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Review

Structural overview of technetium compounds (2000–2004)

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Contents

Abstract

This paper provides an overview of the about 80 crystal structures of technetium complexes described in the past 5 years and exhibiting some peculiar structural features. In almost 90% of the compounds, technetium shows an odd oxidation number, and by a large majority the revised complexes are mononuclear and neutral. The review especially focuses on nitrido-Tc(V), oxo-Tc(V) and *fac*-$[Tc(CO)_3]^+$ complexes, which cover approximately one-half of the X-ray structural reports.

Keywords: $[Tc(CO)_3]^+$ complexes; Tc(III) complexes; Nitrido-Tc(V) complexes; Oxo-Tc(V) complexes; X-ray structures

1. Introduction

^{99m}Tc continues to play a prominent role in diagnostic nuclear medicine. In this context, the coordination chemistry of technetium remains an important tool in the design of molecules relevant to nuclear medicine. A number of reviews illustrating the use of this nuclide in diagnostic nuclear medicine have recently appeared and interested readers are referred to them [1–7]. The papers [2,3,5,7] offer, in particular, a more complete coverage of the matter, including also all biological implications. In fact, when ^{99m}Tc radiopharmaceuticals are injected in vivo, metabolic and chemical degradation can hamper or reduce the biological effects in physiologic media. Appropriate modifications of the chemical structure of these compounds would prevent their degradation and might optimize their biological profile. A thorough knowledge of the molecular structure is therefore necessary in order to achieve this goal.

X-ray crystal structure determinations represent a major tool for the elucidation of the stereochemistry of such biologically relevant molecules. The first X-ray investigation of a Tc complex dates back nearly 50 years ago [8]. After this work, only polyhalide and pseudo-polyhalide complexes were considered for structural analysis, until the report of the structure of the carbonyl compound $Tc_2(CO)_{10}$ in 1965 [9]. In the past 30 years, interest toward the structural characterization of Tc complexes has considerably grown, as Fig. 1 shows.

A comparison between the number of X-ray papers appearing in the 2000–2004 period (highlighted in Fig. 1) with those published before (1973–1999) shows that the ‘golden age’ during the 1988–1996 years is now followed by a steady decline in the

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Nomenclature

9-MeG 9-methylguanine
9S3 1,4,7-trithiacyclononane
Benzox benzoxazole-2-thiolate (1−)
Bpy 2,2′-bipyridine
BzCOCp η^5-phenylacetyl-cyclopentadienide (1−)
Bzdbsalpn bis(3,5-di-*t*-butylsalicylidene)-2-benzyl-1,3-propanediaminate (2−)
Carbo η^5-7,8-dicarba-*nido*-undecaborate
CCD Cambridge Crystallographic Database
c.n. coordination number
Dppe 1,2-bis(diphenylphosphino)ethane
Dppm 1,2-bis(diphenylphosphino)methane
DppmO 1,2-bis(diphenylphosphino)methane monoxide
$H_2B(tim^{Me})_2$ dihydrogenbis(2-mercapto-1-methylimidazol-3-yl)borate (1−)
HEt_4tcb *N*,*N*-diethylthiocarbamoylbenzamidinate (1−)
Hmorphtcb *N*,*N*-morpholinylthiocarbamoylbenzamidinate (1−)
His-N_ε-benzyl 2-amino-3-(benzyl-1H-imidazol-4-yl)propanate (1−)
HL^2 *S*-methyl-2-methyldithiocarbazate (1−)
HL^3 2,2′-dipyridylthiosemicarbazone
HL^4 4-acetylpyridinethiosemicarbazone
H_2L^5 5-methyl-1H-benzoimidazole-2-thiol
Imid 1H-imidazole-4-carboxylate (1−)
L *N*,*N*-diethylaminoethylthiolate (1−)
L′ 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene
L^1 bis(2-pyridylmethyl)-1,3-dioxopropane-1,3-diamide (2−)
L_{Oet} η^5-C_5H_5-Co[$PO(OEt)_2$]$_3$ (1−)
Me methyl
$NBCl_2Ph$ dichlorophenylborylnitrido
NBH_3 borylnitrido
$N{=}NPh_2$ 1,1-diphenylisodiazene
N_3O 1-(2-oxybenzamido)-2-(pyridinecarboxamide)benzene (3−)
NPh phenylimido (2−)
NS 2-(4′-(2″-methoxyphenyl)piperazinyl)ethylthiolate (1−)
NS_3 2,2′,2″-nitrilotris(ethanethiolate) (3−)
OMePhCOCp η^5-(4-methoxybenzoyl)cyclopentadienide (1−)
o.n. oxidation number
Ph phenyl
$Ph_2P(O)py$ diphenyl(2-pyridyl)phosphine monoxide
Ph_2Ppy diphenyl(2-pyridyl)phosphine
Ph_2PS 2-(diphenylphosphine)ethylthiolate (1−)
$PnAO^1$ 6-benzyl-3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate (3−)
$PnAO^2$ 6-(3-(2-methoxyphenyl)propyl)-3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate (3−)
$PnAO^3$ 6-(2-(2-pyridyl)ethyl)-3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate (3−)
PnAO-6-CN 6-cyano-3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate (3−)
PnAO-6-OH 6-hydroxy-3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate (3−)
PNHP bis[2-(diphenylphosphino)ethyl]amine
PNP bis[2-(diphenylphosphino)ethyl]methoxyethylamine
POP bis[(2-diphenylphosphino)ethyl]ether
PSP bis[(2-diphenylphosphino)ethyl]thioether
Py pyridine
S_2CPh dithiobenzoate (1−)
S_3CPh perthiobenzoate (1−)
SNS *N*-methyl-1,7-dithia-4-azaheptane-1,7-diyl (2−)
SNSS 2-methoxycarbonyl-3-aza-4-oxo-6-thiaoctane-1,8-dithiolate (3−)
Sp square pyramidal
SOS 1,7-dithia-4-oxaheptane-1,7-diyl (2−)
SphMe *p*-methylbenzenethiolate (1−)
SphOMe *p*-methoxybenzenethiolate (1−)
SSS 1,4,7-trithiaheptane-1,7-diyl (2−)
tbp trigonal bipyramidal
Terpy 2,2′:6′,2″-terpyridine
Tht tetrahydrothiophene
TRIPHOS bis(2-phenylphosphinoethyl)phenylphosphine

number of structural investigations. The trend was already apparent at the end of the 1990s, and indicates the shift of the research focus from raw coordination chemistry to substrate–receptor interactions and to the metabolic modifications encountered by the radiodrug, beyond the inner coordination sphere. Nowadays, X-ray structural investigations on Tc complexes appear at a rate of approximately one per month.

This review deals with the crystal structures of Tc complexes published in the 2000–2004 period and with five structure determinations published in early 2005 [20,29,42,57]. It naturally follows the other surveys made by our research group since the beginning of the 1980s [10–12]. The work is based on data extracted from *Chemical Abstracts*, but all major pertinent chemistry journals have been independently surveyed as well. The Cambridge Crystallographic Database (CCD; Version 5.26 of November 2004 + 1 update) has been extensively searched [13,14] and proved invaluable to our study efforts.

Fig. 1 also highlights the oxidation number (o.n.) of the Tc complexes reviewed in this paper and shows that compounds in which Tc has an odd o.n. are largely predominant. Especially, abundant are complexes with o.n. V, III and I, corresponding to low-energy, spin-paired d^2, d^4 and d^6 electronic configurations.

In this work, compounds have been classified according to their o.n., arranged in order of similarity of the coordination sphere and numbered according to their references. When a single paper reports more structures, like, for example, Ref. [34] that describes three complexes, they have been labeled as [34]. Additional metric data and indices not included in the original papers and describing the coordination geometry around the

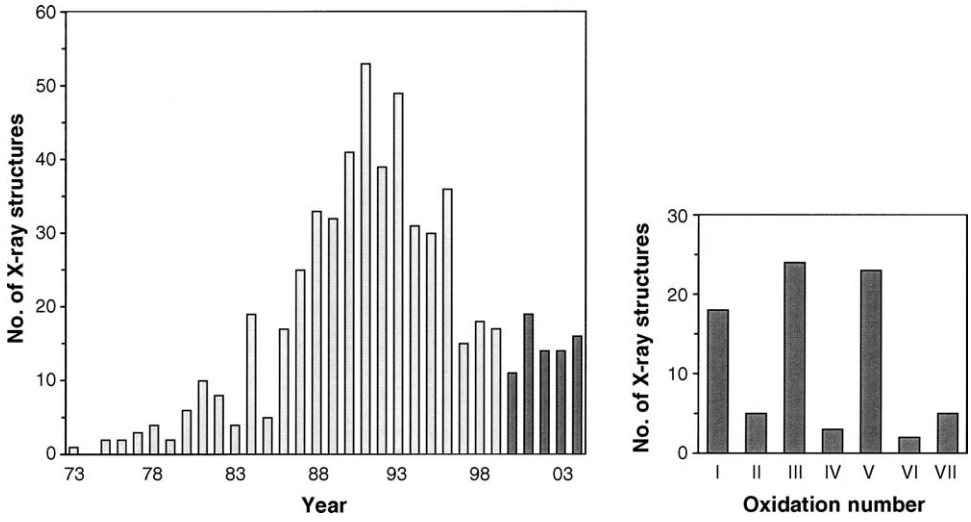


Fig. 1. Number of Tc crystal structures vs. year of publication (left) and oxidation number (right).

metal center (e.g. the τ [15] and χ [16] indices) have been calculated and reported for the 80 revised compounds.

In the tables, the column headed 'donors' shows the set of donor atoms belonging to the coordination sphere. Bis-, ter- or tetradentate ligands have been indicated by joining the involved atoms with the symbol '∩'. So, ON ∩ SS_2 denotes a complex with c.n. five showing three monodentate donors (the oxygen and two sulfur atoms) and a bidentate N,S ligand. Similarly, ON ∩ N ∩ N ∩ NO indicates a complex with c.n. six, two monodentate oxygen donors and a tetradentate N,N,N,N ligand. In the drawings of the relevant compounds the thermal ellipsoids represent 40% probability. For clarity, only atoms other than carbon have been labeled, whereas hydrogen atoms and solvent molecules have been generally omitted.

2. Tc(I) complexes

This section describes 18 complexes with Tc in oxidation state I, 14 of which contain the distinctive *fac*-$[Tc(CO)_3]^+$ fragment (Table 1). The diversity of donor atoms and the variety in the type of the ligands defining invariably the coordination number (c.n.) six in an octahedral geometry confirm the remarkable versatility of this synthon. A new route for the synthesis of mixed-ligand carbonyl complexes was indeed opened with

Table 1
Relevant structural data for Tc(I) complexes

Compound	Donors (D)	Θ (°)[a]	Tc···X(1A) (Å)[b]	Tc···X(1B) (Å)[c]	X(1A)···Tc···X(1B) (°)	Reference
(i) *fac*-$[Tc(CO)_3]^+$ complexes						
$[Tc(CO)_3(CN)_3]^{2-}$	C_3	0.8	1.099	1.238	175.3	[17]
$[Tc(CO)_3(HNPPh_3)_3]^+$	N_3	2.2	1.162	1.446	179.2	[18]
$[Tc(CO)_3(9MeG)_2(MeOH)]^+$	N_2O	0.5	1.136	1.406	178.2	[19]
$[Tc(CO)_3Cl(HL^3)]$[d]	N ∩ NCl	2.1	1.132	1.427	177.0	[20]
$[Tc(CO)_3(imid)(OH_2)]^+$	N ∩ OO	0.8	1.127	1.477	178.8	[21]
$Tc(CO)_3$(Hmorphtcb)(H_2morphtcb)	N ∩ SS	2.8	1.118	1.465	172.6	[22]
$Tc(CO)_3$(His-N_ε-benzyl)	N ∩ N ∩ O	2.3	1.135	1.465	178.6	[23]
$Tc(CO)_3(H_2B(tim^{Me})_2)$[d]	S ∩ H ∩ S	16.3	1.117	1.298	172.6	[24]
$Tc(CO)_3L_{Oet}$	O_3	0.1	1.135	1.381	178.7	[25]
$Tc_2(CO)_6Cl_2(\mu\text{-}HL^4)$	NSCl	2.7	1.114	1.434	174.8	[20]
$[Tc(CO)_3(Het_4tcb)]_2$	N ∩ SS	6.8	1.139	1.542	175.4	[22]
$[Tc(CO)_3(carbo)]^+$	B_3C_2	2.3	1.113	1.812	177.1	[26]
$Tc(CO)_3$(BzCOCp)	C_5	1.7	1.115	1.960	178.7	[27]
$Tc(CO)_3$(OMePhCOCp)	C_5	3.3	1.128	1.956	177.8	[28]
(ii) Other complexes						
$[TcCl(\mu\text{-}Cl)(CO)_2(NO)]_2$[d]	C_2NCl_3	4.5[e]	1.062	1.474	174.4	[29]
$[Tc(CH_3CN)_4(PPh_3)_2)]^+$	N_4P_2					[30]
$Tc(S_2CH)(dppe)_2$	P_4S_2					[31]
$TcCl(CS)(dppe)_2$	CP_4Cl					[32]

[a] Dihedral angle between the CO carbon atoms plane and the opposite face determined by three or five donors (D).
[b] X(1A) is the centroid of CO carbon atoms plane.
[c] X(1B) is the centroid of the opposite face.
[d] Mean value between the two independent units.
[e] Dihedral angle between the triangular face Cl_3, whose X(1A) is the centroid, and the opposite face whose X(1B) is the centroid.

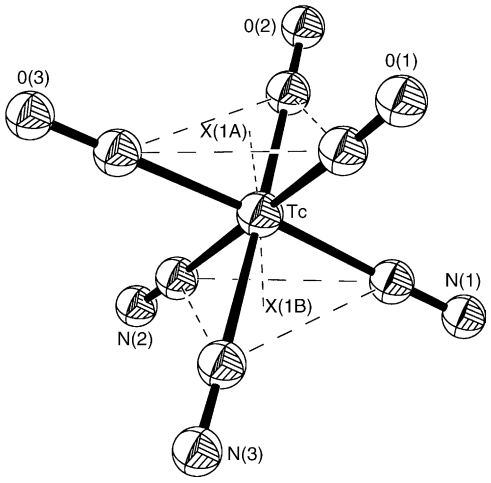


Fig. 2. The molecular structure of the anion $[Tc(CO)_3(CN)_3]^{2-}$ [17].

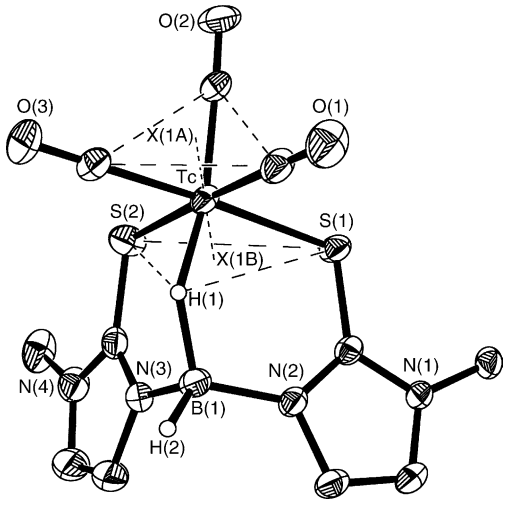


Fig. 4. The molecular structure of $Tc(CO)_3(H_2B(tim^{Me})_2)$ [24].

the preparation of the complex *fac*-$[Tc(CO)_3(OH_2)_3]^+$. In fact, the replacement of the fairly labile coordinated water molecules with other ligands affords suitable Tc species with potential relevant applications in radiopharmaceuticals [1,7 and references therein].

Only one of the 18 complexes investigated is anionic (Fig. 2) and two-thirds are neutral species. In these compounds, the triangular pyramid $[Tc(CO)_3]^+$ is linked to another pyramid, showing either a triangular or a pentagonal basis. The former is found in 11 complexes, the latter just in [26–28] (Fig. 3).

The ligand(s) *trans* to the tricarbonyl moiety can be monodentate, either homo- or hetero-nuclear, or bidentate, while terdentate ligands are found only in [23,24]. Dihydrobis(2-mercapto-1-methylimidazolyl)borate, the terdentate ligand in Fig. 4 [24], is noteworthy because it is the unique example of a structurally characterized Tc-carbonyl complex showing an agostic B–H···Tc interaction, with a short Tc–H separation of 1.65(6) Å.

In the 11 compounds where the $[Tc(CO)_3]^+$ moiety is *trans* to another triangular pyramid, the two basal triangles virtually parallel each other, making dihedral angles close to 0°, the sole exception being compound [24]. However, the large standard deviation of the Tc···H interaction indicates that the reported value (16.3°) must be treated with caution. The average distance between the Tc atom and the centroid of the 'above' (tricarbonyl) triangle [X(1A)] is 1.126 ± 0.015 Å, that between Tc and the centroid of the opposite 'below' face [X(1B)] is more variable and ranges between 1.238 Å [17] and 1.542 Å [22].

When the opposite face is pentagonal, the Tc–X(1B) separation widens markedly, varying from 1.812 Å in the first Tc-carborane complex reported to date [26] to 1.960 Å in a derivatized cyclopentadienyl complex [27]. The X(1A)···Tc···X(1B) angle shows little variation and is always close to 180°, regardless the shape of the opposite face. The largest deviation is 7.4° in [22,24].

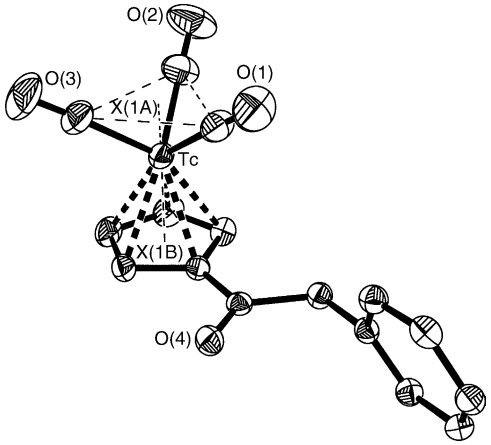


Fig. 3. The molecular structure of $Tc(CO)_3(BzCOCp)$ [27].

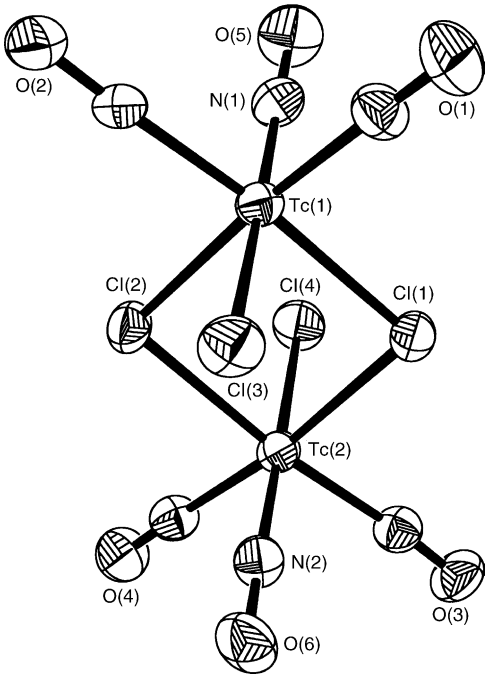


Fig. 5. The molecular structure of $[TcCl(\mu\text{-}Cl)(CO)_2(NO)]_2$ [29].

The complex $[TcCl(\mu\text{-}Cl)(CO)_2(NO)]_2$ [29] is the first mixed dicarbonyl–mononitrosyl complex and is also the sole Tc(I) binuclear compound in Table 1. In this complex, the two CO and the NO^+ ligands are facially arranged around the metal center, which shows a pseudo-octahedral environment. The Tc–NO distances, both 1.75(1) Å, are much shorter than the mean Tc–CO distance, 1.95(2) Å, as expected on the basis of the strong π-acceptor character of NO^+ (Fig. 5).

Moving to other Tc(I) species, in the complex $[Tc(CH_3CN)_4(PPh_3)_2]^+$ [30] the four MeCN ligands occupy the equatorial plane and the two phosphine ligands are placed *trans*-axially about the metal core. This complex might prove a useful starting material in the search for a new route to low-valent Tc compounds. Finally, we report two neutral and octahedral Tc complexes showing the bidentate dppe ligand [31,32]. In [31], the dithioformate (1−) ligand fills the equatorial plane; in [32], the P donors occupy the equatorial plane and the chloride ion and the thiocarbonyl residue take the apical positions.

3. Tc(III) complexes

In the 2000–2004 period, 24 Tc(III) complexes have been described (Table 2), 9 showing c.n. five and the others with c.n. six. Compounds whose c.n. is five and 3 of those having c.n. six [37,40,42] are neutral complexes; the 12 remaining compounds are cationic species. The coordination geometry does not vary very much and is always trigonal bipyramidal (tbp) in penta-coordinated complexes and octahedral in hexa-coordinated molecules. Exceptions are the two fully sulfur-coordinated complexes [36,37], where Tc lies in a distorted trigonal prismatic environment. The tbp geometry of compounds with c.n. five is confirmed by the values of the τ [15] and χ [16] indexes.

Table 2
Relevant structural data for Tc(III) complexes

Compound	Donors	τ[a]	χ[a]	$\Delta_{Tc\ from\ S_3}$(Å)	Tc—S (Å)	Reference
(i) c.n. five						
$Tc(SNS)(Ph_2PS)$	P∩SS∩N∩S	0.895	0.944	0.08	2.221(1), 2.240(1), 2.243(1)	[33]
$Tc(SSS)(Ph_2PS)$	P∩SS∩S∩S	0.842	0.874	0.04	2.216(6), 2.239(7), 2.251(6), 2.402(7)	[33]
$Tc(SNS)(SPhOMe)(PMe_2Ph)$	PSS∩N∩S	0.832	0.920	0.15	2.220(1), 2.233(1), 2.255(1)	[34]
$Tc(SOS)(SPhOMe)(PMe_2Ph)$	PSS∩O∩S	0.893	0.960	0.09	2.221(1), 2.226(1), 2.239(1)	[34]
$Tc(SSS)(SPhOMe)(PMe_2Ph)$	PSS∩S∩S	0.847	0.901	0.00	2.220(1), 2.236(1), 2.254(1), 2.399(1)	[34]
$Tc(NS_3)(PMe_2Ph)$	PS∩N∩S∩S	0.927	0.961	0.16	2.223(1), 2.226(1), 2.230(1)	[35]
$Tc(NS_3)(CNCH_2Ph)$	CS∩N∩S∩S	0.965	0.979	0.16	2.227(3), 2.232(2), 2.242(3)	[35]
$Tc(NS_3)(CNC_6H_{11})$	CS∩N∩S∩S	0.968	0.974	0.16	2.214(2), 2.215(1), 2.242(2)	[35]
$Tc(NS_3)(CNCH_2C(O)OEt)$	CS∩N∩S∩S	0.965	0.977	0.17	2.224(1), 2.229(1), 2.236(1)	[35]

Compound	Donors	Φ (°)[b]	Tc—S (Å)	Reference
(ii) c.n. six sulfur-rich				
$[Tc(9S3)(SSS)]^+$	$(S∩S∩S)_2$	6.9	2.251(1), 2.274(1), 2.354(1), 2.414(1), 2.456(1), 2.481(1)	[36]
$Tc(S_3CPh)_2(S_2CPh)$	$(S∩S)_2S∩S$	9.6	2.227(4), 2.231(4), 2.349(4), 2.354(4), 2.478(5), 2.510(4)	[37]

Compound	Donors	θ (°)[c]	Tc—P (Å)	Tc—Cl (Å)	Reference
(iii) c.n. six					
$[TcCl_2(N{=}NPh_2)(PMe_2Ph)_3]^+$	NP_3Cl_2	170.7(1)	2.458(1), 2.490(1), 2.491(1)	2.424(1), 2.416(1)	[38]
$[TcCl(N{=}NPh_2)(dppe)_2]^{2+}$	$N(P∩P)_2Cl$	179.5(3)	2.502(2), 2.503(2), 2.555(2), 2.558(2)	2.387(2)	[38]
$[TcCl_2(N{=}NPh_2)(TRIPHOS)]^+$	$NP∩P∩PCl_2$	175.9(1)	2.405(1), 2.450(1), 2.452(1)	2.412(1), 2.444(1)	[38]
$[TcCl_2(N{=}NPh_2)(bpy)(PPh_3)]^+$	NN∩NOPCl	172.9(1)	2.487(1)	2.422(1)	[39]
$[TcCl_2(N{=}NPh_2)(terpy)]^+$	$NN∩N∩NCl_2$	176.9(1)		2.382(1), 2.396(1)	[39]
trans-$[TcCl_2(dppm)_2]^+$	$(P∩P)_2Cl_2$	176.7(1)	2.458(1), 2.462(1), 2.499(1), 2.511(1)	2.301(1), 2.333(1)	[40]
trans-$[TcCl_2(Ph_2P(O)py)_2]^+$[d]	$(N∩O)_2Cl_2$	180		2.351(2)	[40]
trans-$[TcCl_2(dppmO)_2]^+$[d]	$(O∩P)_2Cl_2$	180	2.449(3)	2.329(2)	[40]
mer-$TcCl_3(Ph_2Ppy)_2$	$N∩PPCl_3$	173.4(1)	2.432(2), 2.455(2)	2.334(1), 2.340(2), 2.417(1)	[40]
trans-$[TcCl_2(PMe_2Ph)_4]^+$	P_4Cl_2	177.0(1)	2.490(1), 2.508(1), 2.516(1), 2.536(1)	2.325(1), 2.330(1)	[41]
trans-$[TcCl_2(PMe_3)_4]^+$[d,e]	P_4Cl_2	180	2.451(2), 2.454(2), 2.484(2), 2.486(2)	2.342(2), 2.346(2)	[41]
trans-$[TcCl_2(PMe_3)_4]^+$[f]	P_4Cl_2	179.9(1)	2.469(3), 2.475(3), 2.479(3), 2.485(2)	2.340(3), 2.347(3)	[41]
$TcCl_2(benzox)(PPh_3)_2$[g]	$N∩SP_2Cl_2$	177.1(1)	2.478(1), 2.499(1)	2.368(1)	[42]

[a] $\tau = (\beta - \alpha)/60$, where α and β are the two largest angles around Tc defined by four of five donors (Ref. [15]); $\chi = (\beta + \gamma + \delta - 2\alpha)/180$, where γ and δ are the angles concerning the fifth donor atom (Ref. [16]).

[b] Φ (°) is the twist angle between the upper and the lower triangular faces in trigonal prism description.

[c] θ is the X_{apical}—Tc—L_{trans} angle.

[d] The metal center lies on an inversion center.

[e] BPh_4 as counteranion.

[f] PF_6 as counteranion.

[g] The benzox ligand is disordered; low accuracy of the bond distances.

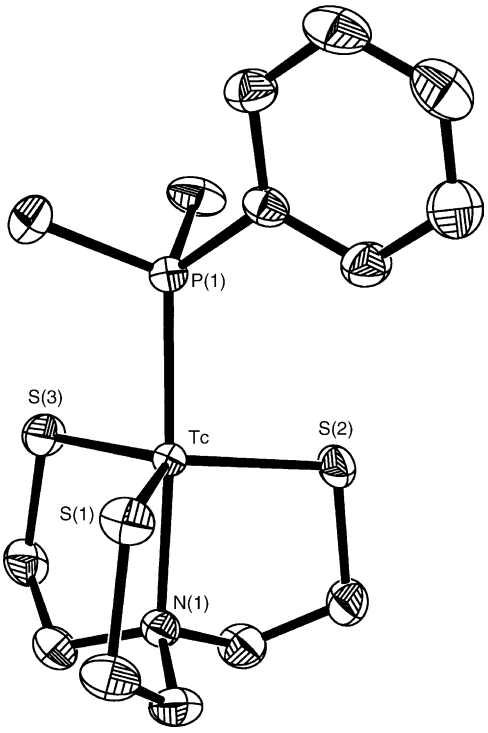


Fig. 6. The molecular structure of $Tc(NS_3)(PMe_2Ph)$ [35].

In tbp complexes, the most represented donor atom is sulfur, which accounts for 29 of the 45 possible donors. When the equatorial plane is filled by three sulfur atoms, the apical positions are occupied by donors having π-acceptor character. In these compounds, the deviation of the metal atom from the mean equatorial plane becomes a significant feature, up to about 0.16 Å with the tripodal ligand 2,2′,2″-nitrilotris(ethanethiol) (NS_3) [35] (Fig. 6). Besides, the Tc–N distance (mean value: 2.201(4) Å) is 0.06 Å shorter than that found in compounds showing terdentate ligands [33,34] (Fig. 7).

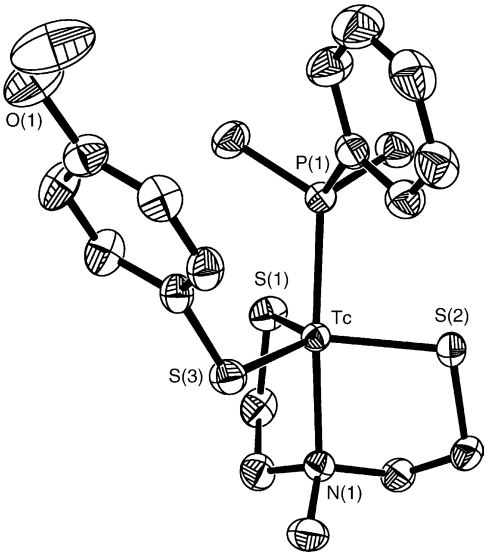


Fig. 7. The molecular structure of $Tc(SNS)(SPhOMe)(PMe_2Ph)$ [34].

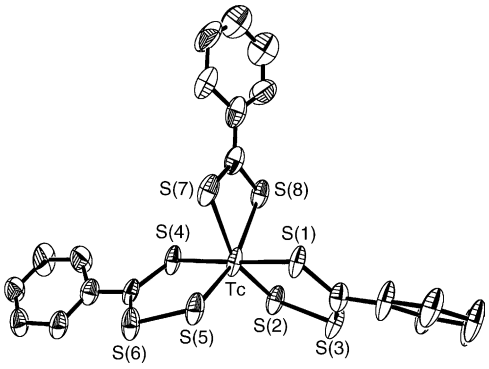


Fig. 8. The molecular structure of $Tc(S_3CPh)_2(S_2CPh)$ [37].

Tc–P distances do not differ too much from the average value of 2.307(3) Å but for [34]. In the latter the Tc–P bond is 2.359(1) Å, a lengthening due to nature of the *trans*-axial hetero-atom (thioether sulfur) of the terdentate ligand. On the other hand, the Tc–S distances vary within a rather wide range, from 2.214(2) Å in [35] to 2.402(7) Å in [33]. There are actually two different types of Tc–S bonds: $Tc–S_{thiolato}$ and $Tc–S_{thioether}$ (averages of 2.232(2) and 2.401(3) Å, respectively). The range spanned by Tc–S distances broadens further in the compounds having only sulfur atoms in the coordination sphere, from 2.227(4) to 2.510(4) Å [36,37] (Fig. 8). Again, this happens because there are three types of Tc–S bonds: $Tc–S_{thiolato}$, $Tc–S_{‘thiourea’}$ and $Tc–S_{dithiocarbamato}$, whose mean lengths are 2.246(2), 2.368(2) and 2.481(2) Å, respectively. The highest value fits also with those found in the Tc(I) complex [31] containing a dithioformate ligand where the two Tc–S bonds measure 2.487(1) and 2.455(1) Å.

The other 13 complexes with c.n. six all show octahedral geometry and the metal center is found virtually within the equatorial plane. The preferred donor atoms are P (42%) and Cl (32%), while sulfur is present only in compound [42].

The Tc=N bond length of the five isodiazene complexes reported in Table 2 varies between 1.739(3) Å in [39] and 1.758(7) Å in [38]. These distances are markedly shorter than the Tc–N ones (single bond) found in [39,40], whose average value is 2.130(4) Å.

It is worth noting that the Tc–P and Tc–Cl bond lengths show a similar variation. The former ranges between 2.405(1) Å in [38] and 2.558(2) Å in [38] (Δ = 0.15 Å), the latter varies from 2.301(1) Å in [40] to 2.444(1) Å in [38] (Δ = 0.14 Å). Additionally, in the complexes with c.n. five, no chloride is bound to the Tc, while the Tc–P bond is much shorter than in the octahedral complexes (mean: 2.307(3) Å).

It is also interesting to compare the isostructural Tc(III)/Tc(II) $[TcCl_2(dppm)_2]^{+/0}$ [40]. The reduction of the metal from o.n. III to II is matched by an increase of the Tc–Cl (+0.12 Å) and a shortening of the Tc–P distances (−0.06 Å).

4. Tc(V) complexes

This section includes 11 penta-coordinated and 10 hexa-coordinated complexes (Table 3). Compounds with c.n. five are neutral molecules, of which nine are oxo-complexes and two

Table 3
Relevant structural data for Tc(V) complexes

Compound	Donors	Δ_{Tc} (Å)[a]	τ[b]	Tc≡N (Å)	Tc—N (Å)	Tc═O (Å)	Tc—P (Å)	Reference
(i) c.n. five								
trans-Tc(N)$Cl_2(Ph_3PNH)_2$	NN_2Cl_2	0.59	0.023	1.585(4)	2.078(4), 2.102(4)			[43]
syn-Tc(N)(bzdbsalpn)[c]	NO∩N∩N∩O	0.43		1.588(5)	2.064(6), 2.077(6)			[44]
Tc(O)($PnAO^1$)	ON∩N∩N∩N	0.67	0.048		1.905(4), 1.911(4), 2.081(4), 2.084(4)	1.679(3)		[45]
Tc(O)($PnAO^2$)	ON∩N∩N∩N	0.67	0.007		1.912(1), 1.919(1), 2.067(2), 2.077(2)	1.676(1)		[45]
Tc(O)($PnAO^3$)	ON∩N∩N∩N	0.66	0.067		1.910(1), 1.921(2), 2.079(2), 2.085(2)	1.672(2)		[45]
anti-Tc(O)(PnAO-6-OH)	ON∩N∩N∩N	0.66	0.052		1.905(4), 1.917(5), 2.066(5), 2.089(4)	1.672(4)		[46]
syn-Tc(O)(PnAO-6-CN)	ON∩N∩N∩N	0.66	0.080		1.913(3), 1.918(2), 2.075(3), 2.080(3)	1.674(2)		[46]
Tc(O)(SNSS)	OS∩N∩S∩S	0.77	0.418		1.995(3)	1.668(3)		[47]
Tc(O)(N_3O)	ON∩N∩N∩O	0.69	0.150		1.971(4), 1.984(4), 2.109(4)	1.657(3)		[48]
Tc(O)(L)$(SphOMe)_2$	ON∩SS_2	0.72	0.162		2.256(7)	1.659(5)		[49]
Tc(O)(NS)$(SphMe)_2$[d]	ON∩SS_2		0.550					[50]
			N(O)—Tc—X_{trans} (°)[e]					
(ii) c.n. six								
mer,*cis*-Tc(N)Cl_2(PNHP)	NP∩N∩PCl_2	0.19	170.2(1)	1.614(3)	2.167(3)		2.424(1), 2.429(1)	[51]
trans-Tc(N)Cl_2(POP)	NP∩O∩PCl_2	0.52	179.4(2)	1.665(5)			2.424(2), 2.447(2)	[52]
fac,*cis*-Tc(N)Cl_2(PSP)	NP∩S∩PCl_2	0.44	169.7(2)	1.633(5)			2.441(1), 2.445(1)	[51]
fac-[Tc(N)(HL^2)(PNP)]$^+$	NP∩N∩PN∩S	0.43	161.8(8)	1.61(1)	2.06(1), 2.81(1)		2.432(5), 2.440(5)	[53]
fac-[Tc(N)(HL^2)(POP)]$^+$	NP∩O∩PN∩S	0.48	159.7(2)	1.623(4)	2.038(3)		2.432(1), 2.440(1)	[53]
Tc$(NBH_3)Cl_2(PPhMe_2)_3$	NP_3Cl_2	0.16	175.7(4)	1.704(4)			2.436(1), 2.467(1), 2.485(1)	[54]
Tc$(NBCl_2Ph)Cl_2(PPhMe_2)_3$	NP_3Cl_2	0.22	176.3(2)	1.681(2)			2.461(1), 2.495(1), 2.504(1)	[54]
trans-[Tc(O)(L^1)(OH_2)]$^+$	ON∩N∩N∩NO	0.35	162.4(2)		1.968(4), 1.980(4), 2.145(4), 2.170(4)	1.641(3)		[55]
Tc(O)(bpy)$(SPRMe)_3$	ON∩NS_3	0.33	154.5(1)		2.229(3), 2.259(3)	1.670(3)		[56]
trans-[Tc(O)Cl_2(H_2L^5)(OH_2)]$^+$	OOS_2Cl_2	0.38	180			1.635(5)		[57]

[a] Distance of Tc from basal plane (c.n. = 5) in square pyramidal geometry or from equatorial plane (c.n. = 6).
[b] See Table 2.
[c] Mean value of two independent molecules in asymmetric unit.
[d] Isostructural with Re analogue, atomic coordinates unavailable.
[e] The angle between the nitrido (or oxo) N (or O) atom and the donor atom *trans* to it.

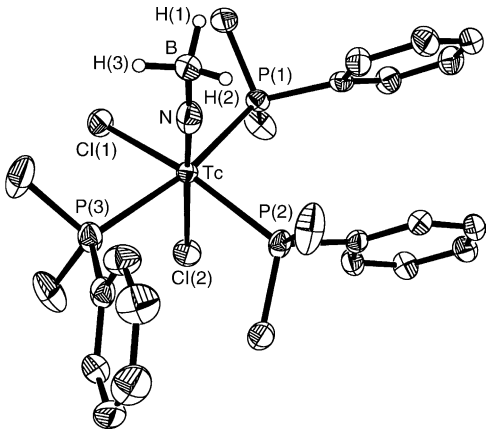


Fig. 9. The molecular structure of $Tc(NBH_3)Cl_2(PPhMe_2)_3$ [54].

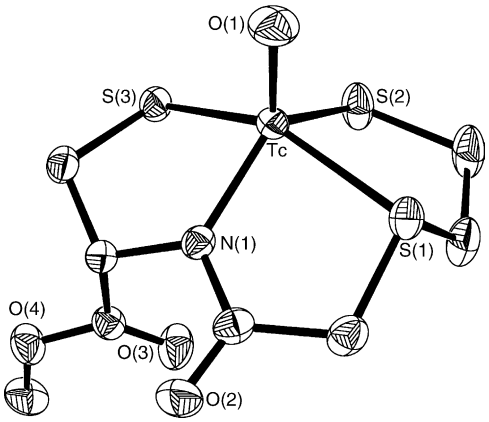


Fig. 11. The molecular structure of Tc(O) (SNSS) [47].

nitrido-species [43,44]. The most represented donor is nitrogen, which accounts for 32 of the 55 possible donors, while phosphorous does not show at all.

Compounds with c.n. six are partly neutral (six molecules) and partly monocationic, including one dioxo-, three monooxo-, five nitrido-species and two complexes showing a nitrido-bridge between Tc and boron [54] (Fig. 9). The most represented donors are N (17/66), P (16/66; only in nitrido-species), Cl (12/66) and S (8/66).

In penta-coordinated complexes most ligands are polydentate. There are eight compounds containing a tetradentate ligand, two with a bidentate N ∩ S ligand [49,50] and one showing only monodentate ligands [43]. The denticity of the ligands varies more in molecules with c.n. six: in this group there are three compounds with a tetradentate ligand, three with a terdentate ligand and one containing only one bidentate ligand [56]. The remaining four complexes show just monodentate ligands [54,57,58].

The compound described in [58] (Fig. 10) is only the third reported example of a Tc-carbene complex. The core of the molecule is a *trans*-TcO_2^+ moiety in which the two oxygens take the axial positions of the octahedron, while the equatorial positions are occupied by four carbene ligands. The average Tc–C distance (2.226(4) Å) demonstrates the σ-bonding character of the interaction.

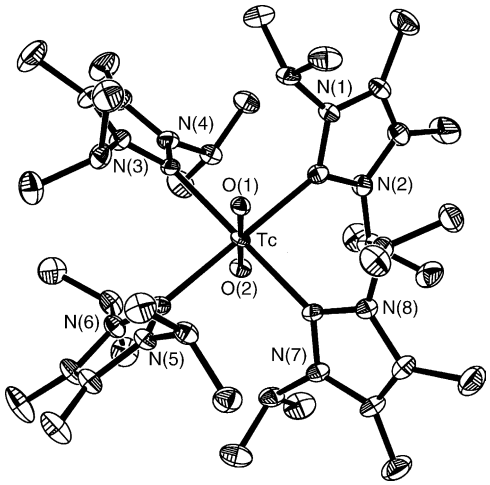


Fig. 10. The molecular structure of the cation $[TcMO_2(L^1)_4]^+$ (L^1 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) [58].

Five-coordinated compounds show the metal surrounded by a square pyramidal (sp) environment except for complex [47] (Fig. 11), the only one containing a tetradentate 'S-rich' ligand. The coordination geometry of this molecule is intermediate between sp and tbp, with three sulfur atoms defining the triangle. Tc is reported to have a tbp environment also in compound [50], chiefly because the complex is isostructural with the rhenium analogue. In this molecule, the basal plane is occupied by an oxo-group and two sulfur atoms belonging, respectively, to the bidentate ligand and to an aromatic thiol. In the 10 sp complexes, the metal atom deviates markedly from the basal square plane, always toward the apex. The deviations range between 0.66 and 0.72 Å in oxo-complexes and from 0.49 to 0.53 Å in nitrido-species.

All compounds with c.n. six show a more or less distorted octahedral geometry. The position *trans* to the oxo- or nitrido-moiety can be occupied by different atoms, although oxygen is somehow preferred, especially in oxo-compounds. The deviation of Tc from the equatorial plane spans a wider range than that observed in five-coordinated complexes but is smaller in size, ranging between 0.16 and 0.52 Å. The distortion of the octahedron is measured by the departure of the O(N)–Tc–X_{trans} angle from the ideal value of 180°. The deviation reaches 25.5° and 20.3° in the complexes described in [56,53] (Fig. 12), respectively.

The average Tc=O (1.664(4) Å) and Tc≡N (1.634(4) Å) bond lengths in oxo- and nitrido-complexes are in good agreement

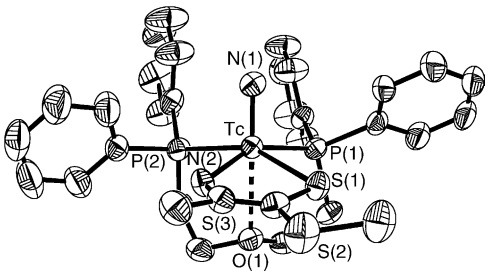


Fig. 12. The molecular structure of the cation *fac*-$[Tc(N)(HL^2)(POP)]^+$ [53].

with the mean values of 1.675(3) and 1.618(5) Å found in the 156 oxo- and 74 nitrido-complexes reported in the CCD [13]. The agreement with existing data for nitrido-complexes is even better by restraining the comparison to compounds with c.n. six. The average Tc≡N distance for the seven complexes listed in Table 3 is then 1.647(6) Å, very close to the mean value of 1.636(5) Å found in the 30 hexa-coordinated nitrido-complexes already reported in the CCD.

In compounds with c.n. five the Tc–N distance varies between 1.905(4) Å [45,46] and 2.256(7) Å [49]. Close inspection reveals that there are actually three types of Tc–N bonds, spanning accordingly three different ranges: (i) Tc–N_{amide} from 1.905 to 1.921 Å; (ii) Tc–N'_{amide} from 1.971 to 1.995 Å; (iii) Tc–N_{oxime} from 2.064 to 2.109 Å. Type (i) distances are found in the five complexes [45,46] belonging to the 'PnAO' ligand class, while type (ii) distances are found only in compounds [47,48]. The lengthening is likely related with a trigonal distortion of the square pyramidal geometry about the metal. The anomalous Tc–N distance in [49], 2.256(7) Å, has also been previously observed in other severely distorted complexes [13].

In compounds with c.n. six the Tc–N_{amide} distance lengthens, as expected, by about 0.08 Å. The average Tc–$N_{pyridine}$ bond length is 2.16 Å; the two longest distances found in compound [56], 2.229(3) and 2.259(3) Å, refer to the nitrogen atoms of the bipyridine ligand. On the other hand, the Tc–P distance varies very little, between 2.424(1) Å [51,52] and 2.504(1) Å [54]. The lower and higher values are found when the phosphorous donor belong to polydentate or monodentate ligands [54], respectively.

5. Even o.n. Tc complexes

The 10 structures of this section are listed in Table 4, and include 5 Tc(II), 3 Tc(IV) and 2 Tc(VI) complexes. Most compounds show octahedral geometry, except the two nitrido-Tc(VI) complexes described in [63,64]. With respect to charge, there are five neutral, three anionic and two cationic complexes. The most represented donors are phosphorous, halide atoms and nitrogen; oxygen is observed only in the dinuclear complex [64].

In these compounds, the Tc–P distance lengthens about 0.07 Å when the o.n. rises from II to IV, following a decrease in π-donation. The Tc–Cl bonds are of two types: equatorial and axial. The former varies between 2.313(1) Å [62] (Fig. 13) and 2.324(3) Å [63]; the latter is 2.445(1) Å [39]. Likewise, the Tc(IV)–N equatorial distances found in [61] (Fig. 14), 1.991(6)

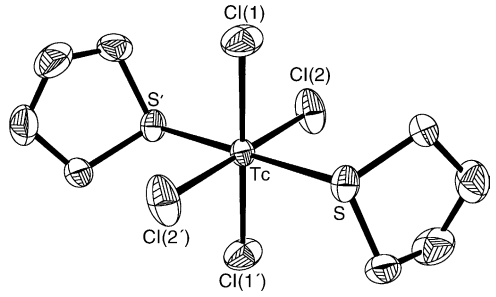


Fig. 13. The molecular structure of *trans*-$TcCl_4(tht)_2$ [62].

Table 4
Complexes of technetium in even o.n.

Compound	Donors	Δ_{Tc} (Å)[a]	X–Tc–Y (°)[b]	Tc–N (Å)	Tc–P (Å)	Tc–halogen (Å)	Reference
(i) Technetium(II)							
$[Tc(CH_3CN)_4(PPh_3)_2]^{2+}$[c]	N_4P_2	0.0	180	2.049(5), 2.048(5)	2.441(1)		[30]
trans-$Tc(NCS)_2(PMe_2Ph)_4$[c]	N_2P_4	0.0	180	2.052(6)	2.429(2), 2.482(2)		[61]
trans-$Tc(NCS)_2(P(OMe)Ph_2)_4$[c]	N_2P_4	0.01	177.9(1)	2.037(4), 2.039(4)	2.423(1), 2.434(1), 2.434(1), 2.442(1)		[61]
trans-$TcCl_2(dppm)_2$[c]	P_4Cl_2	0.0	180		2.402(3), 2.441(3)	2.432(3)	[40]
$[Tc(N{=}NPh_2)(C{\equiv}NCH_2Ph_2)(PPh_3)_2]^+$	C_2NP_2Cl	[d]	176.9(2)	1.832(5)	2.470(2), 2.476(2)	2.445(1)	[39]
(ii) Technetium(IV)							
trans-$TcCl_4(tht)_2$[c]	S_2Cl_4	0.0	180			2.310(1), 2.316(1)	[62]
$[TcBr_5(tht)]^-$	SBr_5	0.12	173.5(1)			2.455(2), 2.471(2), 2.480(2), 2.481(2), 2.484(2)	[62]
trans-$Tc(NCS)_4(P(C_3H_7)_3)_2$[c]	N_4P_2	0.0	180	1.991(6), 2.003(6)	2.519(3)		[61]
(iii) Technetium(VI)							
$[TcNCl_4]^-$[e]	NCl_4	0.50				2.324(3)	[63]
$[Tc(NCl_2)_2(\mu\text{-}O_2)_2)]^{2-}$	NO_2Cl_2	[d]				2.382(2), 2.416(2)	[64]

[a] Distance of Tc from basal plane (c.n. = 5) in square pyramidal geometry or from equatorial plane (c.n. = 6).
[b] The angle between the two donors X and Y in apical positions.
[c] Tc lies on an inversion center.
[d] Unavailable data.
[e] Mean value of the six units.

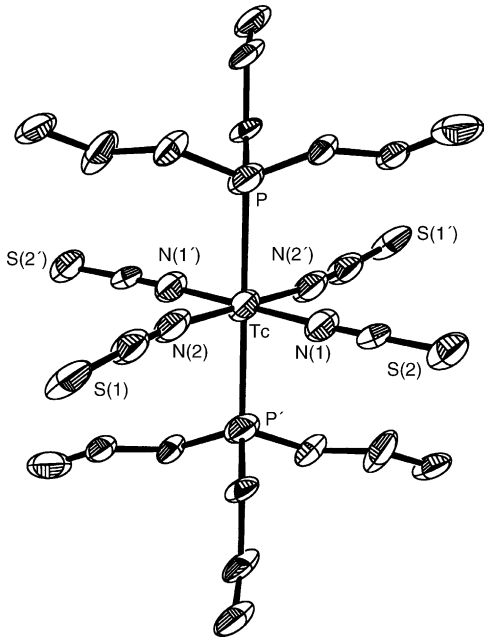


Fig. 14. The molecular structure of *trans*-$Tc(NCS)_4(P(C_3H_7)_3)_2$ [61].

and 2.003(6) Å, are shorter than the average Tc(II)–N axial distance of 2.046(5) Å [61,30]. The extremely short Tc–N distance of 1.832(5) Å found in [39] does not fit with the other ones reported because it pertains to a diphenylisodiazene ligand.

A few additional pertechnetate anions reported in [58,60] and the oxide-fluorides $TcOF_5$, $[TcOF_4]^+$ and $[Tc_2O_2F_9]^+$ described in [59] do not deserve any comment.

6. Conclusions

6.1. General remarks

Fig. 15 depicts the ligating atoms as a function of the o.n. in the complexes examined in this survey. The overall pattern reasonably matches that of Fig. 32 of our previous survey [12], referring to the structures reported in the 1993–1999 period.

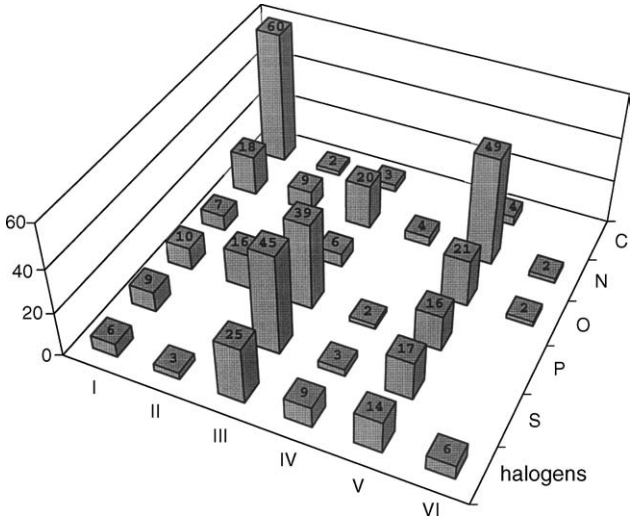


Fig. 15. Distribution of coordinating atoms vs. o.n.

Some remarks can be done: (i) largely regardless of the o.n. the most represented donors are, respectively, N, P, S and the halides; (ii) *hard* metal cores with high o.n. prefer *hard* donors such as the amine nitrogen. Conversely, when the metal ion becomes softer by reducing its o.n. below V, *hard* nitrogen and oxygen donors are replaced by *soft* phosphorous and sulfur; (iii) disregarding the 12 oxo-complexes listed in Table 3, Tc has little preference for oxygen, regardless of the o.n.; (iv) halides are easily 'exchangeable' ligands, thus they appear in all o.n. complexes; (v) sulfur donors prefer o.n. III and are often matched with phosphorous donors.

6.2. The metal–nitrogen interaction

Since nitrogen is the most represented donor, the Tc–N bond distance deserves additional comment. By considering all structural reports deposited so far in the CCD [13] it comes out that the average length of Tc≡N, Tc=NR and $Tc–NR_2$ bonds in nitrido-, imido- and amido-complexes are very different, being 1.618 Å (74 reports), 1.746 Å (11 reports) and 1.966 Å (52 reports), respectively. Unlike Tc≡N and Tc=NR bond lengths, $Tc–NR_2$ distances vary over a wider range (1.880–2.216 Å), according to the different R substituents.

Despite the shortage of data, it is interesting to comment on bond lengths and angles of complexes showing 'organohydrazide' ligands, that is, complexes containing a Tc–N–N linkage. As pointed out by Nicholson and coworkers [65,66], these ligand types may afford eight monohapto structural types. Some of them are documented only for rhenium [67]. The first report of a diazenido Tc complex ($[TcCl(PPh_3)_2(NNC_6H_4Br)_2]$) was published in 1989 [68] and it has been followed by eight structural determinations [69]. All the reported complexes are distorted octahedral and diamagnetic species.

With respect to bond distances, the Tc=N(1) bond length ranges between 1.762 and 1.798 Å, with a mean value of 1.777 Å. The average value of the N(1)=N(2) distance and of the Tc=N(1)=N(2) angle are 1.235 Å and 172.0°, respectively. These properties suggest that the ligand behaves as an uninegative, linear four-electron donor and that, in the o.n. formalism, Tc is low-spin III (d^4), or, alternatively, as a trinegative, linear two-electron donor with Tc low-spin V (d^2).

As for isodiazene compounds, the first complex ($[TcCl_3(N=NPh_2)(PPh_3)_2]$) was described in 1998 [70]. Six more structural reports followed: $[TcCl_2(N=NPh_2)(PMe_2Ph)_3]^+$ [38], $[TcCl(N=NPh_2)(dppe)_2]^{2+}$ [38], $[TcCl_2(N=NPh_2)(TRIPHOS)]^+$ [38], $[TcCl_2(N=NPh_2)(bipy)(PPh_3)]^+$ [39], $[TcCl_2(N=NPh_2)(terpy)]^+$ [39] and $[TcCl(N=NPh_2)(C{\equiv}NCH_2Ph)_2(PPh_3)_2]^+$ [39]. In these octahedral complexes, the average Tc=N(1) and N(1)=N(2) distances are 1.749 and 1.297 Å, respectively, while the mean Tc=N(1)=N(2) angle is 175.6°. This reflects the multiple bonding throughout the isodiazene moiety and the sp^2 hybridization of the β-nitrogen atom of the zwitterionic isodiazene ligand. In these compounds the o.n. of Tc is III, except for [39] where Tc shows the unusual o.n. II. However, unlike diazenido compounds, isodiazenido

complexes are paramagnetic. The magnetic behavior might be better understood by holding paramagnetic isodiazene compounds as octahedral high spin (d^4) Tc(III) species and diamagnetic diazene complexes as Tc(V) (d^2) molecules, as somewhat suggested in [71].

6.3. *fac*-[Tc(CO)$_3$]$^+$: any isomer here?

Finally, the growing importance of *fac*-[Tc(CO)$_3$]$^+$ complexes stimulated us to discuss the possible isomerism of these compounds. As illustrated in Section 2, the technetium tricarbonyl metal fragment invariably exhibits the facial configuration. The occurrence of this unique stereochemistry for the three carbonyl groups markedly diminishes the formation of isomers. However, when the other face of the octahedron is filled with three different donor atoms, as it appears in compounds [21,23], the metal becomes an asymmetric center, and the formation of isomers becomes possible.

The chirality of Tc can be better understood if we imagine the face of the octahedron filled with the three carbonyl groups as a unique substituent, described by its centroid (see also Fig. 2). In this representation, the metal shows four different substituents, like an asymmetric carbon (Fig. 16), with the pertinent absolute configurations (R and S) and, eventually, the presence of enantiomers.

The mirror image typical of tetrahedral carbon (in our case tetrahedral Tc) can also be applied to the octahedral geometry. According to the IUPAC provisional recommendations for the nomenclature of inorganic chemistry [72], octahedral coordination compounds are identified with a specific annotation, for example, OC-6-21-*C* or OC-6-21-*A*. Such acronyms allow one to distinguish between diastereoisomers and to determine the absolute configuration about the metal as clockwise (*C*) or anticlockwise (*A*).

On these grounds, compound [21] can be described with the annotation OC-6-44-*C*. OC-6 indicates an octahedral compound with coordination number six. The coordinating donor atoms are then numbered according to the Cahn, Ingold and Prelog (CIP) priority rules [73]. The essence of these rules is that the ligands attached to the metal are compared to one another, beginning with the donor atom and then moving outwards in the structure.

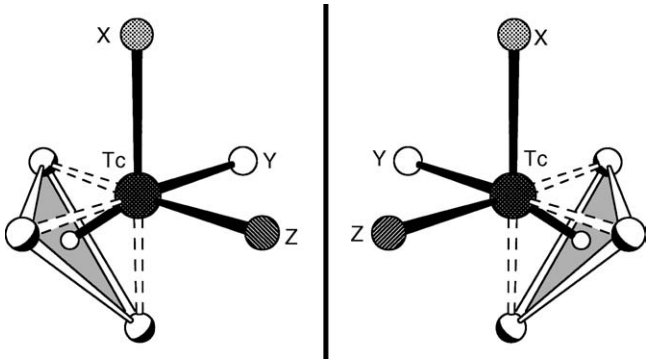
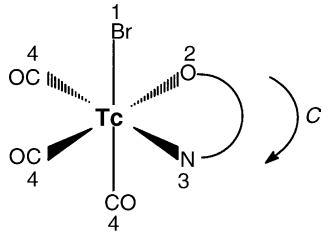


Fig. 16. Two mirror images of a 'chiral' octahedral Tc complex (see text). The octahedral face defined by the three CO groups is grayed and the centroid highlighted as a small circle.



OC-6-44-*C*

Fig. 17. The absolute configuration of the octahedral complex [21].

The comparison is made on the basis of atomic number. Once the ligands have been compared, the priority numbers are assigned as follows: (i) identical ligands are assigned the same rank; (ii) the ligand(s) with highest priority is(are) assigned the priority number 1; those with the next highest priority, 2; so on.

Ligand 1 and its *trans*-coordinated ligand define the axis of the octahedron, the remaining ligands define the equatorial plane. Hence, as shown in Fig. 17, the two digits 44 indicate: (a) the priority number of the atom (C) *trans* to the highest priority number atom (Br) that define the octahedral axis; (b) the priority number of the atom (C) *trans* to the highest priority number atom (O) on the equatorial plane. The absolute configuration around the metal is then determined correlating the highest priority number atom on the equatorial plane (O) with the subsequent priority number atom (N) on the same plane. If the arrow describing the path turns clockwise the annotation is *C*, otherwise *A* (anticlockwise).

The compound index for complex [23] is also OC-6-44-C (Fig. 18). In this case, the value of the Flack parameter allowed the authors to determine the absolute configuration of the asymmetric histidine C close to the amine donor. Interestingly, it turns out that, while the absolute configuration at C is anticlockwise (i.e. L) as generally described for tetrahedral arrangements, in agreement with the known stereochemistry (L) of the histidine used in the synthesis, the absolute configuration at Tc is clockwise (*C*).

Similar arguments may also be applied to the examination of a series of pseudo-octahedral nitrido-complexes (i.e. mixed-ligand *fac*-[Tc(N)(PXP)(HL^2)]$^+$ species [53]) for which the absolute configuration at the metal has not been previously described. Fig. 19 shows that the absolute configuration is anticlockwise in the PNP-containing *fac*-[Tc(N)(PNP)(HL^2)]$^+$

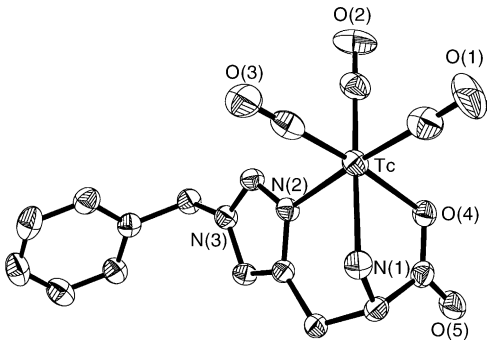


Fig. 18. The molecular structure of Tc(CO)$_3$(His-N$_\varepsilon$-benzyl) [23].

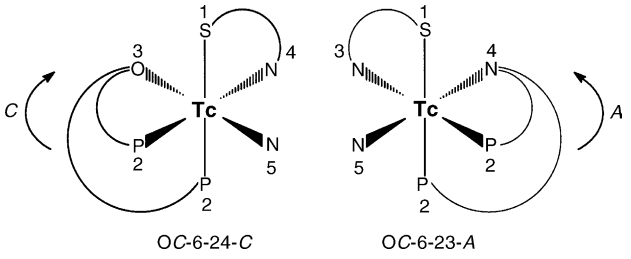


Fig. 19. The absolute configuration of two pseudo-octahedral complexes [53].

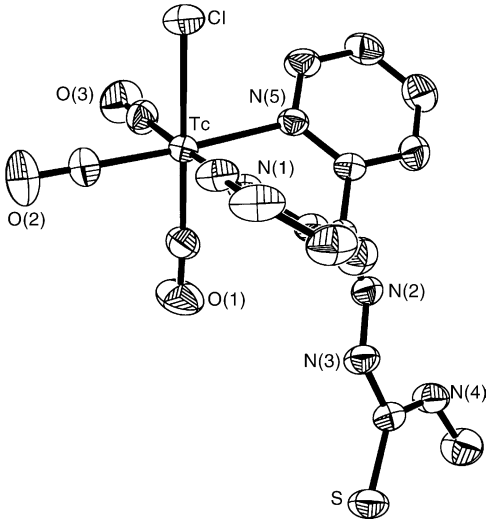


Fig. 20. The molecular structure of $Tc(CO)_3Cl(HL^3)$ [20].

complex [53] and clockwise in the close analogue *fac*-$[Tc(N)(POP)(HL^2)]^+$ [53].

In addition to the enantiomeric pairs described above, *fac*-$[Tc(CO)_3]^+$ complexes may exhibit additional geometric isomers, as it appears in compound [20] (Fig. 20). In this case, the unique Cl donor and the thiosemicarbazide substituent at the central carbon atom of the bidentate ligand can be oriented toward the same side (*syn*) or opposite sides (*anti*) of the octahedral face defined by the N_2Cl donors. The crystal structure solved and reported by the authors in [20] contains only the *anti*-isomer.

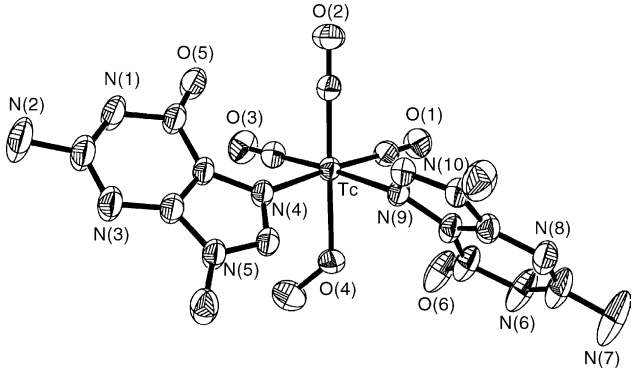


Fig. 21. The molecular structure of the cation $[Tc(CO)_3(9MeG)_2(MeOH)]^+$ [19].

Finally, in the complex $[Tc(CO)_3(9MeG)_2(MeOH)]^+$ [19] a unique conformation of the two model DNA bases is observed in the solid state, resulting from hindered rotation about the single metal–N bonds (Fig. 21).

The two purine bases adopt a head-to-tail orientation, which resembles the conformation exhibited by one of the active forms of cisplatin. $[Tc(CO)_3(9MeG)_2(MeOH)]^+$ is a special type of stereoisomer, called atropisomer [74], an isolated conformer which is defined to exist when the half-life of interconversion (into the head-to-head or tail-to-tail forms in the present case) is greater than 1000 s [75].

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