = 99.4°$.

6) [35]. The four "short" equatorial Tc–O bonds have an average length of 2.01(1) Å, while the two "long" axial Tc–Cl and Tc–P bonds are 2.42(1) and 2.46(1) Å, respectively. *trans*-[$TcO_2(en)_2$]Cl (Fig. 7) with its four "long" equatorial Tc–N bonds of 2.166(2) Å and two "short" axial Tc–O bonds of 1.746(1) Å, is a typical example of tetragonal contraction [36]. The second type of distortion involves rhombic changes in the length of two of the C_4 axes such that as they become equal, the resulting symmetry is D_{2_h}. The crystal structure of the *trans*-[$Tc(diars)_2Cl_2$]$^+$ cation is a typical example of such a symmetry (Fig. 8). The mean Tc–As bond length is 2.515(2) Å (±0.007 Å), whereas the Tc–Cl bond is 2.329(1) Å. The third type of distortion is a trigonal distortion, elongation or contraction along one of the C_3 axes, resulting in D_{3_d} symmetry. The cation [Tc{$SC(NH_2)_2$}$_6$]$^{3+}$ (Fig. 9) is a typical example [37]. The cation is roughly octahedrally coordinated by six sulfur atoms, even though all donor atoms are part of thiourea substituent groups. This distortion, also known as the Jahn–Teller distortion, can be accounted for by either a tetragonal or a trigonal distortion. Both effects are present in [Tc{$SC(NH_2)_2$}$_6$]$Cl_3 \cdot 4H_2O$, as discussed in detail by Abrams et al. [38].

Among the data presented in Table 5, the tetragonal distortion is by far the most common. Crystallographic analysis of *trans*-[TcO_2(cyclam)]$ClO_4 \cdot H_2O$ [39], *trans*-[$Tc(DPPE)_2(NCS)_2$] [40], *mer*-[$TcCl_3(PMe_2Ph)_3$] [41] and α-*trans*-[$Tc(pd)_2(PPh_3)Cl$] [39] indicate the presence of two independent molecules which differ mainly in their Tc–L bond lengths (Table 5) resulting in different tetragonal distortions. These results indicate the presence of two distortion isomers for each of these technetium compounds [28].

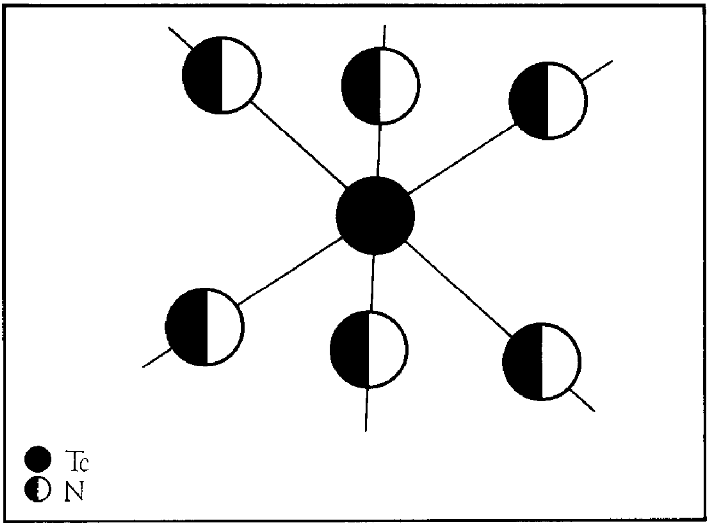

Fig. 5. A view of the technetium(III) environment in [$Tc(NCS)_6$]$^{3-}$ [33].

TABLE 5

Structural data for mononuclear technetium compounds with coordination number six [a]

Compounds	Crystal class [b]	Space group	*Z*	Chromophore	*a*(Å) *b*(Å) *c*(Å)	α(°) β(°) γ(°)	M–L$_{eq}$ (Å)	M–L$_{ax}$ (Å)	L$_{eq}$–M–L$_{eq}$ L$_{ax}$–M–L$_{eq}$ L$_{ax}$–M–L$_{ax}$ (°)	Ref.
$H_2[Tc(IV)Cl_6]\cdot 9H_2O$	tr	*P*1	1	$TcCl_6$	8.30(4) 7.35(4) 8.04(4)	95.0(5) 98.0(5) 117.5(5)	Cl [c] 2.33(3.11)	Cl [c] 2.50(3.1)	89.2(2.5,8.2) 89.3(2.5,7.5) 175.0(2.5)	115,116
$(NH_4)_2Tc(IV)Cl_6$	c	*Fm*3*m*	4	$TcCl_6$	9.972(8)		Cl 2.3531(5.0)	Cl 2.3531(5.0)	[d]	30
$K_2Tc(IV)Cl_6$	c	*Fm*3*m*	4	$TcCl_6$	9.830(15)		Cl 2.35(1.0)	Cl 2.35(1.0)	[d]	31
$(Ph_4As)_2[Tc(IV)Cl_6]$	tr	*P*$\bar{1}$	1	$TcCl_6$	10.111(4) 12.165(3) 10.263(5)	93.86(3) 114.51(4) 99.08(3)	Cl 2.3538(7.97)	Cl 2.3649(7.0)	88.63(2) 90.10(3) [d]	111
$(NH_4)_2Tc(IV)Br_6$	c	*Fm*3*m*	4	$TcBr_6$	10.417(1)		Br 2.500(1.0)	Br 2.500(1.0)	[d]	32
$(n\text{-}Bu_4N)_3[Tc(III)(NCS)_6]$	c	*Pa*3	8	TcN_6	24.444(6)		N 2.04(2.1)	N 2.05(2.1)	90.0(7.2.0) 90.0(7.2.0) 117.0(8)	33
$(Me_4N)[Tc(V)(NCS)_6]$	hx	*R*3 [e]	3	TcN_6	11.71 – 17.10		[d]	[d]	[d]	117
$[Tc(III)\{SC(NH_2)_2\}_6]Cl_3\cdot 4H_2O$	m	*C*2/*c*	4	TcS_6	11.876(2) 12.048(2) 19.662(3)	95.32(1)	S 2.435(1.5)	S 2.412(1.0)	85.78(4) 98.70(4,48) [d]	38
$[Tc(IV)Cl_5(PPh_3)]\cdot[Ph_3PC(Me)_2CH_2COMe]$ [f]	m	*P*2$_1$/*n*	4	$TcCl_5P$	21.909(4) 18.963(4) 9.869(3)	103.05(5)	Cl 2.33(1.2)	Cl 2.36(1) P 2.57(1)	90.2(4.2.4); 176.5(4.2.5) [g] 89.3(4.2.6) 178.4(4)	118
$(Ph_4P)[Tc(IV)Cl_4(sal)]$	m	*P*2$_1$/*c*	4	$TcCl_4O_2$	14.20(1) 12.93(1) 16.96(1)	105.1(1)	O 2.01(2.3) Cl 2.31(1.1)	Cl 2.34(1.2)	90.0(5.2.4), 177.6(5.0.9) [g] 90.0(5.4.5) 173.5(3)	119
trans-$[Tc(V)O_2(en)_2]Cl$	m	*P*2$_1$/*c*	4	TcN_4O_2	5.637(1) 11.177(2) 16.112(3)	101.11(1)	N 2.166(2.16)	O 1.746(1.6)	90.00(6,10.25); 178.5(7.1) [g] 90.00(6.1.59) 178.6(3)	36,

trans-$[Tc(V)O_2(en)_2]$ [h]	tr	$P\bar{1}$	2	TcN_4O_2	5.767(4) 8.759(7) 10.929(7)	84.13(5) 92.18(6) 97.63(5)						36
trans-$[Tc(V)O_2(cyclam)]$ $ClO_4 \cdot H_2O$ [i]		$P\bar{1}$	2	TcN_4O_2	9.964(3) 9.475(3) 11.815(3)	101.38(2) 112.54(2) 113.50(2)	N N	2.125(4,6) 2.126(4,13)	O O	1.749(3,0) 1.754(3,0)	90.2(1) 90.3(1,1) d 96.8(2) 90.4(1,7)	39
trans-$[Tc(V)O_2(im)_4]Cl \cdot 2H_2O$	m	$C2/c$	4	TcN_4O_2	13.249(3) 11.239(2) 14.358(3)	115.56(2)	N	2.15(2,0)	O	1.71(2)	90 (1) 89 (1) d	120
trans-$[Tc(V)O_2(Meim)_4]$ $Cl \cdot 3H_2O$	m	$C2/c$	4	TcN_4O_2	20.980(5) 8.599(3) 16.105(3)	124.22(2)	N	2.15(2,1)	O	1.71(2)	90 (1) 91 (1,3) d	120
$[Tc(V)O_2(py)_4]Cl \cdot nH_2O$	m	Cc	4	TcN_4O_2	14.40 12.34 15.06	116						121
$[Tc(V)N(NCS)_2(CH_3CN)$ $(PPh_3)_2] \cdot 0.5CH_3CN$	m	$P2_1/c$	4	TcN_4P_2	9.296(3) 18.614(5) 23.307(6)	109.63(2)	N P	2.056(4,12) 2.509(1,15)	N N	1.629(4) 2.491(4)	91.7(2,5.4), 167.8(2,7.1)g 87.8(1,10.9) 174.6(2)	37
$[Tc(V)O(H_2O)(acac)_2en]$ $Br_{0.25} \cdot C_{0.75}$	tr	$P\bar{1}$	2	TcO_4N_2	10.935(4) 9.877(4) 7.324(3)	87.266(9) 102.498(12) 97.845(9)	N O	2.002(2,1) 2.016(2,4)	H_2O O	2.282(2) 1.648(2)	88.0(1,5.6) 90.0(1,12.3) 176.8(1)	42
trans-$[Tc(III)(DPPE)_2 \cdot Br_2]$ BF_4	trg	$P3$	3	TcP_4Br_2	20.926(5) – 11.178(2)		P	2.500(1,13)	Br	2.440(1,0)	80.8(1) 93.0(1,1.0) d	122
$[Tc(III)(DMPE)_2Cl_2]$ (F_3CSO_3)	m	$P2_1/c$	4	TcP_4Cl_2	8.076(2) 24.401(4) 13.435(4)	96.61(2)	P	2.436(5,7)	Cl	2.324(4,3)	90.0(8,9.28) 90.0(8,1.39) d	123
$[Tc(V)(DMPE)_2(OH)O]$ $(F_3CSO)_2$	m	$P2_1/c$	2	TcP_4O_2	8.052(2) 11.527(2) 16.070(3)	101.96(2)	P	2.476(1,4)	O	1.795(3,0)	81.20(4) 90.28(11,46) d	123
cis-$[Tc'(CO)_2\{P(OEt)_2$ $Ph\}_4]ClO_4$	tr	$P\bar{1}$	2	TcP_4C_2	17.708915) 13.977(13) 10.185(10)	93.22(8) 90.48(9) 96.13(11)	P C	2.41(1,3) 1.90(2)	P C	2.44(1) 1.90(3)	89.9(5,9.3), 172.8(3,2.5) 90.0(5,3.9) 176.5(7)	57
trans-$[Tc(II)Cl_2\{P(OEt)_2$ $Ph\}_4]$	m	$P2_1/n$	4	TcP_4Cl_2	21.740(19) 11.750(10) 18.312(12)	92.92(9)	P	2.41(1,1)	Cl	2.41(1,1)	91.1(1,0.6); 164.1(1,1) [g] 90.0(1,9.6) 178.8(1)	34

TABLE 5 (continued)

Compounds	Crystal class[b]	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	α(°) β(°) γ(°)	M–L$_{eq}$ (Å)	M–L$_{ax}$ (Å)	L$_{eq}$–M–L$_{eq}$ L$_{ax}$–M–L$_{eq}$ L$_{ax}$–M–L$_{ax}$ (°)	Ref.
trans-[Tc(II)(DPPE)$_2$(NCS)$_2$][i]	tr	$P\bar{1}$	2	TcP$_4$N$_2$	21.384(6) 12.878(5) 9.549(4)	71.51(3) 81.94(4) 83.38(4)	P 2.428(5,8)	N 2.047(8,0)	79.9(1) 82.7(2,7) d	40
							P 2.445(5,5)	N 2.035(9,0)	79.9(1) 83.2(2,1,2) d	
trans-[Tc(III)(diars)$_2$Cl$_2$]Cl)	m	$C2$	2	TcAs$_4$Cl$_2$	13.001(10) 10.409(3) 11.796(8)	114.49(15)	As 2.515(2,4)	Cl 2.318(8,30)	83.5(1) 89.5(1,2) d	77,79
trans-[Tc(III)(diars)$_2$Cl$_2$]Cl	m	$P2_1/c$	2	TcAs$_4$Cl$_2$	9.354(5) 9.662(2) 15.341(4)	98.75(6)	As 2.508(1,2)	Cl 2.329(1,0)	82.4(1) 90.4(1,10) d	79
mer-[Tc(III)Cl$_3$(PMe$_2$Ph)$_3$][i]	m	$P2_1/n$	8	TcP$_3$Cl$_3$	10.935(9) 39.191(11) 13.738(7)	107.33(7)	P 2.45(1,3) Cl 2.46(1)	Cl 2.33(1,0)	90.0(2,7,1); 172.0(2,4,6)[g] 90.0(2,4,8) 177.0(2)	41
							P 2.45(1,3) Cl 2.45(1)	Cl 2.33(1)	90.1(2,3,7) 170.5(2,3,7)[g] 90.0(2,4,0) 178.0(2)	
HTcN$_2$(DPPE)$_2$	m	$P2_1/n$	4	TcP$_4$NH	11.090(3) 24.550(5) 16.379(4)	96.02(2)	P 2.359(3,18)	H 1.7(1) N 2.05(1)	89.8(1,9,0), 172.6(1,1,1)[g] 93.6(2,3,3)[j], 86(3,11)[k] 169(3)	124
trans-[Tc(V)O(sal)$_2$en}Cl][i]		$P2_12_12_1$	8	TcO$_4$NCl	26.653(11) 11.697(5) 10.529(3)	90 90 90	N 2.045(12,13) O 1.990(9,3)	O 1.626(11) Cl 2.527(4)	89.0(4,7,1) 89.8(4,10,9) 172.5(4)	42
α-*trans*-[Tc(III)(pd)$_2$(PPh$_3$)Cl][i]	tr	$P\bar{1}$	4	TcO$_4$PCl	13.152(8) 15.042(10) 15.532(13)	112.26(11) 91.01(7) 104.70(9)	O 2.02(1,2)	P 2.46(1) Cl 2.42(1)	89.9(3,1,2), 176.4(3,1,5)[g] 89.9(3,7,2) 176.3(1)	35
							O 2.01(1,2)	P 2.47(1) Cl 2.42(1)	89.9(3,2,3), 177.6(3,3)[g] 90.0(3,5,5) 174.4(1)	

β-*trans*-[Tc(III)(pd)$_2$(PPh$_3$)Cl]	tr	$P\bar{1}$	2	TcO$_4$PCl	15.330(8) 10.369(5) 9.309(6)	105.82(11) 104.58(8) 92.15(7)	O	2.01(1)	P Cl	2.44 2.42	89.9(2,2.3); 177.6(3,3) ^{g} 90.0(2,5.4) 175.8(1)	44
[Tc(V)(HBPz$_3$)Cl$_2$O]	tr	$P\bar{1}$	2	TcN$_3$Cl$_2$O	7.786(2) 9.052(2) 11.328(2)	103.20(2) 92.07(3) 113.83(3)	N Cl	2.087(4,1) 2.328(1,4)	O N	1.656(3) 2.259(4)	88.9(1,1.5), 164.3(1,0.5) ^{g} 89.9(1,12.9) 168.2(2)	46
cis-[Tc(V)O(OXMe)$_2$Cl	tr	$P\bar{1}$	2	TcO$_3$N$_2$Cl	7.693(2) 9.337(2) 2.739(3)	86.52(2) 85.99(2) 84.12(2)	Cl N O	2.360(1) 2.197(3,18) 1.947(3)	O O^{ox}	1.994(3) 1.649(3)	89.4(1,11.5), 166.3(1,2.1) ^{g} 90.4(1,14.2) 161.8(1)	47
[Tc(V)OCl(phsal)$_2$]	m	$P2_1/n$	4	TcO$_3$N$_2$Cl	12.854(4) 15.840(7) 11.433(4)	93.43(2)	O N Cl	1.99(1) 2.15(1,4) 2.38(1)	O O	1.94(1) 1.67(1)	89.6(5,2.6), 169.8(5,1.2) ^{g} 90.1(5,11.8) 167.1(5)	125
[Tc(V)OCl(salpd)]	or	$Pn2_1a$	4	TcO$_3$N$_2$Cl	12.010(4) 11.702(4) 11.625(6)		O N	1.98(1,0) 2.11(2,1)	O Cl	1.66(1) 2.44(1)	89.3(8,7.8), 165.2(1.0,1.7) ^{g} 90.4(8,15.1) 162.1(7)	48
[Tc(V)O(C$_5$H$_9$NO$_2$S)-(C$_5$H$_{10}$NO$_2$S)]	or	$P2_12_12_1$	4	TcN$_2$O$_2$S$_2$	21.878(5) 11.711(2) 5.924(1)		N S	2.197(6,12) 2.290(2,7)	O O	1.657(4) 2.214(4)	90.5(2,7.2), 158.2(2,3.6) ^{g} 90.1(2,16.9) 158.5(2)	45
Tc'(PMe$_2$Ph)$_2$(CO)$_2$(dtt)	or	*Pbca*	8	TcN$_2$C$_2$P$_2$	11.036(2) 14.657(4) 38.92(1)		N C	2.184(4,6) 1.869(5,3)	P	2.411(1,21)	^{m} 89.8(2,6.0) 173.80(4)	126
Tc'(PMe$_2$Ph)$_2$(CO)$_2$(dpa)	or	*Pbca*	8	TcN$_2$C$_2$P$_2$	8.954(3) 16.727(2) 41.435(5)		N C	2.203(2,1) 1.875(3,1)	P	2.409(1,22)	^{n} 89.8(1,6.5) 173.97(3)	126
[Tc(V)OBr$_2$(CH$_3$CH$_2$O)-(Npy)$_2$]	m	$P1$	2	TcN$_2$O$_2$Br$_2$	10.820(1) 11.164(2) 9.006(1)	102.82(1) 108.11(1) 64.53(1)	N Br	2.144(8,3) 2.554(8,16)	O O	1.684(6) 1.855(6)	90.0(2,0.9); 176.5(2,2.2) ^{g} 90.0(3,7.2) 172.9(3)	127

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[a] Mean value of chemically equivalent bond lengths or angles. The first number in parentheses is the standard deviation, the second number is the maximum deviation from the mean. [b] c, cubic, hx, hexagonal; m, monoclinic; or, orthorhombic; tr, triclinic; trg, trigonal. [c] The chemical identity of the coordinated atom is specified in these columns. [d] Not available. [e] Or $R\bar{3}$, $R32$, $R3m$ and $R\bar{3}m$. [f] At 173 K. [g] *Trans* L$_{eq}$–M–L$_{eq}$ angle. [h] *Trans*-[Tc(V)O$_2$(en)$_2$]X (X = Cl or I), difference result from the configuration of the en ligands. In the iodide compound en has δλ, in the chloride compound enantiomeric δδ- and λλ-conformation. [i] There are two crystallographically independent molecules. [j] The N–Tc–P angle. [k] The H–Tc–P angle. [l] The complex contains two independent molecules with only minor differences in ligand conformations. [m] The N–Tc–N = 57.2(1)°; C–Tc–C = 86.9(2)°; N–Tc–C = 107.9(2,3) and 165.2(2,3)°. [n] The N–Tc–N = 59.0(1)°; C–Tc–C = 88.1(1)°; N–Tc–C = 106.4(1,1.4) and 165.2(1,1.3)°.

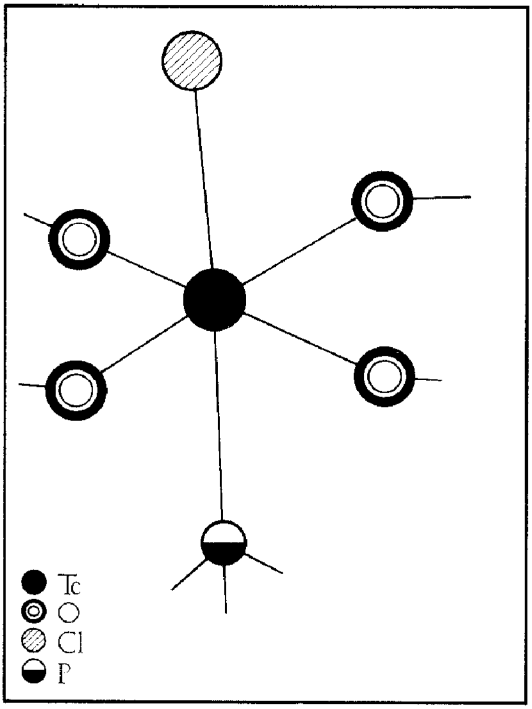

Fig. 6. A schematic view of the molecular structure of α-*trans*-[Tc(pd)$_2$(PPh$_3$)Cl] [35].

trans-[TcO{(Sal)$_2$en}Cl] contains two independent molecules with only minor differences in their ligand conformations [42]. Similar differences found between *trans*-[TcO$_2$(en)$_2$]Cl and *trans*-[TcO$_2$(en)$_2$]I (Table 5) have

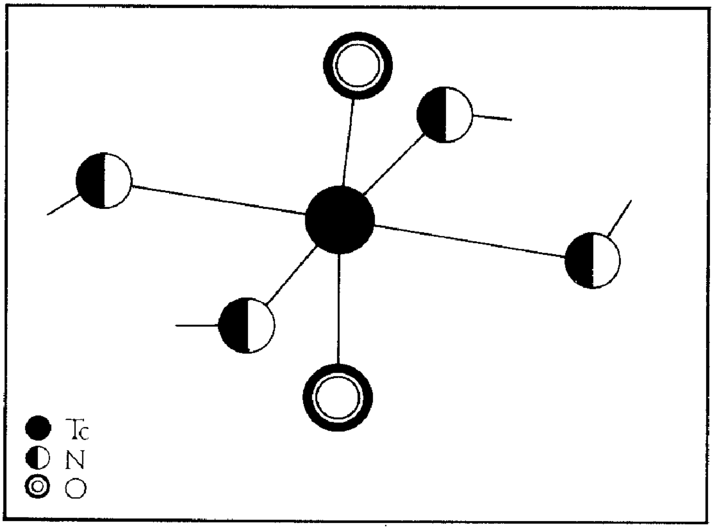

Fig. 7. A view of the technetium(V) environment in *trans*-[TcO$_2$(en)$_2$]$^+$ [36].

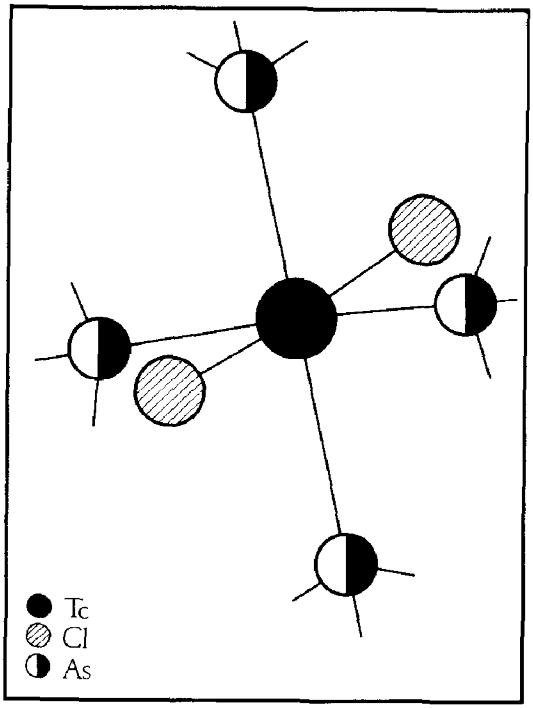

Fig. 8. A view of the technetium(III) environment in *trans*-[Tc(diars)$_2$Cl$_2$]$^+$ [79].

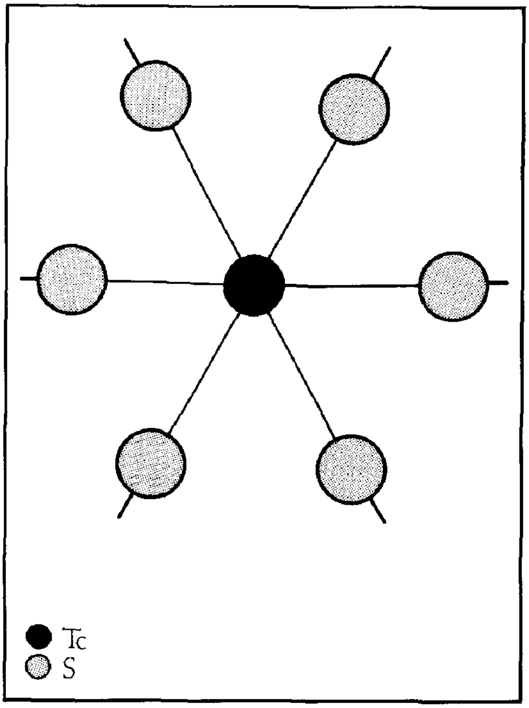

Fig. 9. A view of the technetium(III) environment in [Tc{SC(NH$_2$)$_2$}$_6$]$^{3+}$ [38].

been attributed to the configuration of the ethylenediamine ligands [43]. As indicated in Section C, second row transition metals including technetium, prefer higher coordination numbers at lower oxidation states. From the data in Table 5, it may be seen that technetium can be found in electronic configuration d^2 to d^6.

Another significant factor in stabilizing the coordination arrangement about the central atom, is the size and shape of the ligands. There are several examples of complexes with six equivalent ligands whereas tetradentate ligands are less common (Table 5). Examples of the latter include *trans*-$[TcO_2(cyclam)]ClO_4H_2O$ [39] and *trans*-$[TcO\{(sal)_2en\}Cl]$ [42] with ligands in an equatorial position and $[Tc(HBPz_3)Cl_2O]$ [44], with the tridentate $HBPz_3$ occupying two ligands in the equatorial position and one in the axial position. Two different types of chelate ligands are present in $[TcO(C_5H_9NO_2S)(C_5H_{10}NO_2S)]$ [45]. Bidentate $(C_5H_{10}NO_2S)$ is coordinated in the equatorial position and tridentate $(C_5H_9NO_2S)$ is coordinated through the S and N atoms in the equatorial position and through the O atom in the axial position. The second axial position is occupied by a monodentate O atom (Fig. 10). There are more examples of bis(bidentate) and mono(bidentate)-ligands as compared to tridentate-ligands (Table 5).

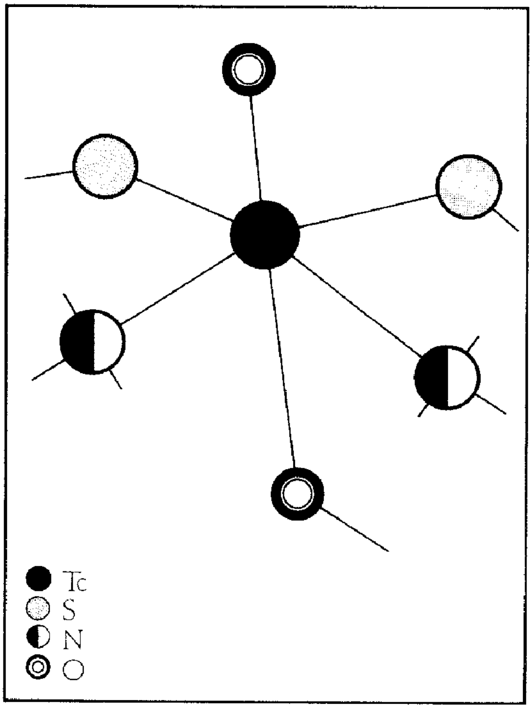

Fig. 10. A schematic view of the molecular structure of $[TcO(C_5H_9NO_2S)(C_5H_{10}NO_2S)]$ [45].

The data in Table 5 reveal that equatorial positions are occupied by donor atoms with Tc–L bond lengths increasing in the order $C < O < N < Cl \sim S < P < As < Br$. A similar trend is observed for the donor atoms coordinated in the axial position, e.g. $H < C < O < N < Cl < S < P \sim Br$. The order is in correspondence with the van der Waals radii of the donor atoms [26]. There is also a correlation between the oxidation state of the central technetium atom and the Tc–L bond length. The Tc–P(N) bond length (equatorial as well as axial) increases with higher oxidation states of technetium. This phenomenon may be related to variations in the effective ionic radii of technetium in the different oxidation states. In the case of the Tc–Cl bond length, only the axial ligand follows this general pattern.

The angle data presented in Table 5 reveal that the *cis*-L_{eq}–M–L_{eq} angles observed for technetium compounds with unidentate ligands are comparable to those of chelate ligands (80.6–99.4° versus 79.7–100.5°). The differences between unidentate and chelate ligand *trans*-L_{eq}–M–L_{eq} angles are more extreme and vary from 160–179° for the former but only from 171.5–178.5° for the latter. There are however a few exceptions: in *trans*-$[TcCl_2\{P(OEt)_2Ph\}_4]$ [34], $Tc(HBPz_3)Cl_2O$ [46], *cis*-$[TcO(oxMe)_2Cl]$ [47], TcOCl(salpd) [48], and $TcO(C_5H_9NO_2S)(C_5H_{10}NO_2S)$ [45], *trans*-L_{eq}–M–L_{eq} exhibit angles of 164, 164, 166, 165 and 158° respectively, which differ from the average values. Such deviations result from the steric requirements of the chelate ligands coordinated in both equatorial and axial positions. This is also reflected on the L_{ax}–M–L_{ax} angles, which range from 168–158° as compared to 174–179° for technetium compounds with unidentate and chelate ligands. Furthermore, chelate ligands are coordinated only in an equatorial position. Similar deviations are found for the L_{ax}–M–L_{eq} angles (Table 5).

Tsutsui and Hrung [49] studied {[tricarbonyl technetium(I)]-μ(mesoporphyrin IX dimethyl-es-terato)-[tricarbonyl rhenium(I)]}; $[(OC)_3Tc'MPRe'(CO)_3]$, and found that the central metal atoms are hexacoordinated with the chromophore MC_3N_3. The distance between the two central atoms is 3.13 Å.

(ii) Binuclear compounds

X-ray data for binuclear technetium compounds are summarized in Table 6. From the structural point of view these data can be divided into four groups. The structures of $Tc_2(OAc)_4Cl$ [50], $Tc_2(OAc)_4Br$ [51], $KTc_2(OAc)_4Cl_2$ [52], $Tc_2(O_2CCMe_3)_4Cl$ [53], and $Tc_2(OC_5H_4N)_4Cl$ [54] consist of tetra-carboxylato-(in$Tc_2(OC_5H_4N)_4Cl$, chelated with tetra-(2-oxopyridinato-)-bridged binuclear $[Tc_2(O_2CR)_4]^+$ and $[(Tc_2(OC_5H_4N)_4]^+)$ units symmetrically linked via Cl^- ions. The crystal structure of

TABLE 6

Structural data for binuclear technetium compounds [a]

Compounds	Crystal class [b]	Space group	Z	Chromophore	a(Å) b(Å) c(Å)	β[°]	M–L_{eq} (Å)	M–L_{ax} M–M (Å)	M–M′–L_{ax} M–M′–L_{eq} (°)	Ref.
$Tc_2(OAc)_4Cl$	m	$C2/c$	1	TcO_4ClTc'	15.035(3)		O [c] 2.064(5,7)	Cl [c] 2.656(1)	176.07(5)	50
					7.801(1)	109.65(2)		2.1172	91.4(2,8)	
					12.894(4)					
$Tc_2(OAc)_4Br$	m	$C2/m$	1	TcO_4BrTc'	7.102(3)		O 2.060(4)	Br 2.843(1)		179.63(3)51
					14.772(4)	113.36(3)		2.112(1)	91.4(1)	
					7.095(2)					
$KTc_2(OAc)_4Cl_2$	tg	$P4_2/n$	4	TcO_4ClTc'	11.9885(3)		O 2.077(3,12)	Cl 2.589(1)	175.90(3)	52
								2.1260(5)	91.45(9,1.28)	
					11.2243(2)					
$Tc_2^{III}(O_2CCMe_3)_4Cl_2$		$I4/m$	2	TcO_4ClTc'	11.515(2)		O 2.032(4)	Cl 2.408(4)	180.00	53
								2.192(2)	90.67(11)	
					10.625(3)					
$Tc_2(OC_5H_4N)_4Cl$ [d]		$I4/m$	2	TcO_2N_2ClTc'	11.793(3)		O 2.087(3)	Cl 2.679(1)	180.00	54
							N 2.087(3)	2.095(1)	93.07(1)	
					7.454(1)					
$Tc_2^0(CO)_{10}$	m	$I2/a$	4	TcC_5Tc'	14.73(5)					128
					7.22(2)	104.6(1)				
					14.90(2)					

$Tc_2^0(CO)_{10}$ [e]	m	$I2/a$	4	TcC_5Tc'	14.65(3) 7.18(2) 14.93(3)	 105.6(1)	C	2.000(12,23)	C	1.899(11) 3.036(6)	177.3(4) 86.3(3,3.4)	56
$[TPP\{Tc'(CO)_3\}_2]$ [f]		$P2_1/c$	2	TcN_3C_3	11.934(1) 16.295(1) 11.596(1)	 117.02(1)	C N	1.882(4,2) 2.404(2,10)	C N	1.911(4) 2.161(2) 3.101(1)		58
$(Tc(V)O)_2$ $(SCH_2CH_2S)_3$	m	$P2_1/c$	4	TcS_4O	8.833(2) 15.034(3) 11.350(2)	 108.17(1)	S	2.328(2,90)	O	1.663(4,2) 3.654(1)	[h]	129
$[\{Tc(V)O(salpd)\}_2]O$ [g]	m	$P2_1/c$	4	TcO_4N_2	15.041(2) 12.630(3) 16.522(4)	 95.35(3)	N O	2.11(1,2) 2.02(1,1)	O O [i]	1.68(1) 1.90(1)		48
							N O	2.13(1,1) 2.00(1,0)	O O [i]	1.69(1) 1.90(1)		

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[a] Mean value of chemically equivalent distances or angles. The first number in parentheses is the standard deviation, the second number is the maximum deviation from the mean. [b] m, monoclinic, tg, tetragonal. [c] Chemical identity of the ligand. [d] $L_{ax}-M-L_{eq} = 96.93(7)°$; *trans*-$L_{eq}-M-L_{eq} = 173.8(1)°$. [e] $L-_{ax}-M-L_{eq} = 93.8(5,1.4)°$; *trans*-[*cis*]-$L_{eq}-M-L_{eq} = 172.4(4,2.3)°$; [89.8(4,1.3)°]. [f] $L_{ax}-M-L_{eq} = 90.0(2,11.4)°$; *trans*-[*cis*]-$L_{eq}-M-L_{eq} = 171.2(2,2)^3$; [89.8(4,9.8)°]; $L_{ax}-M-L_{ax} = 176.5(2)°$. [g] There are two independent TcO(salpd) moieties A and B: $L_{ax}-M-L_{ax} = 167.0(5)°$ (A); 165.7(4)° (B). $L_{ax}-M-L_{eq} = 90.3(5,8.4)^3$ (A), 90.2(5,10.0°) (B); *trans*-[*cis*]-$L_{eq}-M-L_{eq} = 171.4(5.4)°$ [89.8(5,5.9)°] (A); 170.4(5,4)°, [89.9(5,5.7)°](B); Tc–O–Tc = 180.0°. [h] The S–Tc–S = 83.66(6,8.05) and 140.93(6, 2.41)°; S–Tc–O = 109.3(2, 2.3)°; Tc–S–Tc = 99.77(6, 26)°; [i] Bridging atom.

$Tc_2(O_2CCMe_3)_4Cl_2$ is shown in Fig. 11 as a representative example of this group. In these binuclear complexes the two technetium atoms are linked via multiple bonds. The average Tc–Tc bond distance in $[Tc_2(OR)_4]^+$ (OR = OAc^- or $OC_5H_4N^-$) is 2.11 Å. This is at least 0.08 Å shorter than the same bond in $[Tc_2(O_2CCMe_3)_4]^{2+}$ and corresponds to a change in the oxidation state of the central atom from +2.5 in $[Tc_2(OR)_4]^+$ to +3 in $[Tc_2(O_2CCM_3)_4]^{2+}$. Similar differences are observed between $[Tc_2Cl_8]^{3-}$, with a Tc oxidation state of +2.5, and $[Tc_2Cl_8]^{2-}$ with a Tc oxidation state of +3 (Section C (ii), Table 3). We also note that the Tc–L bond in $[Tc_2(OR)_4]^+$ is in general longer than the same bond in $[Tc_2(O_2CCMe_3)_4]^{2+}$ (Table 6), and also that the sum of all interatomic distances around Tc in $[Tc_2(OR)_4]^+$ (oxidation state +2.5) is somewhat longer than that in $[Tc_2(O_2CCMe_3)_4]^{2+}$ (oxidation state +3). This is also in agreement with similar differences between $[Tc_2Cl_8]^{3-}$ (Tc is +2.5) and $[Tc_2Cl_8]^{2-}$ (Tc is +3) (Section C (ii)).

In general the Tc(III)–Tc(III) distance is longer than the Tc(2.5)–Tc(2.5) distance, but at the same time the Tc(III)–L bond is shorter than the Tc(2.5)–L. This is also reflected in the sum of all interatomic distances, which is smaller around Tc(III) than around Tc(2.5) (Tables 4 and 6). These

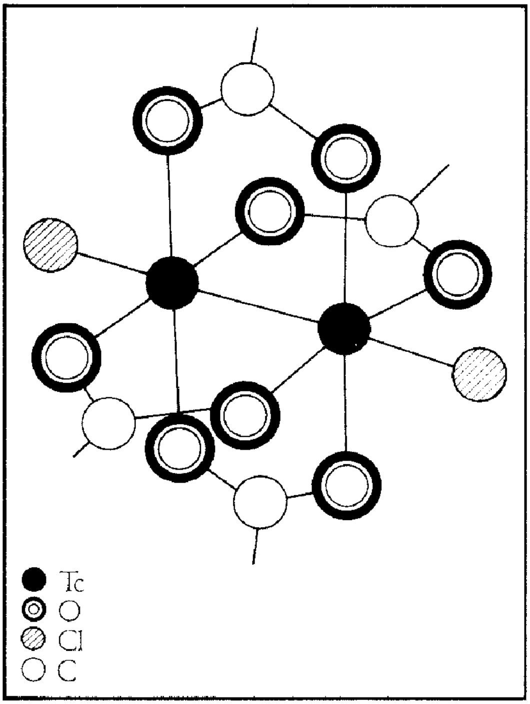

Fig. 11. A schematic view of the molecular structure of $Tc_2(O_2CCMe_3)_4Cl_2$ [53].

variations most likely result from differences in the σ, π and δ bond strengths between Tc(III) and Tc(2.5) binuclear complexes [55].

In the structure of $Tc_2(CO)_{10}$, which exhibits an approximately D_{4_d} symmetry, each Tc(0) atom is octahedrally coordinated to five carbonyl ligands (Tc–C = 1.899–2.023(12) Å; Tc–Tc = 3.036(6) Å) such that the equatorial carbons are arranged in a staggered configuration [56]. The Tc–CO bond length of 1.90(3) Å in *cis*-$[Tc(CO)_2\{P(OEt)_2Ph\}_4]ClO_4$ [57] is still within the range observed for $Tc_2(CO)_{10}$, and the angle values found in these two compounds are also comparable (Tables 3 and 6).

The crystal structure of $TPP\{Tc(CO)_3\}_2$ is shown in Fig. 12 and bond lengths and bond angles are given in Table 6 [58]. The M–C bond lengths appear to be normal and comparable to those found in other familiar technetium compounds. However, the average Tc–N bond length of 2.32 Å, is larger than that found in *trans*-$[Tc(cyclam)O_2]ClO_4 \cdot H_2O$ (2.125 Å) [39]. In the latter the tetradentate N donor cyclam ligand builds up a plane which together with two oxygen atoms in the apex complete a tetragonal distortion around Tc(V). In $TPP\{Tc(CO)_3\}_2$ the metal atom is situated 1.42 Å above the plane of the four pyrrole nitrogen atoms (distance from the Tc(I) to the N atoms is 3.208 Å) and the porphyrin macrocycle is highly distorted. It is

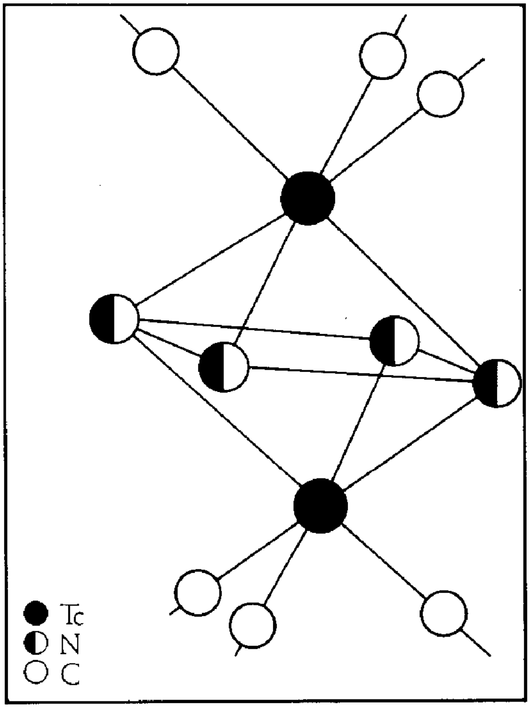

Fig. 12. A schematic view of the molecular structure of $[TPP\{Tc(CO)_3\}_2]$ [58].

possible to enumerate a few factors that seem to influence the Tc–N bond length. First of all, the size of the central atom is of some importance. As expected, the effective ionic radii of a technetium ion with d^2 electronic configuration such as in TPP{Tc(CO)$_3$}$_2$, is larger than the radii of a technetium ion with d^6 configuration such as in *trans*-[Tc(cyclam)O$_2$]ClO$_4$ · H$_2$O. Secondly, and of more significance, the size and shape of the ligands strongly influence the bond length. Finally, there is a Tc–Tc (bond length 3.101(1) Å) interaction between the central atoms in compounds like TPP{Tc(CO)$_3$}$_2$, which is absent in others, such as *trans*-[Tc(cyclam)O$_2$] ClO$_4$ · H$_2$O. X-ray analysis of the orange (TcO)$_2$(SCH$_2$CH$_2$S)$_3$ complex shows two Tc(V) atoms with similar environments [58]. Two sulphur atoms of a square pyramidal TcOS$_4$ core are bonded to another TcOS$_4$ unit forming two square pyramids sharing a corner, with an angle of 106.0(1) Å between the basal planes. The technetium atoms are 0.7410(3) and 0.8025(4) Å above the sulfur atom planes and these values are similar to those reported for other TcL$_5$ systems (Table 2). The Tc–Tc distance of 3.654(1) Å rules out direct bonding. The values of bond distances and angles are summarized in Table 6.

The binuclear structure of [{TcO(salpd)}$_2$]O [48] consists of two crystallographically independent TcO(salpd) moieties bridged by an oxygen atom, with the bridging Tc–O–Tc angle symmetrically imposed at 180°. The Tc(V) atoms have octahedral coordination with the equatorial plane formed by the N$_2$O$_2$ donor set of the salpd-ligand, whereas the O and the "bridging" O atom are *trans* to each other in axial positions. Selected bond distances and angles are given in Table 6. The average value of Tc–L$_{eq}$ (L = O or N) bond lengths is 2.01 and 2.12 Å, respectively, which may be compared with 2.00 and 2.11 Å found in hexacoordinated technetium compounds (Table 5). The non-bridged Tc–O$_{ax}$ bond length of 1.69 Å is comparable with the bond length of 1.70 Å found in mononuclear hexacoordinated Tc compounds (Table 5). The bridging Tc–O$_{ax}$ distance of 1.90 Å is well within the average Tc–O$_{ax}$ bond length of 1.70 Å and the average Tc–O single bond length of 2.00 Å (Table 6).

(iii) Trinuclear compounds

Edwards et al. [59] studied the crystal structure of technetium(VI) oxide tetrafluoride. Crystals of the hexagonal form have space group $P6_3/m$ ($a = 9.00(1)$, $c = 7.92(1)$ Å; $Z = 6$), and consist of distinct trinuclear units, (TcOF$_4$)$_3$, positioned in the mirror planes of the space group with the three technetium(VI) atoms forming a triangle, linked asymmetrically by *cis*-bridging fluorine atoms (Fig. 13). The distorted octahedral arrangement around the technetium atom consists of two fluorine atoms (terminal) (Tc–F$_t$ =

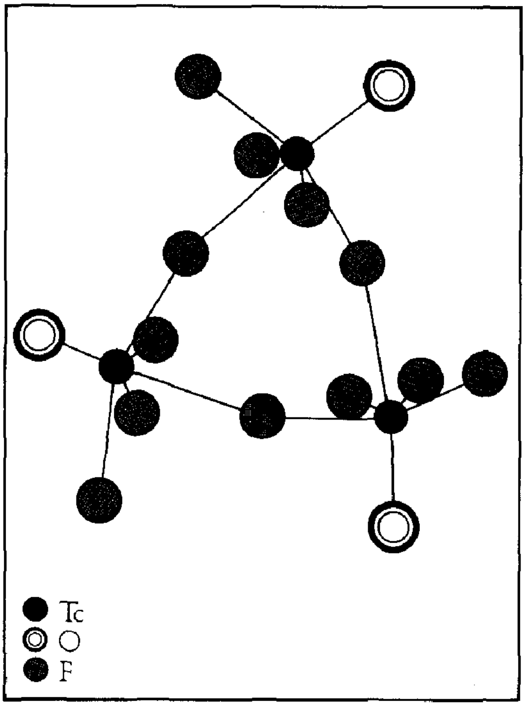

Fig. 13. A schematic view of the molecular structure of $(TcOF_4)_3$ [59].

1.80(2) and 1.82(4) Å), an oxygen atom (Tc–O = 1.66(3) Å) and fluorine atoms (bridge) ($Tc–F_{br}$ = 1.89(2) and 2.26(2) Å). Distortion is also reflected in the various bond angles: $F_t–Tc–F_{br}$ = 78.0(2.9) and 78.7(1.5)° (*cis*); and 157.2(3.0) (*trans*); $O–Tc–F_{br}$ = 96.8(2.2)° (*cis*) and 175.9(2.1)° (*trans*); $F_t–Tc–F_t$ = 89.1(1.5)°; $F_t–Tc–O$ = 101.1(1.5) and 106.0(3.3)°; $F_{br}–Tc–F_{br}$ = 79.1(1.5)°; and $Tc–F_{br}–Tc'$ = 160.9(2.1)° [59].

(iv) Hexanuclear compounds

Two examples of hexanuclear technetium compounds are reported. The crystal structure of $[Tc_6(Br,OH)_6Br_6][(H_2O)_3H_3O]_2$ is monoclinic with space group $P2_{1/c}$ and the following cell dimensions: $a = 9.258(4)$, $b = 9.211(3)$ and $c = 17.437(7)$ Å; $\beta = 101.09(3)$° and $Z = 2$ [60]. The crystals of the compound consists of the $[Tc_6(Br,OH)_6Br_6]^{2-}$ anion and $[(H_2O)_3H_3O]^+$ cations. The six technetium atoms in the $[Tc_6(Br,OH)_6Br]^{2-}$ anion form a proper octahedron positioned within a cube with six apices occupied by bromine atoms and probably oxygen atoms of hydroxyl groups and with two apices unoccupied. In addition, the technetium atoms are bound to the terminal bromine atoms positioned above the midpoints of the six surfaces of the cube. Each technetium atom is bound to four adjacent technetium atoms with bond lengths of 2.59–2.60 Å. The lengths of the bonds of the technetium atoms with the bridging ligands, which partially occupy the cube apices, are in the range 2.41–2.51 Å. The bond distances between the technetium atoms and the terminal bromine atoms are uniform (2.55 Å). The Tc–Br terminal bond distance is somewhat longer than those of mononuclear technetium compounds (Table 5).

Another example of a hexanuclear technetium compound is $[Tc_6Cl_{14}][(Me_3)_4N]_3$ [60]. The compound crystallizes in the orthorhombic space group *Pcmn* with four formula units in a cell with the following dimensions: $a = 11.583(2)$, $b = 13.527(3)$, and $c = 24.387(3)$ Å. The crystals consist of the $[Tc_6Cl_{14}]^{3-}$ anion and tetramethylammonium cations. The structure of the anion shows D_{3_h} symmetry. The six technetium atoms form a trigonal prism with a base in the form of a right triangle. There are three quaternary Tc–Tc bonds (2.16 Å) which form the lateral edges of the prism, and six weak Tc–Tc bonds (2.70 Å) which form the sides of the triangles of the prism. The three bridging chlorine atoms which are bound in pairs to three technetium atoms ($Tc–Cl_{br} = 2.36–2.40$ Å) and three terminal chlorine atoms ($Tc–Cl_{ter} = 2.37–2.38$ Å) in each half of the complex. All six chlorine atoms occupy equatorial positions relative to the triangle consisting of technetium atoms. The seventh chlorine atom interacts with three technetium atoms forming a unique axial ligand ($Tc–Cl_{ax} = 2.88–3.08$ Å) above the center of this triangle. The complex consists of three identical fragments of $[Tc_3Cl_8]^{n-}$ dimers, excluding the axial chlorine atoms [60].

(v) Octanuclear compounds

The crystal structure of $Tc_8Br_{13} \cdot 2H_2O$ was determined by Kozmin et al. [61]. Crystals of the compound are monoclinic with the following dimensions, $a = 7.561(2)$, $b = 13.553(5)$, $c = 12.620(3)$ Å, $\beta = 102.62(2)°$, including two formula units and space group $P2_{i/n}$. The compound consisted of octanuclear Tc_8Br_{12} moieties, Br^- ions, as well as H_2O molecules, $(OH)^-$ anions, and $(H_3O)^+$ cations. In the Tc_8Br_{12} structure (Fig. 14), eight technetium atoms occupy the vertices of a prism. The base of this prism is a rhombus and the side edges are perpendicular to the base. There are two types of technetium atoms, Tc_3 and Tc_4 (both in a formal oxidation state of +1), located at the vertices of the short diagonals, while atoms Tc_1 and Tc_2 (formal oxidation state of +2) are located at the vertices of the long diagonals of the rhombi. All the technetium atoms interact in a pairwise manner to form four Tc–Tc bonds of high multiplicity with lengths of 2.155(2) and 2.156(2) Å (the side edges of the prism). In addition, each technetium(I) atom forms three metal–metal bonds with a length of 2.531(2) (short diagonals of the rhombus) and 2.679(2) and 2.721(2) Å (sides of the

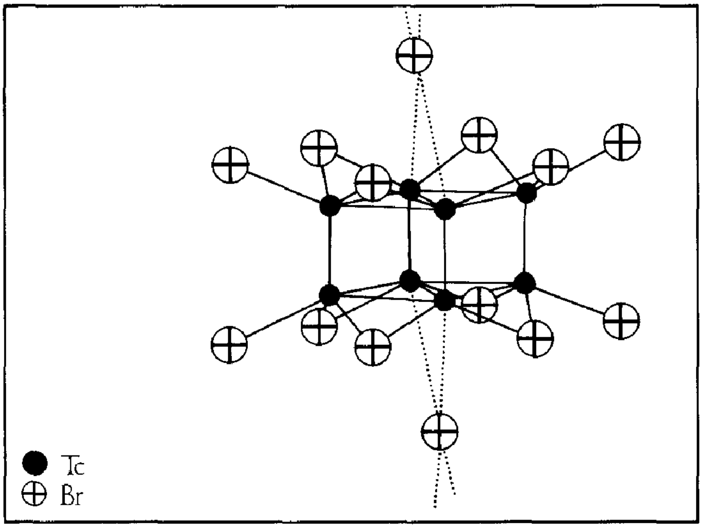

Fig. 14. A schematic view of the structure of $[Tc_8Br_{12}]$ [61].

rhombus). Each of the Tc(II) atoms is bound to Tc(I) atoms (3.30–3.46 Å). Eight bromine bridging atoms link the Tc(I) and Tc(II) atoms in a pairwise manner (Tc(1)–Br = 2.504(2)–3.066(2) Å, 2.677 Å (mean); Tc(II)–Br = 2.496(2)–2.519(2) Å, 2.508 Å (mean)); while the four terminal bromine atoms are linked only to the Tc(II) atoms (Tc(II)–Br = 2.513(2), 2.549(2) Å, 2.531 Å (mean)). The average Tc(I)–Br bond is longer than the Tc(II)–Br bond, and the average Tc(II)–Br bond is also longer than the bonds found in hexanuclear $[Tc_6(Br,OH)_6Br_6]^{2-}$ (oxidation state of technetium is close to +3). It thus seems that there is a tendency towards larger Tc–Br bond lengths at lower oxidation states of technetium. The Tc–Tc–Tc valence angles between a side edge and a side of the base of the prism vary between 89.4 and 90.7°. In the plane of the rhombus the angles are 55.7 and 56.3° (between sides of the rhombus formed by the Tc(II) atoms) and 61.7 to 62.6° (between a sides and a short diagonal of the rhombus). The remaining angles include $Tc–Tc–Br_{term}$: 106.6 and 112.8°, $Tc–Tc–Br_{bridge}$: 110.1 to 112.9°, and $Tc–Br_{bridge}–Tc$: 64.3 to 65.6° [61]. The octanuclear complex consists of two pairs of different fragments: in contrast, the hexanuclear complex consists of three identical fragments.

(vi) Polynuclear compounds

The X-ray powder pattern of polynuclear TcO_2 has been reported by Mooney [62], Lam et al. [63], and Muller et al. [16]. While the unit cell dimensions for hexagonal TcO_2 reported by the last two laboratories are in

TABLE 7

Structural data for polynuclear technetium compounds [a]

Compounds	Crystal class [b]	Space group	*Z*	Chromo- phore	*a*(Å) *b*(Å) *c*(Å)	M–L M–M′ (Å)	L–M–L M–L–M′ (°)	Ref.
$(Tc(IV)Cl_4)_n$	or	*Pbca*	8	$TcCl_6$	11.65(1) 14.06(1) 6.03(1)	Cl [c] 2.372(0,126) 3.31	90(0,6) [d]	64
$\{[Tc(IV)(OH)(MDP)]\text{-}[Li(H_2O)_3]\cdot 1/3H_2O\}_n$	hg	$R\bar{3}$	18	TcO_6	21.771(8) – 12.208(3)	O 2.012(14,29) HO 1.942(14,26)	[d]	65
$(Tc(III)P_3)_n$	or	*Pnma*	4	TcP_6	15.359(5) 3.029(1) 5.142(2)	P 2.386(2,63) Tc′ 3.092(1)	99.0(1) 80.8(1,2.5)	66
$(TcP_4)_n$	or	*Pbca*	8	TcP_6	6.238(1) 9.215(3) 10.837(3)	P 2.398(2,132) Tc′ 3.002(2)	[d]	67
$(Tc_3P)_n$	tg		8		9.568(5) – 4.736(3)	P 2.482(3,35) [e] Tc′ 2.620–3.231(3) P 2.458(3,58) [f] Tc′ 2.652–3.211(3) P 2.486(3,169) [g] Tc′ 2.652–3.015(3)	[d]	67
$(Tc_2As_3)_n$ [h]	tr	$P\bar{1}$	4	6.574(1) 6.632(1) 8.023(2)				130

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[a] Mean value of chemically equivalent distances or angles. The first number in parentheses is the a standard deviation, the second number is the maximum deviation from the mean. [b] hg, hexagonal; or, orthorhombic; tg, tetragonal; tr, triclinic. [c] In this column is specified the coordinated atom (ligand). [d] Not given. [e] For Tc(1). [f] For Tc(2). [g] For Tc(3). [h] $\alpha = 95.69(1)°$, $\beta = 102.03(1)°$, $\gamma = 104.31(2)°$.

good agreement ($a = 2.743$ and $c = 4.400$ Å versus $a = 2.741(1)$ and $c = 4.400(1)$ Å), Mooney's [62] cell dimensions are smaller ($a = 2.735$ and $c = 4.388$ Å). The lower values may indicate impurities in the technetium sample. No other structural data of TcO_2 are available. Structural data for polynuclear technetium compounds are presented in Table 7. The crystal structure of $(TcCl_4)_n$ [64] is shown in Fig. 15 as a representative example of this class. There are three chemically distinct Tc–Cl bond lengths, e.g. 2.24, 2.38 and 2.49 Å (mean values) and two crystallographically independent examples of each. The shortest Tc–Cl bonds involve the non-bridging Cl(4) and Cl(5), whereas the longest bonds involve the bridging Cl(2) and Cl(3) atom, with ligands perpendicularly to the chain. The intermediate Tc–Cl bonds involve the bridging Cl(2)′ and Cl(3)′ atoms, parallel to the chain. All bond angles are within 6° of 90°, as expected for a regular octahedron. The Tc–Cl bond lengths are within the same range as found in other Tc(IV) compounds (Table 5). On the other hand, the mean Tc–Cl bridge bond length in the polynuclear compounds is longer than in hexanuclear $[Tc_6Cl_4]^{3-}$, whereas the reverse holds for Tc–Cl terminal bond lengths.

In the case of the infinite polymeric chain of $[Tc(OH)(MDP)]^-$ [65] each MDP ligand bridges two symmetrically related technetium atoms, and the

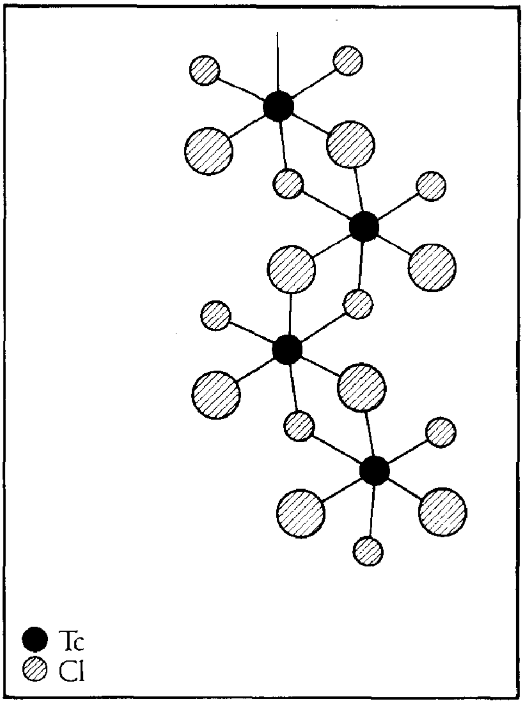

Fig. 15. A schematic view of a section of a $(TcCl_4)_n$ chain [64].

charge of each unit is neutralized by the hydrated lithium cation $[Li(H_2O)_3]^+$. In addition, there is a single oxygen atom (H_2O) on the threefold axis of the space group. The coordination geometry around each technetium atom is approximately octahedral, with the two bridging oxygen atoms (Tc–O = 1.917(12) and 1.968(15) Å) occupying *cis* coordinate sites and the oxygen atoms of the MDP ligands (Tc–O = 2.01 Å average) occupying the remaining four sites. The Tc–O bond length is generally in accordance with observed Tc–O single bond lengths (Tables 4 and 5). In the case of TcP_3 [66], the average phosphorus to technetium bond distance of 2.386 Å compares well with the corresponding distance of 2.398 Å in TcP_4 [67] (Table 7). The average Tc–P distance in Tc_3P (2.48 Å) [67] is longer than in TcP_3 and TcP_4, but all distances are comparable to those found in other hexacoordinate Tc compounds (Table 5).

E. STRUCTURAL DATA FOR TECHNETIUM COMPOUNDS WITH COORDINATION NUMBER SEVEN

(i) Mononuclear compounds

(a) Pentagonal bipyramidal geometry

Seven-coordinate compounds are probably the most complicated in coordination chemistry [68]. Structural and dynamic aspects of their stereochemistry are also of importance for a better understanding of dissociation reactions of six- and eight-coordinate compounds [69]. The majority of seven-coordinate compounds analyzed by X-ray crystallography exhibit geometries related to one of three possible polyhedra, e.g. the pentagonal bipyramid, the capped octahedron, and the capped trigonal prism. An additional type, the tetragonal base-trigonal base, is less frequently found [70]. Structural data of the tetragonal base-trigonal base type for technetium are not available but some interesting examples of the other three types have been reported. In Table 8 we summarize structural data for mononuclear technetium compounds with a pentagonal bipyramidal geometry. The structures are tabulated in order of increasing number of different ligands. Figure 16 illustrates a representative example of this class of compounds, the structure of $Tc(S_2CNEt_2)_3(CO)$ [71]. The technetium is surrounded by one unidentate and three bidentate ligands in a distorted pentagonal bipyramidal conformation, and the equatorial plane consists of two $S_2CNEt_2^-$ ions (Tc–S bond, 2.475(3)–2.491(3) Å) and a $S_2CNEt_2^-$ ion which occupies both an equatorial (Tc–S(6) = 2.440(3) Å) and an axial position (Tc–S(5) = 2.520(3) Å). The remaining axial site is occupied by the carbonyl group (Tc–C = 1.861(2) Å).

TABLE 8

Structural data for mononuclear technetium(III) compounds with a pentagonal bipyramidal geometry [a]

Compounds	Space group	*Z*	Chromophore	Tc–L_{ax} Tc–L_{eq} (Å)		L_{ax}–Tc–L_{ax} L_{ax}–Tc–L_{eq}	L_{eq}–Tc–L_{eq} *cis*(°) *trans*(°)	Ref.
[Tc(III)($S_2CNEt_2)_3$(CO)]	$P\bar{1}$	2	TcS_6C	C [b]1.861(12)	S [b]2.520(3)	172.9(3)	72.4(1)	71,131
				S 2.474(3)		90.6(2)	142.5(1)	
[Tc(III)($S_2CNEt_2)_3$(PMe_2Ph)]	$P2_12_12_1$	4	TcS_6P	P 2.330(3)	S 2.505(3)	168.9(1)	72.2(1)	132
				S 2.476(3)		90.2(1)	143.1(1)	
[Tc(III)($S_2CNEt_2)_2Cl_2$(NS)] [c]	*Pcmn*	8	TcS_4Cl_2N	Cl 2.492(6)	N 1.80(2)	178.9(8)	71.8(2)	133
				Cl 2.401(7)	S 2.646(5)	90.1(4)	144.2(1)	
				Cl 2.414(5)	S 1.70(2)	176.8(9)	72.0(2)	
				Cl 2.376(8)	S 2.477(5)	89.9(6)	144.2(1)	

[a] Mean value of chemically equivalent distances or angles with standard deviations in parentheses. [b] Chemical identity of the coordinated atom. [c] There are two crystallographically independent molecules.

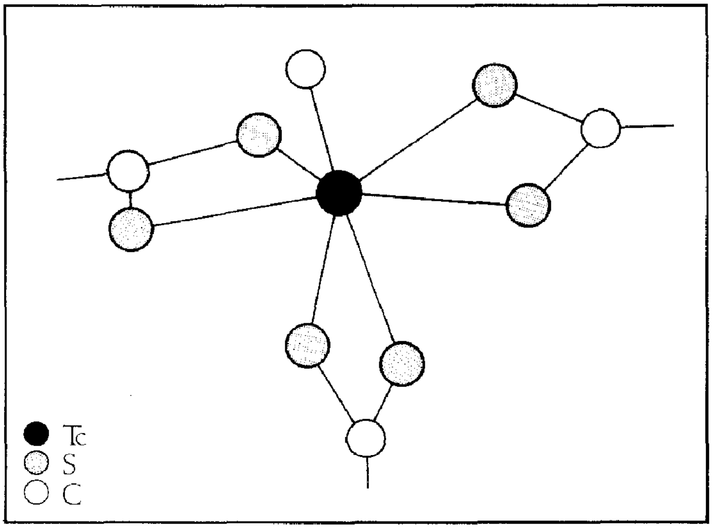

Fig. 16. A schematic view of the molecular structure of $[Tc(S_2CNEt_2)_3(CO)]$ [71].

It is of interest to note that in all possible polyhedra the central Tc atom is in an oxidation state + 3 (Table 8). Furthermore, the data in Table 8 reveal that the mean Tc–L_{ax} bond of 2.20 Å is shorter than the Tc–L_{eq} bond (2.45 Å). This relatively large difference is in agreement with the notion that the two apical sites of a pentagonal bipyramid are less sterically hindered than the five equatorial sites [72]. The TcL_5 girdle is distorted in such a way that the central atom is above the equatorial plane, at the site of the apical ligand with the shorter Tc–L_{ax} bond length. There are no examples with equivalent Tc–L_{ax} bond lengths.

One of the important shape characteristics for describing a pentagonal bipyramidal geometry is the ratio of the bond distances M–L_{ax}/M–L_{eq}. In $Tc(S_2CNEt_2)_2Cl_2(NS)$ this ratio is 0.97, versus 0.88 for the remaining tris(diethyldithiocarbamato) compounds. This indicates that the geometry about technetium in $Tc(S_2CNEt_2)_2Cl_2(NS)$ resembles closely an ideal pentagonal bipyramid, whereas in tris(diethyldithiocarbamato) compounds a considerably distorted pentagonal bipyramidal geometry prevails. The latter distortion results from the restricted bite of the dithiocarbamato ligand which spans both the axial and equatorial sites. Any deviation from the ideal geometry is also reflected in the the bond angles L_{ax}–M–L_{ax}, L_{ax}–M–L_{eq} and L_{eq}–M–L_{eq}. In the ideal pentagonal bipyramidal the angles are: L_{ax}–M–L_{ax}, 180°; L_{ax}–M–L_{eq}, 90°; L_{eq}–M–L_{eq}, 72 and 144° [72]. In tris(diethyldithiocarbamato) compounds the angle differs from the ideal geometry by 7–11°, in bis(diethyldithiocarbamato) compounds only by 2–3° (Table 8). The L_{ax}–Tc–L_{eq} angles are also indicative of larger distortion in tris- than in bis(diethyldithiocarbamato) compounds: 87.1–93.7° for bis-compounds versus 71–102.2° for tris-compounds. As can be expected, the smaller L_{eq}–M–L_{eq} angles (68–78°) in the pentagonal base between intraligand coordinated atoms are similar for both bis- and tris(diethyldithiocarbamato) compounds. In contrast, the larger L_{eq}–M–L_{eq} angles between interligand atoms vary to some extent. Angles in bis-compounds resemble those found in the pentagonal bipyramid (144.2° versus 144°), whereas in triscompounds they range from 139 to 152°. Again, they reflect deviation from the ideal pentagonal bipyramidal geometry. It should be noted that the average values are comparable to those of an ideal bipyramid (Table 8).

(b) Capped octahedral geometry

Pale, yellow plates of carbonyltrichlorotris(dimethylphenylphosphine) technetium(III) ethanol ($[TcCl_3(CO)(PMe_2Ph)_3]C_2H_5OH$), were observed when carbon monoxide was passed through a boiling solution of *mer*-$TcCl_3(PMe_2Ph)_3$ [73]. The compound crystallizes as monoclinic crystals in space group $P2_1/c$ with 4 molecules per unit. The crystal structure consists of molecular units of $Tc(III)Cl_3(CO)(PMe_2Ph)_3$ and C_2H_5OH (Fig. 17) [73]. The coordination polyhedron around technetium(III) is a distorted capped

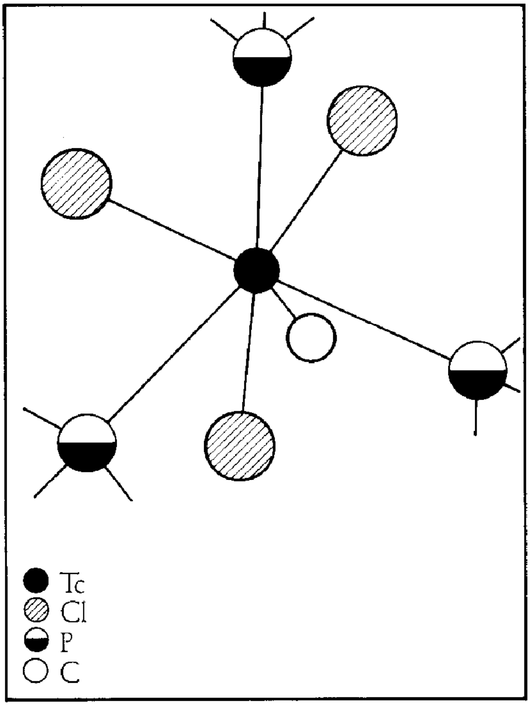

Fig. 17. A schematic view of the molecular structure of $[TcCl_3(CO)(PMe_2Ph)_3]$ [73].

octahedron, with the capped face consisting of the three phosphorus atoms (Tc–P: 2.44(1) (2 ×) and 2.45(1) Å) and the uncapped face consisting of the three chlorine atoms (Tc–Cl: 2.47, 2.48 and 2.49(1) Å); the carbonyl group occupies the unique capping position (Tc–C: 1.86(2) Å). In seven-coordinated Mo compounds the bond distances in the capped octahedron increase in the following order: $(\mathrm{Mo{-}L_c}) < (\mathrm{Mo{-}L_{cf}}) < (\mathrm{Mo{-}L_{uf}})$ [70]. The mean values of similar bonds in $\mathrm{TcCl_3(CO)(PMe_3Ph)_3}$ follow the same trend. This, in spite of the fact that the phosphorus atom has a larger atomic radius (r_P 1.10 Å) than chlorine (r_Cl 0.99 Å) [26], suggesting that the capped position is more populated than the uncapped face. Average bond angles about technetium are: $\mathrm{L_c{-}Tc{-}L_{cf}}$, 74.2°; $\mathrm{L_{cf}{-}Tc{-}L_{cf}}$, 112.9°; $\mathrm{L_{cf}{-}Tc{-}L_{uf}}$ (*cis* to $\mathrm{L_{uf}}$) 77.3°. In the capped octahedron, the freedom, or confinement of the atom in the uncapped face is usually revealed by the $\mathrm{L_{uf}{-}M{-}L}$ angles. The mean values of the $\mathrm{L_{uf}{-}Tc{-}L}$ angles are 88.0, 159.1 and 126.6°, for $\mathrm{L_{uf}}$, $\mathrm{L_{cf}}$ and $\mathrm{L_c}$ respectively, which is fairly close to values reported for related structures with different central atoms (90, 162 and 127°) [70,72].

(c) Capped trigonal prism geometry

X-ray analysis of a technetium compound with clinical applications as a $^{99\mathrm{m}}\mathrm{Tc}$ radiopharmaceutical was accomplished by Deutsch et al. [74]. They

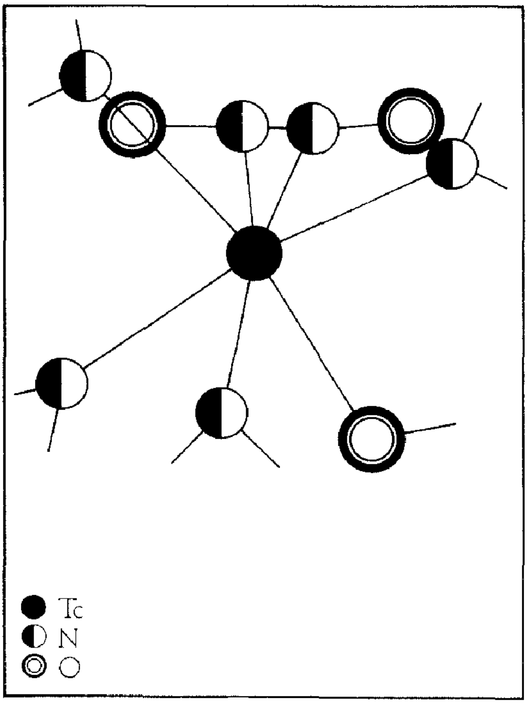

Fig. 18. A schematic view of the molecular structure of $[\mathrm{Tc(dmg)_3(SnCl_3)(OH)}]$ [74].

reported the synthesis and structure of the yellow compound [Tc(dmg)$_3$(SnCl$_3$)(OH)] · 3H$_2$O. The compound crystallizes in the triclinic system in the space group $P\bar{1}$ with 2 molecules per unit cell ($Z = 2$). The coordination polyhedron around technetium(V) is a capped trigonal prismatic (Fig. 18). The coordination sphere is built up by the six imino nitrogen atoms from the dmg ligands (Tc–N, 2.074(9)–2.104(9) Å) and the bridging nitrogen atom (Tc–N, 2.074(9)–2.104(9) Å) together with the bridging oxygen atom (Tc–OH, 2.030(6) Å) comprise the coordination sphere. The Sn atom is octahedrally coordinated. The Tc and Sn atoms are joined by three bridges, including a single bridge from the OH group and two diatomic N–O bridges from different dmg ligands. The distance between the metal centers is 3.47 Å [74].

(ii) Binuclear compounds

The crystal structure of diamagnetic binuclear red-brown (H$_2$EDTA)Tc(IV)(μ-O)$_2$Tc(IV)(H$_2$EDTA) · 5H$_2$O, prepared via the reaction between ammonium pertechnetate and Na$_2$H$_2$EDTA, reveals that the coordination of the central Tc(μ-O)$_2$Tc unit includes two H$_2$EDTA molecules, one for each Tc atom (Fig. 19) [75]. The coordination number about each Tc atom is seven with TcO$_4$N$_2$Tc′ as a chromophore. The technetium(IV) atoms are bridged by two oxygen atoms with the Tc–O distances averaging 1.912(5) Å and the Tc–Tc atoms 2.331(1) Å apart. Each technetium atom is bound in the axial positions to two oxygen atoms derived from two different carboxy-

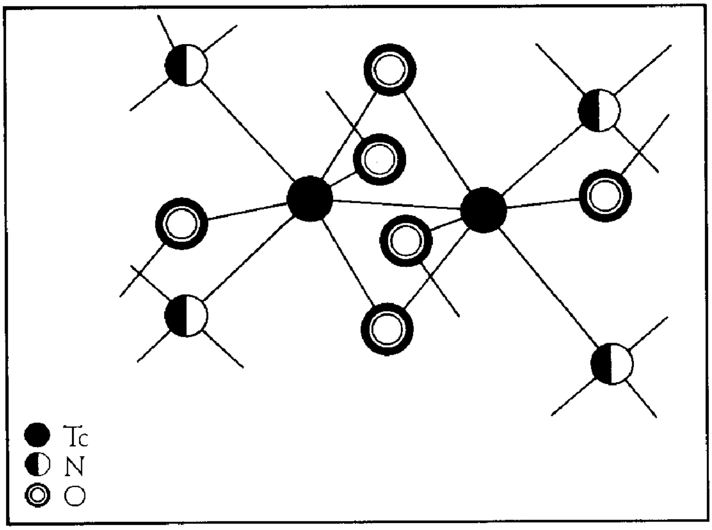

Fig. 19. A schematic view of the molecular structure of [(EDTA)Tc(μ-O)$_2$Tc(EDTA)] [75].

late groups (Tc–O, 2.011(7) Å), and in the equatorial position (except for the two bridged O atoms) to two amine nitrogens (Tc–N, 2.207(16) Å). This complex contains some of the shortest Tc(IV)–Tc(IV) bonds observed so far.

Burgi et al. [76] prepared and studied the crystal structure of diamagnetic binuclear sevencoordinate $Na_2[NTATc(IV)(\mu\text{-}O)_2Tc(IV)NTA] \cdot 6H_2O$, with the TcO_5NTc' chromophore. The crystal and molecular structure of this compound reveal that two Tc–NTA moieties are joined via two oxo-bridging O-atoms (Tc–O, 1.919(2) Å) and that the Tc–Tc atoms are 2.363(2) Å apart. Coordination polyhedron around each technetium atom is built up by bonding to the N-atom (Tc–N, 2.148(2) Å) and to three carboxylate O-atoms (Tc–O, average 2.047(3) Å) of the NTA-ligand. The elongation of the Tc–Tc distance is reflected in simultaneous opening of the Tc–O–Tc bridging angle. In $[NTATc\text{-}(\mu\text{-}O)_2TcNTA]^{2-}$ the Tc–O–Tc bridge angle is 76.0(1)° and the Tc–Tc atoms are 2.363(2) Å apart, whereas in $(H_2EDTA)Tc(\mu\text{-}O)_2Tc(H_2EDTA)$ these values are 75.2(1)° and 2.331(1) Å, respectively.

F. STRUCTURAL DATA FOR TECHNETIUM COMPOUNDS WITH COORDINATION NUMBER EIGHT

Glavan et al. [77] investigated $[Tc(V)(diars)_2Cl_4] \cdot (PF_6)$ and found that the dark brown compound belongs to the orthorhombic space group *Fddd*

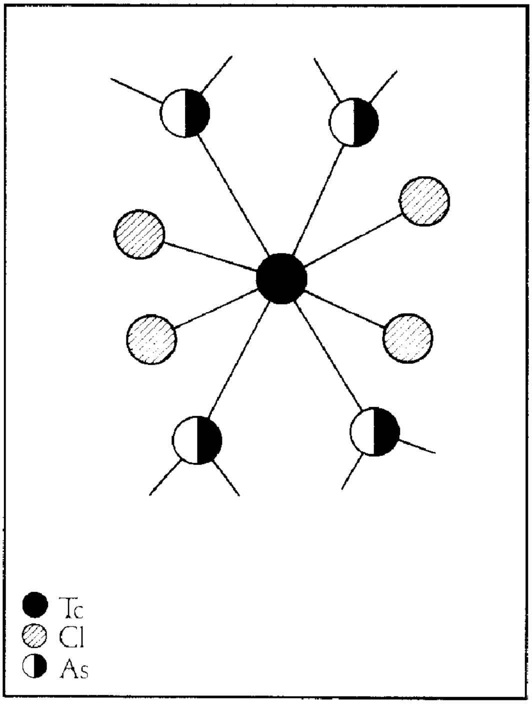

Fig. 20. A schematic view of the molecular structure of $[Tc(diars)_2Cl_4]^+$ [77].

with eight independent molecules per unit cell ($Z = 8$) and with unit cell dimension: a, 13.821(4); b, 21.159(8); and c, 21.227(18) Å. The technetium(V) atom is eight coordinate in a D_{2d} dodecahedral coordination geometry (Fig. 20). This geometry consists of a compressed tetrahedron, built up by four chlorine ligands (Tc–Cl, 2.442(4) Å; Cl–Tc–Cl, 91.21(12)°) and four As atoms (from the diars ligands), which form a second elongated tetrahedron (Tc–As, 2.578(2) Å; As–Tc–As, 126.46(5)°). This is the only example of a Tc-complex with coordination number eight.

G. CONCLUSIONS

This review reports on the crystal and structural data of technetium compounds which appeared through 1985. It describes over 140 technetium compounds for which crystal data are available, and X-ray and molecular structural data for over 80 compounds.

From the stereochemistry point of view, there are technetium compounds with coordination number four, five, six, seven, and eight. Six-coordinate compounds are the most common, while only one example was found of an eight-coordinate complex.

From the electronic configuration point of view, the technetium atom can exist in eight oxidation states, e.g. from Tc(0) (d^7) to Tc(VII) (d^0). The oxidation states of Tc(0) (d^7), Tc(I) (d^1) and Tc(II) (d^2) are rare, the other four are common. There are examples of Tc oxidation states of +2.5. In general, second-row elements prefer a lower coordination number in their higher oxidation states. It appears that technetium is no exception. For example, Tc(VII) (d^0) exists only in a four-coordinate compound, whereas compounds with coordination number seven only feature Tc(III) or Tc(IV). There is however an exception, Tc(diars)$_2$Cl$_4$ contains Tc(V) (d^2), even though its coordination number is eight.

The lowest coordination number of technetium compounds is four. There is no example available with a square-planar form. Bond lengths, as well as bond angles in mononuclear or binuclear technetium(VII) compounds, with tetrahedral environments about Tc(VII), are similar. There is a clear correlation between the axial ratio c/a and the ionic radii of the cation (Table 1): substitution for cations with smaller ionic radii results in decrease of the axial ratio c/a. In the series of $M(Tc(VII)O_4)_3 \cdot H_2O$ and $M_2Tc_2(VII)O_7$ (M = lanthanide), both the unit cell volume, as well as the axial ratio c/a, exhibit monotonic decrease with lanthanide contraction (Table 1 and Section B (ii)).

A distorted square pyramidal geometry around the technetium atom is a commonly found geometry for five-coordinate Tc compounds. Except for $[TcCl_4N]^-$, where Tc is in the +6 oxidation state, all examples listed in

Table 2 feature Tc(IV) as the central metal ion. The apical position in distorted square-pyramidal geometries is occupied by multiple Tc–N or Tc–O bonds, with a mean value of 1.593 Å for Tc≡N and 1.655 Å for Tc=O. Equatorial positions are built up by ligands of oxygen, nitrogen, chlorine, and sulfur. The average Tc–L_{eq} bond length increases in the following order: 1.949 Å (0) < 2.019 Å (N) < 2.303 Å (Cl) < 2.326 Å (S); this increase parallels the van der Waals radii of the various coordinated atoms. Furthermore, the sum of all interatomic distances around the technetium atom increases with larger van der Waals radii of the coordinated atoms, e.g.: $TcN_4O < TcO_3NCl < TcO_3S_2 < TcCl_4O < TcS_4O < TcS_4N$.

It is of interest to note that the mean value of the Tc(V)–L_{eq} and Tc(V)–L_{ax} bond lengths in pentacoordinate technetium compounds is lower than in hexacoordinate technetium(V) compounds (Table 9). This is in agreement with the notion that the substituents around pentacoordinate technetium are less sterically hindered than those around hexacoordinate technetium.

Two types of binuclear anions were studied by X-ray analysis, e.g. $[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$. Their structures are comparable, although a few differences exist. The Tc–Tc bond length in $[Tc_2Cl_8]^{2-}$ (2.142 Å, mean value) is about 0.023 Å longer than in $[Tc_2Cl_8]^{3-}$ (2.119 Å); however, the Tc–Cl bond length in the former (2.33 Å, mean value) is about 0.03 Å shorter than in the latter (2.36 Å). The lower oxidation state (+2.5 versus +3) of the central atoms results in decreased repulsion, which in turn may explain the variations in bond lengths between the central atoms.

In a series of hexahalogeno-quadrivalent technetium compounds (Table 4) the lattice constants increase with both the ionic radii of the alkali metal cation and the van der Waals radii of the substituents, e.g. hexafluoro < hexachloro < hexabromo < hexaiodo compounds.

Six-coordinate technetium compounds are by far the most common. Three principal forms of octahedron distortion are observed; among them the tetragonal distortion is the predominant conformation. Finally, of the possible d^2–d^6 electronic configurations of the Tc atom, the d^2, d^3 and d^4 configurations are most frequently encountered.

Among the 35 examples of dentate ligands (Table 5) are 15 examples with unidentate ligands, three with tetradentate and only two with tridentate ligands; the remaining examples exhibit bidentate ligands. It should be noted that tri- and tetradentate ligands are only observed in coordination compounds of Tc(V)(d^2). In contrast, unidentate ligands form an octahedral environment around Tc(IV)(d^3) in six out of the seven known examples. Further inspection of the data presented in Table 5 reveals that the equatorial Tc–L_{eq} bond lengths increase with the van der Waals radii of the donor atoms (ligands) in the following order: C < O < N < Cl < S < P ~ Br.

TABLE 9

Summary data for Tc–L bond lengths

C.N.[b]	L	M–L_{eq} (Å)[a]			
		Tc(III)	Tc(IV)	Tc(V)	a.v.(Å)[c]
6	C[d]				1.95
5	O			1.930–1.963(1.949)	1.949
6	O	2.00–2.03(2.015)	1.98,2.04(2.01)	1.947–2.012(1.985)	2.005
7	O[e]		2.034–2.072(2.046)		2.046
5	N			1.908–2.093(2.019)	2.019
6	N	2.04,2.05(2.045)		2.001–2.215(2.122)	2.114
7	N		2.148		2.148
6	P[f]	2.42–2.513(2.46)	2.473,2.480(2.476)		2.429
5	S			2.283–2.405(2.326)	2.326
6	S	2.431,2.440(2.435)		2.283,2.296(2.289)	2.363
7	S	2.43–2.502(2.467)			2.467
5	Cl[g]			2.291,2.317(2.303)	2.313
6	Cl	2.45,2.46(2.455)	2.22–2.39(2.340)	2.324–2.360(2.338)	2.357
7	Cl	2.367,2.401(2.384)			2.384
8	Cl			2.442	2.442
6	As	2.507–2.518(2.512)			2.512
6	Br		2.500	2.538,2.570(2.554)	2.536
		M–L_{ax} [Å]			
6	H[h]				1.7
6	C[i]				1.90
5	O[j]			1.604–1.697(1.655)	1.655
6	O			1.626–1.795(1.911)	1.691[k]
				1.795–2.282(2.985)	1.985[l]
7	O			1.861	1.861
5	N[m]			1.604	1.593
6	N[m]			1.629	1.629
6	N[n]	2.05		2.259,2.491(2.375)	2.156
7	N	1.70,1.80(1.75)			1.75
6	P[o]	2.44–2.47(2.46)	2.57		2.47
7	P	2.330			2.33
6	S	2.412			2.412
7	S	2.505,2.520(2.512)			2.512
6	Cl[p]	2.288–2.42(2.353)	2.32–2.51(2.41)	2.44,2.527(2.483)	2.39
7	Cl	2.414,2.492(2.453)			2.453
6	Br	2.440	2.36,2.50(2.43)		2.433

[a] The number in parentheses is an average value. [b] C.N., coordination number. [c] a.v., average value. [d] Tc(0)–C = 2.00 Å (mean); Tc(I)–C = 1.88–1.90 Å; (1.89 Å, mean). [e] Tc(IV)–O_{bridge} = 1.919 Å. [f] Tc(I)–P = 2.341–2.44 Å (2.335 Å, mean); Tc(II)–P = 2.40–2.436 Å, (2.42 Å, mean). [g] Tc(VI)–Cl = 2.322 Å. [h] Tc(I)–H = 1.7 Å. [i] Tc(O)–C = 1.899 Å; Tc(I)–C = 1.90, 1.91 Å, (1.905 Å, mean). [j] Tc=O. [k] There are three types of Tc(V)–O bond lengths: a, Tc=O = 1.626–1.684 Å (1.656 Å, mean) (Tc(V)OL); b, Tc–O = 1.746–1.754 (1.750 Å, mean) (Tc(V)O_2L); c, Tc–O(OH) = 1.795 Å in [Tc(V)O(OH)(DMPE)]·$(F_3CSO_3)_2$. [l] Type of ligands: OH^-, $CH_3CH_2O^-$, H_2O, etc. [m] Tc(VI)≡N = 1.581 Å; Tc≡N. [n] Tc(I)–N = 2.05, 2.161 Å (2.105 Å, mean); Tc(II)–N = 2.035, 2.047 Å (2.041 Å, mean). [o] Tc(I)–P = 2.44 Å. [p] Tc(II)–Cl = 2.41, 2.42 Å (2.415 Å, mean).

The Tc=O_{ax} bond lengths are not taken into account in this sequence. Again, there is a tendency for longer Tc–L bonds with increased effective ionic radii of the different oxidation states of technetium (Table 9).

The Tc(III)–Tc(III) bond in binuclear $[Tc_2(O_2CCMe_3)_4]^{2+}$ (2.192 Å) is at least 0.08 Å longer than the Tc(2.5)–Tc(2.5) bond in $[Tc_2(OR)_4]^+$ (OR = AcO^- or $OC_5H_4N^-$) (2.11 Å mean value). Also, the Tc(III)–L bonds in $[Tc_2(O_2CCMe_3)_4]^{2+}$ are shorter than the Tc (2.5)–L bonds in $[Tc_2(OR)_4]^+$, whereas the sum of all interatomic distances around Tc(III) are also somewhat smaller than those around Tc(2.5). Similar differences were found in $[Tc_2Cl_8]^{2-}$ [Tc(III)] and $[Tc_2Cl_8]^{3-}$ [Tc(2.5)].

Even though coordination number seven is rare for Tc compounds, there are three distinct geometries known: a pentagonal bipyramid, a capped octahedron and a capped trigonal prism. An oxidation state of Tc(III)(d^4) is common in these geometries of the technetium atom.

Finally, the data in Table 9 confirm the following general rules:

(a) M–L bond lengths increase with higher coordination numbers around the central atom;

(b) M–L bond lengths increase with larger van der Waals radii of the ligands;

(c) M–L bond lengths increase with higher oxidation states of the technetium atom in the case of L = N, P or Br, but decreases when L = O or S. However, if L = Cl, the M–L_{eq} bond length decreases whereas the M–L_{ax} bond length increases with higher oxidation states of the technetium atom.

ACKNOWLEDGEMENTS

We thank the Medical Research Council of Canada for financial support and Mrs. Francine Lussier for her expert and dedicated assistance in typing and assembling the manuscript.

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