Synthesis and characterization of technetium(V) and (VII) complexes with bidentate nitrogen donor ligands. X-ray molecular structures of tetrabutylammonium bis(1,2-diimidobenzene)-oxotechnetium(V) and tris(1,2-diimidobenzene)technetium(VII) pertechnetate

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(Received March 11, 1992; revised July 27, 1992)

Abstract

The reaction of pertechnetate with 1,2-diaminobenzene (H_2pda) in the presence of the reducing agent sodium dithionite in alkaline aqueous solution led to the formation and isolation of (n-Bu_4N)[$TcO(pda)_2$] (**1**). If the reaction is performed without reducing agent in methanol, the green compound [$Tc(pda)_3$](TcO_4) (**2**) is formed. Both complexes are diamagnetic, and a single N–H stretching frequency in both indicates that each pda ligand contains one hydrogen per nitrogen, and is dianionic. X-ray crystal structures of both compounds are also reported. Crystal data for complex **1**, $C_{28}H_{48}N_5OTc$: orthorhombic, space group $P2_12_12_1$, $a=11.644(3)$, $b=15.303(4)$, $c=16.950(5)$ Å and $U=3020.3(1.5)$ Å^3 to give $Z=4$ for $D_{calc}=1.25$ g cm^{-3}. Crystal data for **2**, $C_{18}H_{18}N_6O_4Tc_2$: orthorhombic, $Pna2_1$, $a=13.869(4)$, $b=12.799(5)$, $c=10.851(3)$ Å and $U=1926.2(1.1)$ Å^3 to give $Z=4$ for $D_{calc}=1.99$ g cm^{-3}. The structures have been solved by Patterson and Fourier methods and refined by least-squares methods to $R=0.058$ for **1** and 0.090 for **2**. Complex **2** represents the first tris-bidentate cationic complex of technetium to be structurally characterized. Complex **1**, with an unexpectedly low ν(Tc=O) of 891 cm^{-1}, has a Tc=O bond distance of 1.668(7) Å, that is typical for monooxotechnetium(V) square-pyramidal complexes.

Introduction

Complexes formed from the short-lived isotope ^{99m}Tc are widely used in nuclear medicine as organ imaging agents because of the ideal nuclear properties of this isotope ($t_{1/2}=6$ h, $\gamma=140$ keV). As a result, the coordination chemistry of the long-lived isotope ^{99}Tc is currently attracting considerable interest, with the aim of preparing kinetically stable complexes that can be easily synthesized in aqueous media by the reduction of the pertechnetate ion.

Many technetium-based radiopharmaceuticals are formed by the two-electron reduction of TcO_4^- in the presence of suitable ligands which can stabilize the +5 oxidation state. In this state, complexes containing the TcO^{3+} core are by far the most common, and they have been studied extensively. One of their characteristics is a square-pyramidal geometry with the oxo ligand in the apical position and the technetium ion displaced above the basal plane of four ligands, in the direction of the oxo oxygen.

As part of our programme to study technetium complexes with highly delocalized, unsaturated, electron-rich ligands, we have prepared the complex (n-Bu_4N)[$TcO(pda)_2$] (**1**) (pda = $HNC_6H_4NH(2-)$) by the reduction of TcO_4^- with sodium dithionite in the presence of an excess 1,2-diaminobenzene in aqueous solution. The complex exhibits the $TcON_4$ inner core that is common to the family of the tetradentate amine oxime complexes [1] used for brain imaging. When the reaction is performed without a reducing agent in methanol, the product [$Tc(pda)_3$](TcO_4) (**2**) is obtained. This report concerns the preparation, characterization and structure determination of the two complexes.

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0020-1693/92/$5.00

Experimental

Materials

Ammonium [^{99}Tc] pertechnetate was supplied by the Oak Ridge National Laboratory, TN, as the dry salt. ^{99}Tc is a weak β-emitter (0.292 keV) with a half-life of 2.12×10^5 years. When handled in milligram amounts, it does not present a health hazard since common laboratory materials provide adequate shielding, but normal radiation safety procedures must be used at all times to prevent contamination.

All chemicals were of analytical grade. 1,2-Diaminobenzene (H_2pda) was obtained commercially (Merck), and its purity was checked by NMR and melting point. All the solvents used were purified by standard methods.

Apparatus

Scientific instrumentation used in this study is the same as reported elsewhere [2].

Syntheses

(n-Bu_4N)[TcO(pda)$_2$] (1)

A volume of 2.5 cm^3 of a 0.340 mol dm^{-3} aqueous NH_4TcO_4 solution (850 μmol) was added to 276 mg (2250 μmol) of 1,2-diaminobenzene (H_2pda) in 30 cm^3 of a 0.6 mol dm^{-3} aqueous sodium hydroxide solution under vigorous stirring at room temperature. A freshly prepared solution of 40 mg sodium dithionite in 10 cm^3 of a 0.6 mol dm^{-3} NaOH solution was rapidly added to the reaction mixture, followed by the addition of 2 cm^3 of a saturated aqueous solution of n-Bu_4NCl. After 5 min of stirring, the orange precipitate was removed by filtration, and dried under vacuum. Recrystallization was from acetone/water. The yield was 79%; m.p. 197 °C. *Anal.* Calc. for $C_{28}H_{48}N_5OTc$: C, 59.03; H, 8.49; N, 12.29. Found: C, 58.87; H, 8.76; N, 12.53%. IR (KBr): ν(Tc=O) 891(vs); ν(NH) 3247(m); ν(Tc–N) 430(m) cm^{-1}. Conductivity (10^{-3} mol dm^{-3}, CH_3CN): 101 Ω^{-1} cm^2 mol^{-1}.

[Tc(pda)$_3$](TcO_4) (2)

To 2 cm^3 of a 0.340 mol dm^{-3} aqueous NH_4TcO_4 solution was added 340 mg of 1,2-diaminobenzene (H_2pda) in 15 cm^3 methanol, and the mixture was heated under reflux for 1 h. After cooling to room temperature, the solution was filtered and left to stand overnight at ambient temperature. The resulting green crystals were removed by filtration, washed with cold ethanol, and dried under vacuum. The yield was 74% (based on Tc); m.p. > 300 °C. *Anal.* Calc. for $C_{18}H_{18}N_6O_4Tc_2$: C, 37.25; H, 3.13; N, 14.48. Found: C, 37.41; H, 3.56; N, 14.26%. IR (KBr): $\nu(TcO_4)$ 912(s), 897(s), 881(m); ν(NH) 3235(m); ν(Tc–N) 418(m) cm^{-1}. Electronic spectrum (CH_3CN) (λ_{max} (nm) (ϵ, dm^3 mol^{-1} cm^{-1})): 725 (6230), 674sh (5790), 437 (5770), 357sh (1550), 266sh (1880). Conductivity (10^{-3} mol dm^{-3}, CH_3CN): 104 Ω^{-1} cm^2 mol^{-1}.

X-ray analysis

Crystals of (n-Bu_4N)[TcO(pda)$_2$] (**1**), obtained at room temperature from acetone/ether, are transparent, red–brown parallelipeds of dimensions *c.* $0.1 \times 0.2 \times 0.4$ mm; crystals of [Tc(pda)$_3$](TcO_4) (**2**), obtained on slow evaporation of a methanol solution, are green, irregularly shaped parallelipeds of dimensions *c.* $0.15 \times 0.2 \times 0.3$ mm.

Crystal data

(n-Bu_4N)[TcO(pda)$_2$] (**1**). $C_{28}H_{48}N_5OTc$, $M = 568.7$, orthorhombic, $a = 11.644(3)$, $b = 15.303(4)$, $c = 16.950(5)$ Å, $U = 3020.3(1.5)$ Å^3; space group $P2_12_12_1$, $Z = 4$, $D_c = 1.25$ g cm^{-3}, $F(000) = 1208$; μ(Mo Kα) = 0.49 mm^{-1}.

[Tc(pda)$_3$](TcO_4) (**2**). $C_{18}H_{18}N_6O_4Tc_2$, $M = 578.4$, orthorhombic, $a = 13.869(4)$, $b = 12.799(5)$, $c = 10.851(3)$ Å, $U = 1926.2(1.1)$ Å^3; space group $Pna2_1$, $Z = 4$, $D_c = 1.99$ g cm^{-3}, $F(000) = 1144$; μ(Mo Kα) = 1.48 mm^{-1}.

A unique data set was measured to $2\theta = 45°$ for **1** and 60° for **2** by using a Nicolet-Siemens R3m/V four-circle diffractometer in conventional ω-2θ scan mode and monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å).

Structure determination

Complex 1. The intensities were corrected for Lorentz and polarization factors and for absorption by the Ψ-scan empirical method, using four reflections at $\chi \simeq 90°$. A total of 2287 independent reflections was collected, 1568 with $|F_o| > 3\sigma(F_o)$ being considered observed and used in structure determination (by Patterson and Fourier methods) and refinement (by full-matrix least-squares methods). Due to the limited number of data, most atoms were treated isotropically and only Tc, O, N and C(1), C(6), C(7), C(12) atoms were refined anisotropically and thus the number of refined parameters was 199. Hydrogen atoms were included in the structure factor calculation in idealized and fixed positions. The model refined to the residual $R = 0.058$ ($R_w = 0.055$) with goodness of fit being 1.29. The weighting scheme was $w = [\sigma^2(F_o) + 0.0006|F_o|^2]^{-1}$ and the quantity minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$. In the final ΔE map the largest peak was 0.36 e Å^{-3}, the largest hole -0.42 e Å^{-3}. Another refinement to convergence was performed with the inverted atomic coordinates yielding $R = 0.062$, so that the first set of coordinates was retained. Also, the η-test [3] for the absolute configuration was inconclusive, yielding a value of 0.8 with large e.s.d. (0.3).

Complex (2). The intensities of two standard reflections measured every 150 reflections showed significant decay (up to 15%) and consequently intensities were corrected also for crystal deterioration. At the early stage of refinement procedure, a Fourier difference map showed several electron-density peaks in the vicinity of the Tc(2) atom (at *c.* $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$), along with abnormal thermal motions of the heavy atom. A number of reflections seemingly badly in error due to extinction were deleted from the refinement; however, in any case, the TcO_4^- anion is less than well-behaved: the counteranion is disordered and attempts to treat this disorder (via fractionally populated oxygen atoms or treatment as rigid body) were unsuccessful. Finally, we decided to locate the oxygen atoms at the four large peaks (and chemically reasonable positions) found in the difference map. Other peaks observed in the map were slightly smaller in magnitude and were left unmodelled. The model refined to the residual $R=0.090$ ($R_w=0.11$), with goodness of fit being 0.93, for 1743 observed ($|F_o|>3\sigma(F_o)$) reflections. The atomic scattering factors were taken from the usual source [4] and the programs package system was SHELXTL-PLUS [5].

The final non-hydrogen atomic coordinates with their e.s.d.s for both complexes are given in Table 1, while the relevant bond distances and angles are shown in Table 2. See also 'Supplementary material'.

Results and discussion

Syntheses and characterization

Pertechnetate reacts with a molar excess of 1,2-diaminobenzene (H_2pda) in alkaline aqueous solution, using sodium dithionite as reducing agent, to yield the complex $(n\text{-}Bu_4N)[TcO(pda)_2]$ (**1**), an orange crystalline solid. When the reaction is performed without a reducing agent in methanol, the green product $[Tc(pda)_3](TcO_4)$ (**2**) is obtained. Complex **1** could not be prepared by the reaction of $(n\text{-}Bu_4N)[TcOCl_4]$ with H_2pda in ethanol.

Both complexes are diamagnetic and are 1:1 electrolytes in acetonitrile. They are soluble in most organic solvents. Complex **1** is unstable in solution, and it undergoes a rapid colour change from orange to brown in ethanol, DMF, chloroform and DMSO. Decomposition is slowest in acetone and acetonitrile, and even occurs in the absence of air. Complex **2** is stable in organic solvents, and both complexes are stable in the solid state, at least for a period of weeks.

The IR spectrum of complex **1** displays a very intense band at 891 cm^{-1}, which we attribute to the stretching frequency of the Tc=O group. This frequency differs appreciably from the stretching frequencies normally observed for square-pyramidal monooxotechnetium(V) complexes, which typically occur in the range 920–1020 cm^{-1} [6]. It was previously reported [7] that the complex

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **1** and **2**

	x	y	z	U_{eq} [a]
Complex **1**				
Tc	−9139(2)	−444(1)	−9127(2)	65(1)
O	−9653(7)	−530(6)	−8212(4)	78(3)
N(1)	−10411(9)	−611(7)	−9893(6)	78(4)
N(2)	−8775(10)	−1620(7)	−9550(6)	75(5)
N(3)	−9047(13)	792(6)	−9471(6)	72(4)
N(4)	−7473(9)	−239(7)	−9068(7)	75(4)
C(1)	−10471(12)	−1406(10)	−10280(7)	71(6)
C(2)	−11278(11)	−1654(9)	−10853(9)	85(4)
C(3)	−11165(12)	−2469(10)	−11233(8)	88(4)
C(4)	−10282(12)	−2972(10)	−11042(8)	91(5)
C(5)	−9437(11)	−2793(8)	−10482(7)	69(4)
C(6)	−9556(12)	−1979(9)	−10088(8)	67(5)
C(7)	−8016(16)	1193(10)	−9381(7)	75(6)
C(8)	−7742(13)	2104(10)	−9507(7)	84(4)
C(9)	−6676(16)	2403(12)	−9350(9)	120(6)
C(10)	−5816(16)	1868(10)	−9134(9)	115(5)
C(11)	−6001(15)	972(9)	−9016(8)	92(4)
C(12)	−7125(12)	631(10)	−9160(8)	79(6)
N(5)	−8857(9)	1645(7)	−6933(5)	67(4)
C(13)	−9654(11)	1733(8)	−7643(7)	68(4)
C(14)	−10691(14)	2309(11)	−7571(9)	120(6)
C(15)	−11394(15)	2341(12)	−8318(10)	131(7)
C(16)	−11983(18)	1554(13)	−8476(13)	178(9)
C(17)	−7891(11)	1048(8)	−7184(7)	73(4)
C(18)	−6988(13)	869(10)	−6524(8)	95(5)
C(19)	−6144(14)	169(10)	−6779(10)	110(5)
C(20)	−6623(15)	−731(11)	−6801(10)	131(6)
C(21)	−9490(12)	1290(9)	−6232(8)	96(5)
C(22)	−10027(14)	397(12)	−6345(9)	114(5)
C(23)	−10622(17)	91(12)	−5589(10)	136(7)
C(24)	−11137(18)	−685(13)	−5619(12)	180(9)
C(25)	−8397(12)	2549(9)	−6665(8)	82(4)
C(26)	−7701(13)	3047(9)	−7262(9)	100(5)
C(27)	−7433(14)	3966(11)	−6966(10)	114(6)
C(28)	−6704(18)	4449(14)	−7524(13)	180(8)
Complex **2**				
Tc(1)	−2569(1)	−58(1)	−2500	29(1)
N(1)	−2047(12)	−1471(10)	−2184(13)	36(4)
N(2)	−1915(18)	109(14)	−879(21)	42(6)
N(3)	−2044(13)	1398(14)	−2844(17)	45(5)
N(4)	−1991(14)	−160(13)	−4219(17)	32(4)
N(5)	−3712(12)	676(11)	−1759(16)	36(5)
N(6)	−3709(11)	−761(9)	−3268(15)	32(4)
C(1)	−1700(14)	−1673(13)	−1100(16)	32(5)
C(2)	−1382(13)	−2709(14)	−661(19)	37(5)
C(3)	−1036(24)	−2809(27)	528(31)	91(13)
C(4)	−1000(17)	−1829(20)	1349(21)	57(7)
C(5)	−1248(19)	−893(17)	953(22)	58(8)
C(6)	−1614(12)	−818(14)	−326(18)	39(5)
C(7)	−1656(13)	1602(13)	−4022(20)	39(5)
C(8)	−1370(20)	2517(18)	−4513(24)	59(8)
C(9)	−1041(14)	2627(16)	−5602(17)	40(6)
C(10)	−880(20)	1729(27)	−6405(30)	83(11)
C(11)	−1226(16)	714(23)	−5933(20)	63(9)
C(12)	−1618(13)	650(14)	−4723(18)	40(6)
C(13)	−4608(13)	408(11)	−2096(16)	30(4)

(*continued*)

TABLE 1. (*continued*)

	x	y	z	U_{eq}[a]
C(14)	−5470(16)	804(14)	−1665(23)	46(6)
C(15)	−6292(14)	423(16)	−2089(22)	54(7)
C(16)	−6400(17)	−406(17)	−2971(22)	51(7)
C(17)	−5500(15)	−823(14)	−3392(20)	40(6)
C(18)	−4608(14)	−452(12)	−2981(18)	35(5)
Tc(2)	−2539(4)	−2544(3)	−5057(11)	150(2)
O(1)	−2448	−1240	−4935	437(47)
O(2)	−2624	−3086	−3651	333(37)
O(3)	−1549	−2986	−5781	316(35)
O(4)	−3530	−2863	−5865	394(52)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Some relevant bond lengths (Å) and angles (°) for **1** and **2**

Complex **1**	
Tc–O	1.668(7)
Tc–N(1)	1.99(1)
Tc–N(2)	1.98(1)
Tc–N(3)	1.98(1)
Tc–N(4)	1.97(1)
N(1)–C(1)	1.38(2)
N(2)–C(6)	1.40(2)
N(3)–C(7)	1.36(2)
N(4)–C(12)	1.40(2)
C(1)–C(6)	1.42(2)
C(7)–C(12)	1.40(2)
O–Tc–N(1)	109.3(4)
O–Tc–N(2)	110.0(4)
N(1)–Tc–N(2)	78.8(5)
O–Tc–N(3)	111.6(4)
N(1)–Tc–N(3)	88.3(5)
N(2)–Tc–N(3)	138.4(4)
O–Tc–N(4)	108.6(4)
N(1)–Tc–N(4)	142.1(4)
N(2)–Tc–N(4)	87.3(5)
N(3)–Tc–N(4)	79.0(5)
Tc–N(1)–C(1)	117.4(9)
Tc–N(2)–C(6)	117.0(9)
Tc–N(3)–C(7)	116.5(10)
Tc–N(4)–C(12)	115.6(9)
N(1)–C(1)–C(6)	113.4(11)
N(2)–C(6)–C(1)	113.2(12)
N(3)–C(7)–C(12)	114.1(13)
N(4)–C(12)–C(7)	113.5(13)
Complex **2**	
Tc(1)–N(1)	1.98(1)
Tc(1)–N(2)	1.99(2)
Tc(1)–N(3)	2.03(2)
Tc(1)–N(4)	2.03(2)
Tc(1)–N(5)	2.01(2)
Tc(1)–N(6)	2.00(1)
N(1)–C(1)	1.30(2)
N(2)–C(6)	1.39(3)
N(3)–C(7)	1.41(3)
N(4)–C(12)	1.28(2)
N(5)–C(13)	1.34(2)
N(6)–C(18)	1.34(2)
N(1)–Tc(1)–N(2)	77.2(7)
N(1)–Tc(1)–N(3)	137.6(7)
N(2)–Tc(1)–N(3)	84.3(7)
N(1)–Tc(1)–N(4)	87.5(6)
N(2)–Tc(1)–N(4)	129.6(9)
N(3)–Tc(1)–N(4)	75.5(7)
N(1)–Tc(1)–N(5)	130.3(6)
N(2)–Tc(1)–N(5)	87.4(8)
N(3)–Tc(1)–N(5)	85.8(7)
N(4)–Tc(1)–N(5)	135.0(7)
N(1)–Tc(1)–N(6)	87.1(6)
N(2)–Tc(1)–N(6)	140.9(8)
N(3)–Tc(1)–N(6)	128.2(6)
N(4)–Tc(1)–N(6)	84.3(7)
N(5)–Tc(1)–N(6)	75.7(6)
Tc(1)–N(1)–C(1)	118.3(11)
Tc(1)–N(2)–C(6)	115.2(14)
Tc(1)–N(3)–C(7)	118.1(13)
Tc(1)–N(4)–C(12)	119.9(14)
Tc(1)–N(5)–C(13)	120.2(12)
Tc(1)–N(6)–C(18)	120.2(11)

(n-Bu$_4$N)[TcO(HNC$_6$H$_4$S)$_2$], with a ν(Tc=O) at 906 cm^{-1}, has a Tc=O bond length of 1.73(2) Å, which is 0.07 Å longer than previously reported values for technetium(V)–oxo species containing a single Tc=O group. The surprisingly low Tc=O stretching frequency of complex **1** was the main motivating factor for the structure determination of this compound. A single N–H absorption, at 3247 cm^{-1} for complex **1** and at 3235 cm^{-1} for **2**, indicates that each pda ligand in both complexes contains one hydrogen per nitrogen, and is therefore present as the dianion pda^{2-}, and thus establishing the metal oxidation state as +5 in complex **1** and as +7 in **2**. Complex **2** is unusual in that Tc(VII) is normally very readily reduced in the presence of organic ligands.

The UV spectrum of complex **1** was obtained in acetonitrile, but was deemed unreliable due to the colour change observed whenever the complex is in solution. The spectrum is nevertheless characterized by two intense absorption maxima at 311 ($\epsilon \approx 7200$ dm^3 mol^{-1} cm^{-1}) and 353 ($\epsilon \approx 5300$ dm^3 mol^{-1} cm^{-1}) nm. In acetonitrile, the decomposition of **1** is complete after about 12 h, with new maxima at 303 ($\epsilon = 4400$) and 447 ($\epsilon = 2900$ dm^3 mol^{-1} cm^{-1}) nm for 10^{-4} mol dm^{-3} solutions of complex **1**. The decomposition product could not be isolated in a pure form.

Description of the structures

The X-ray analysis of [TcO(HNC$_6$H$_4$NH)$_2$]$^-$ shows it to be five-coordinate and to have square-pyramidal geometry with the oxo group occupying the apical position; the Tc atom lies 0.67 Å above the plane defined by the four nitrogen atoms (Fig. 1). On coordination to the Tc(V) center, the two bidentate ligands both lose two amine protons to form an anionic complex without any relevant interaction with the n-Bu$_4$N$^+$ counterion (Fig. 2), the shortest separation being 2.7 Å between the oxo oxygen and a hydrogen atom at C(13). The Tc=O distance of 1.668(7) Å is typical for

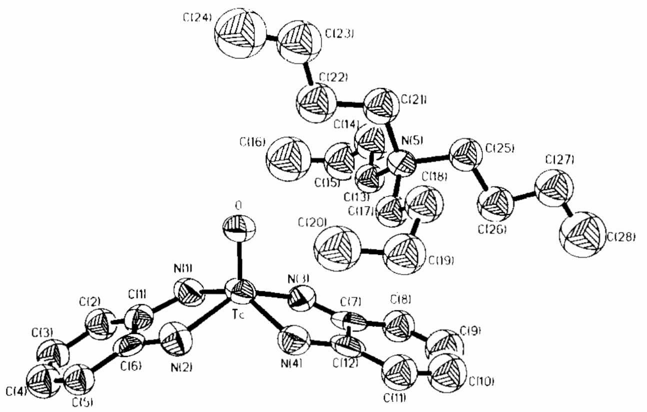

Fig. 1. ORTEP representation of **1**, showing the thermal ellipsoids (40% probability level) and the atom labeling.

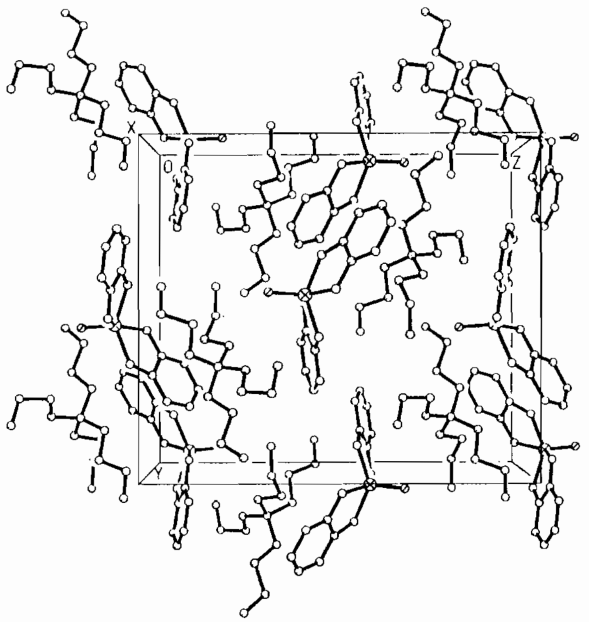

Fig. 2. Unit cell contents of **1**.

monooxotechnetium(V) complexes and the Tc–N distance (mean: 1.98(1) Å) is intermediate between the values of Tc–N (deprotonated) (1.91 Å) and Tc–N (amine) (2.08 Å) found in the seven complexes containing the $TcON_4$ inner core [1]. The dihedral angle between the least-squares planes containing the two ligands is 42.7°; the angles about the nitrogens are in the order of 120°, consistent with sp^2-hybridization, and the 'bite' angles are 78.8 and 79.0°, slightly narrower than those in the parent complex $[TcO(HNC_6H_4S)_2]^-$ (81.4° and 83.9°) [7].

Complex **2** belongs to the class of monomeric complexes of the type $Tc(L^2)_3$, which have a technetium atom coordinated to three bidentate ligands: L^2 = 2-aminobenzenethiolate (Tc(VI)) [8]; toluene-3,4-dithiolate (Tc(VI)) [9]; benzene-1,2-dithiolate (Tc(V)) [10]; 1,2-dicyanoethenedithiolate (Tc(V)) [11]; oxalate (Tc(IV)) [10]; penta-2,4-dionate (Tc(III)) [12]. Of these six complexes, only $[Tc(HNC_6H_4S)_3]$ [8] and $[Tc(SC_6H_4S)_3]^-$ [10] are essentially trigonal-prismatic; the others showing marked changes in coordination geometries, from trigonal to octahedral, for the oxalato complex [10]. Therefore, **2** represents the first tris-bidentate cationic complex of technetium to be structurally characterized; it shows the TcN_6 core in a trigonal-prismatic geometry around Tc(VII) (Fig. 3). As anticipated by Hoffmann *et al.* [13], the trigonal-prismatic coordination seems to be favoured for complexes containing few metal d electrons (in this case, formally d^0) and with metal d orbitals of low energy. Figure 4 shows the 'paddle-wheel' arrangement for the cation projected down the approximate threefold axis; the two triangular faces N(2)N(3)N(5) and

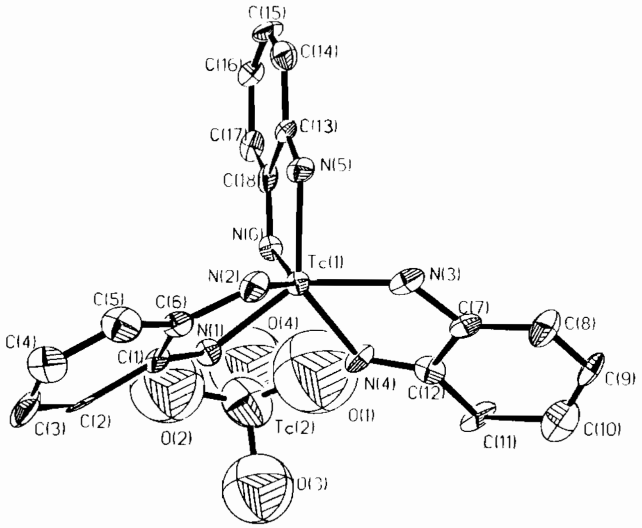

Fig. 3. ORTEP representation of **2**, showing the thermal ellipsoids (40% probability level) and the atom labeling.

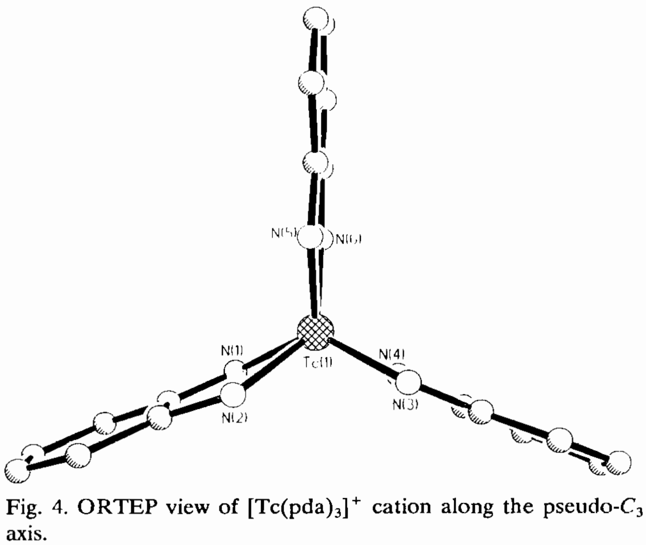

Fig. 4. ORTEP view of $[Tc(pda)_3]^+$ cation along the pseudo-C_3 axis.

N(1)N(4)N(6) are nearly parallel, with a dihedral angle between their normals of 0.7°. The dihedral angles between the mean planes of the triangular faces and the three TcN_2 planes formed by the metal atom and the two donor atoms of each ligand are 94.3, 88.2 and 94.1°, which are close to the trigonal-prismatic ideal of 90°. The distance of Tc(1) from the two N_3 faces is 1.24 Å, compared with 1.26 Å in $[Tc(HNC_6H_4S)_3]$ [8] and the Tc(VII)–N mean bond length (2.00(2) Å) compares very well with the value found for Tc(VI)–N in $[Tc(HNC_6H_4S)_3]$ [8] (1.99(1) Å). Bond distances and angles within the ligands are in general agreement with standard values and, in any event, the differences should not be regarded as being chemically significant because of the low accuracy of the structure determination of compound **2**. In fact, because of the positional disorder for the TcO_4^- counteranion, only gross structure features can be derived from X-ray analysis. The interligand N---N distance (mean 2.74 Å) is relatively short for distances between non-bonded atoms, the sum of van der Waals radii being 3.0 Å and the packing of the molecules in the crystal (Fig. 5) seems to be essentially achieved by hydrogen bonds between N–H and O atoms of TcO_4^-, but the network of hydrogen bonds cannot be defined owing to the disorder of the pertechnetate ion.

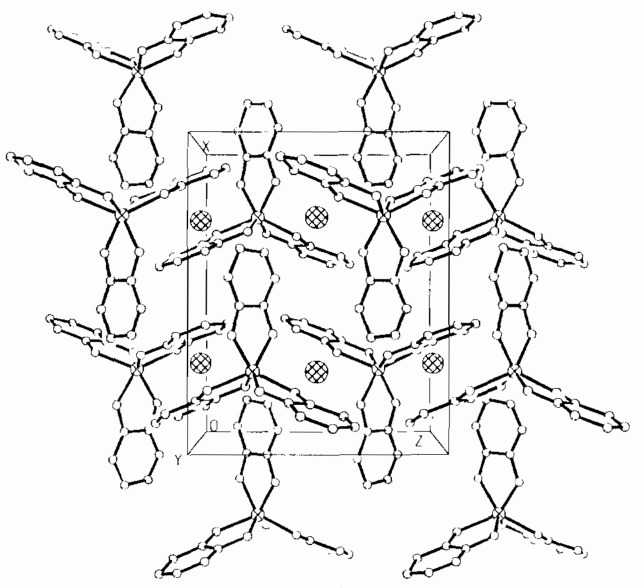

Fig. 5. Unit cell contents of **2**. ⊗ denotes TcO_4^-.

Supplementary material

Full lists of bond lengths (Table A) and bond angles (Table B) for **1**, anisotropic thermal parameters (Table C) and structure factor amplitudes (Table D) for **1** and **2** are available from author T.I.A.G. (University of Port Elizabeth) on request.

Acknowledgements

T.I.A.G. is grateful to the Medical Research Council of South Africa and the Foundation for Research Development for financial support.

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