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Preparation and Structure of Bis(tetraphenylarsonium) *trans*-Aquatetracyanonitridotechnetate(V) Pentahydrate. ESR Studies of the $[TcN(CN)_4(OH_2)]^{2-}/[TcNCl_4]^-$ System

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Abstract

The reaction of $(AsPh_4)[TcNCl_4]$ with KCN and added $AsPh_4Cl$ in CH_3CN/H_2O yields crystals of $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$ (**1**). The complex crystallises in the monoclinic space group $P2_1/n$ with $a = 17.107(5)$, $b = 19.965(7)$, $c = 15.473(5)$ Å, $\beta = 101.70(2)^\circ$ and $Z = 4$. Refinement with 3212 data measured with Cu Kα radiation converged at $R = 0.065$. The geometry of the anion is distorted octahedral with a water molecule coordinated *trans* to the nitrido ligand ($Tc-OH_2$, 2.56(1) Å). The Tc≡N distance is 1.60(1) Å. ESR studies have established the presence of two paramagnetic intermediates in the conversion of $[TcN(CN)_4(OH_2)]^{2-}$ to $[TcNCl_4]^-$ in HCl solutions.

Introduction

Cyano–oxo complexes have been described for many transition metals and have given rise to an extensive chemistry, particularly in the case of molybdenum [1, 2]. Cyanonitrido complexes are less common but a number have been described for rhenium [3–5] and osmium [6]. The nitrido ligand (N^{3-}) is isoelectronic with the oxo ligand (O^{2-}) and is a powerful π-electron donor which stabilises transition metals in high oxidation states [7]. Complexes containing the TcN^{3+} or TcN^{2+} core are of particular interest since these may be regarded as the nitrogen analogues of the ^{99m}TcO complexes which are of importance in nuclear medicine [8, 9]. Several Tc≡N complexes have been characterised by X-ray diffraction and all show very short Tc≡N distances (1.581(5)–1.64(2) Å) corresponding to triple bonds [10, 11]. The preparations of the technetium cyano–oxo complexes $K_2[TcO(CN)_5]\cdot 4H_2O$, $(NBu_4)_2[TcO(OMe)(CN)_4]$ and $K_3[TcO_2(CN)_4]$ have been described in the literature [12] and the preparation and structure of bis(tetraphenylarsonium) *trans*-aquatetracyanonitridotechnetate(V) pentahydrate, $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$ (**1**) are now reported. Complex **1** is characterised by an exceptionally long $Tc-OH_2$ bond and is structurally different to $K_2[ReN(NC)_4]\cdot H_2O$ [5]. ESR studies of the $[TcN(CN)_4(OH_2)]^{2-}/[TcNCl_4]^-$ system are also reported.

Experimental

Ammonium pertechnetate was supplied by Amersham International plc. Infrared spectra were determined for KBr discs on a Perkin-Elmer 197 spectrophotometer. The technetium analysis was performed by liquid scintillation counting with the appropriate correction made for counting efficiency. Tetraphenylarsonium tetrachloronitridotechnetate(VI), cesium pentachloronitridotechnetate(VI) and nitridotechnetic(VI) acid were prepared according to the methods of Baldas *et al.* [10, 13, 14]. Titration of the concentrated hydrochloric acid used against standard base gave a concentration of 11.6 mol dm^{-3}.

Preparation of $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$

(a) From $(AsPh_4)[TcNCl_4]$

A solution of KCN (46 mg, 706 μmol in 1 cm^3 of water) was added to $(AsPh_4)[TcNCl_4]$ (45 mg, 71 μmol) dissolved in 2.5 cm^3 of CH_3CN. The mixture turned a transient purple–red and then became bright yellow. Additional $AsPh_4Cl$ (30 mg, 72 μmol) in 1 cm^3 of water was added and the mixture allowed to evaporate to dryness at room temperature under reduced pressure in a desiccator over KOH. The yellow mass was washed twice with a small amount of cold water to remove KCl, unreacted KCN and excess $AsPh_4Cl$. Since the complex is appreciably soluble in cold water it is essential to keep the amount of water used to a minimum. The crystals were collected by filtration. Yield 50 mg, 65% based on

0020-1693/90/$3.50

$(AsPh_4)[TcNCl_4]$. Recrystallisation from water gave bright yellow crystals, melting point (m.p.) 233–234 °C. *Anal.* Found: Tc, 9.04. Calc. for $C_{52}H_{52}As_2N_5O_6Tc$: Tc, 9.06%. The IR spectrum showed peaks at 3550m, 3460m, 2112s, 1621m, 1481s, 1438vs, 1100s (Tc≡N), 1081vs, 997vs, 745vs and 688vs cm^{-1}.

(b) From $Cs_2[TcNCl_5]$

A solution of KCN (65 mg, 1 mmol) in 4 cm^3 of water was added to $Cs_2[TcNCl_5]$ (56 mg, 0.1 mmol) and the mixture gently swirled until all the solid dissolved to give a yellow solution. The solution was divided into two equal portions and to one portion was added a solution of $AsPh_4Cl$ (50 mg, 0.12 mmol) in 1 cm^3 of water. The mixture was heated until only a small amount of insoluble material remained and was then filtered hot. The yellow filtrate was treated as described for (a) to give 34.5 mg (63% yield) of **1**.

Reaction of $[TcN(CN)_4(OH_2)]^{2-}$ with HCl

To the second portion of the $Cs_2[TcNCl_5]$/KCN solution (2 cm^3) was added 2 cm^3 of conc. HCl. The mixture turned an intense purple and was then heated to near boiling on a hotplate for 3 min. The mixture turned orange and a gelatinous brown precipitate deposited. After cooling, the mixture was centrifuged, the supernate removed and the brown precipitate washed with 1:1 conc. HCl/water and recentrifuged. The combined supernates were treated with $AsPh_4Cl$ (50 mg in 0.5 cm^3 of water) and the orange precipitate of $(AsPh_4)[TcNCl_4]$ (identified by its IR spectrum and m.p.) collected. Yield 9.6 mg (30%). The brown precipitate was dried under vacuum to give an amorphous solid. The IR spectrum showed peaks at 3410 vs, 2152vs (C≡N), 1610s (H_2O), 1074s (Tc≡N) and 1030m cm^{-1}.

ESR Spectroscopy

ESR spectra were recorded at 130 K using a Bruker ESR-200D-SRC spectrometer and associated equipment. Spectral simulations were performed on a Data General MV8000 computer using the programs described previously which employ the standard second-order perturbation theory expressions for the magnetic fields and transition probabilities [15, 16]. The spin Hamiltonian used to represent the spectra was of the form

$$\mathcal{H} = g_{\parallel}\beta B_z S_z + g_{\perp}\beta(B_x S_x + B_y S_y) + A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y) + Q[I_z^2 - I(I+1)/3]$$

where $S = 1/2$, $I = 9/2$ for the Tc(VI) ion and the other symbols have their usual meaning.

X-ray Data Collection and Structure Analysis

Single crystals suitable for X-ray diffraction studies were grown by the slow evaporation at room temperature of an aqueous solution of $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$. Accurate unit cell parameters were determined at 25(1) °C by least-squares refinement of 2θ values measured with Cu Kα radiation for 25 independent reflections well separated in reciprocal space. Integrated intensities were measured on a Rigaku-AFC four-circle diffractometer with Cu Kα radiation (graphite-crystal monochromator) and recorded by an $\omega-2\theta$ scan with 10 s stationary background counts to a maximum $(\sin\theta)/\lambda = 0.497$ Å^{-1}. Three reflections, monitored every 50 reflections, showed a gradual 5% decrease in intensities during data collection and the intensity data were scaled accordingly. The intensities were corrected for Lorentz and polarisation effects, and for absorption [17].

The sites of the Tc and As atoms were determined by a combined Patterson/structure expansion method using SHELXS-86 [18]. Subsequent difference syntheses using SHELX-76 [19] revealed the sites of all the remaining non-hydrogen atoms. The hydrogen atoms of the cations were included in the analysis at calculated positions (C–H = 1.08 Å) and assigned a variable overall isotropic thermal parameter. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters given to the non-hydrogen atoms. The function minimised was $\Sigma w(\Delta F)^2$ (where $\Delta F = ||F_o| - |F_c||$), with the data weighted according to $w = (\sigma^2|F_o| + 1.5 \times 10^{-3}|F_o|^2)^{-1}$.

During the refinement of **1**, based on 3248 non-zero data, it was observed that 34 of the weakest intensity reflections exhibited relatively poor agreement with the calculated structure factors, and in all cases $F_o \gg F_c$. As this effect was clearly systematic, it was decided to omit these low-intensity data from further refinement cycles. Also during the refinement two intense low order reflections which showed severe extinction were omitted from the refinement cycles, viz. (2, 0, 0) and (1, 1, 0). The R indices were defined as $R = \Sigma\Delta F/\Sigma|F_o|$, $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$ and the 'goodness of fit' given by $GOF = [\Sigma w(\Delta F)^2/(N_o - N_v)]^{1/2}$ where N_o is the number of reflections used in the refinement and N_v is the number of variables. The crystal data, data collection and refinement parameters are summarised in Table 1.

Neutral atom scattering-factor curves were taken from refs. 20 and 21 for the non-hydrogen and hydrogen atoms, respectively. Anomalous dispersion corrections were applied to the non-hydrogen atoms [17]. Final atomic positional coordinates are given in Table 2. Figure 1 has been prepared from the output of ORTEP [22]. See also 'Supplementary Material'.

Results and Discussion

The reaction of $(AsPh_4)[Tc^{VI}NCl_4]$ with KCN and added $AsPh_4Cl$ in CH_3CN/H_2O gave a good yield of

TABLE 1. Crystallographic data and summary of intensity data collection and structure refinement of 1

	$(AsPh_4)_2[TcN(CN)_4(H_2O)]\cdot5H_2O$
Formula	$C_{52}H_{52}As_2N_5O_6Tc$
Formula weight	1091.76
Crystal dimensions (mm)	0.52 × 0.104 × 0.316
Crystal colour	yellow
Space group	$P2_1/n$
a (Å)	17.107(5)
b (Å)	19.965(7)
c (Å)	15.473(5)
β (°)	101.70(2)
Cell volume (Å^3)	5175(5)
Molecules/cell	4
F(000)	2224
μ (Cu Kα) (cm^{-1})	38.7
Temperature (°C)	25
Wavelength (Å)	1.5418
Absorption correction factors	0.86 – 0.62
2θ (max) (°)	100
Diffractometer	Rigaku-AFC
Scan rate ($\Delta\omega$) (° min^{-1})	4
Scan range (°)	$1.2 + 0.5 \tan\theta$
Unique non-zero data used	3248
Terms used for refinement	3212
Final no. parameters refined	598
R	0.065
R_w	0.069
GOF for last cycle	1.05
Residual density (e Å^{-3})	+0.94 and −0.56
Max σ/Δ for last cycle	0.03

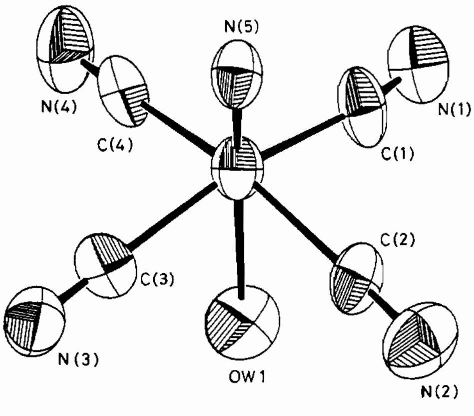

Fig. 1. A perspective view of the $[TcN(CN)_4(OH_2)]^{2-}$ anion in 1 showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

yellow water soluble crystals shown by X-ray diffraction to have the molecular formula $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot5H_2O$ (**1**). The IR spectrum of **1** indicated the presence of both bonded and lattice water (3550, 3460 and 1621 cm^{-1}) and the presence of the Tc≡N group was confirmed by a strong band at 1100 cm^{-1}. There were no peaks in the spectrum attributable to Tc=O. The C≡N absorption occurred as a single sharp peak at 2112 cm^{-1}, indicating the equivalence of the cyano ligands. The complex is readily soluble in acetonitrile and, unusually for the tetraphenylarsonium salt of a complex anion, may be conveniently recrystallised from hot water.

Complex **1** was also prepared by dissolution of $Cs_2[TcNCl_5]$ in aqueous KCN and addition of $AsPh_4Cl$. The addition of one volume of conc. HCl to one volume of $Cs_2[TcNCl_5]$/KCN solution resulted in the formation of an intense purple colour. On heating the solution turned orange with the formation of a brown gelatinous precipitate. Addition of $AsPh_4Cl$ to the orange solution allowed the isolation of a 30% yield of $(AsPh_4)[TcNCl_4]$.

The reaction of $[TcNCl_4]^-$ with CN^- results in the reduction of Tc^{VI} to Tc^{V}. This was confirmed by the absence of ESR signals from solutions of **1** in either acetonitrile or water. A similar reduction from Os(VIII) to Os(VI) has been reported in the reaction of $K[OsO_3N]$ with HCN to give $K[OsN(CN)_4(OH_2)]$ [6]. The stability of the +5 state for **1** is also consistent with the reported reaction of $TcO_2\cdot xH_2O$ with KCN to give $K_2[TcO(CN)_5]\cdot4H_2O$ [12]. In this case oxidation of Tc(IV) to Tc(V) occurs.

TABLE 2. Fractional coordinates for $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$

Atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$
Tc	2601(1)	1727(1)	10308(1)
As(1)	1698(1)	588(1)	4441(1)
As(2)	3910(1)	3100(1)	5584(1)
C(1)	2639(9)	2758(8)	10012(8)
C(2)	3795(9)	1764(6)	11008(8)
C(3)	2707(8)	688(6)	10193(8)
C(4)	1588(10)	1732(6)	9267(9)
N(1)	2555(6)	3303(6)	9802(6)
N(2)	4451(8)	1772(6)	11390(8)
N(3)	2785(6)	121(6)	10131(8)
N(4)	1051(9)	1752(6)	8719(9)
N(5)	2150(6)	1757(5)	11115(5)
OW(1)	3372(5)	1670(5)	9055(5)
OW(2)	164(5)	2960(5)	8224(6)
OW(3)	602(6)	4417(6)	6858(8)
OW(4)	1090(6)	4077(6)	8703(6)
OW(5)	4512(6)	773(6)	8857(9)
OW(6)	968(8)	4189(6)	5043(10)
C(5)	4497(10)	3896(6)	5870(8)
C(6)	5300(11)	3933(8)	5975(9)
C(7)	5700(9)	4547(9)	6128(8)
C(8)	5285(12)	5106(8)	6223(9)
C(9)	4465(12)	5088(8)	6154(9)
C(10)	4074(9)	4473(8)	5971(8)
C(11)	3121(10)	3050(6)	6277(9)
C(12)	3355(11)	3112(6)	7180(11)
C(13)	2824(16)	3065(10)	7716(13)
C(14)	2007(17)	2954(10)	7358(19)
C(15)	1804(12)	2923(8)	6492(17)
C(16)	2307(11)	2966(6)	5917(11)
C(17)	4572(8)	2326(6)	5850(9)
C(18)	4383(9)	1847(6)	6418(9)
C(19)	4873(13)	1303(8)	6609(11)
C(20)	5524(12)	1235(9)	6227(13)
C(21)	5722(9)	1703(9)	5656(10)
C(22)	5228(9)	2254(6)	5457(9)
C(23)	3417(8)	3112(6)	4370(8)
C(24)	3493(8)	2579(6)	3826(9)
C(25)	3114(10)	2587(9)	2942(10)
C(26)	2669(10)	3118(9)	2618(10)
C(27)	2567(10)	3643(8)	3141(11)
C(28)	2934(9)	3634(8)	4044(9)
C(29)	2621(10)	555(6)	3944(9)
C(30)	3355(12)	640(6)	4496(11)
C(31)	4027(10)	633(6)	4104(12)
C(32)	3975(11)	593(6)	3224(12)
C(33)	3233(13)	509(8)	2698(10)
C(34)	2537(10)	502(6)	3057(10)
C(35)	996(10)	−125(8)	3942(9)
C(36)	210(11)	1(8)	3655(10)
C(37)	−271(10)	−519(11)	3298(10)
C(38)	50(13)	−1159(10)	3246(10)
C(39)	853(13)	−1268(8)	3539(11)
C(40)	1326(10)	−737(8)	3885(10)
C(41)	1141(9)	1411(6)	4152(10)
C(42)	1322(10)	1796(8)	3478(12)
C(43)	880(12)	2405(9)	3318(13)
C(44)	339(12)	2591(8)	3766(13)
C(45)	167(11)	2211(10)	4448(12)
C(46)	590(12)	1601(9)	4626(11)
C(47)	2004(8)	520(6)	5680(8)
C(48)	2173(9)	1096(6)	6199(10)
C(49)	2414(10)	1034(9)	7100(10)
C(50)	2516(10)	428(9)	7503(10)
C(51)	2354(10)	−129(8)	7017(11)
C(52)	2103(9)	−91(6)	6089(10)

Molecular Structure of $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$

The crystal structure of **1** consists of discrete $(AsPh_4)^+$ cations and $[TcN(CN)_4(OH_2)]^{2-}$ anions. A perspective view of the anion which includes the atom numbering is shown in Fig. 1 and selected interatomic distances and angles are given in Table 3.

The technetium(V) atom in **1** is coordinated by four cyano groups, one nitrogen and one oxygen (coordinated water) atom to give a distorted octahedron. The cyano ligands occupy the equatorial positions. The short Tc≡N bond distance of 1.596(10) Å in **1** is similar to those observed in $(AsPh_4)[Tc^{VI}NX_4]$ (1.581(5) Å (X = Cl) and 1.596(6) Å (X = Br)) [10, 23] and in $[Tc^{V}N(S_2CNEt_2)_2]$ (1.604(6) Å) [24]. It was not possible in the analysis to establish the presence of the two hydrogens attached to the coordinated oxygen. The alternative possibility that the coordinated oxygen atom was in the form of hydroxide, i.e. $(AsPh_4)_2[Tc^{VI}N(CN)_4(OH)]\cdot 5H_2O$, was discarded on the basis of the observed length of the Tc–O bond (2.559(9) Å) and on the absence of ESR signals from solutions of **1**. Coordinated hydroxyl groups generally exhibit M–O bond distances similar to those of other anionic oxygen ligands. Thus, the Tc–O bond length in *trans*-O=Tc–OR complexes is 1.855(6) Å in $[TcO(OEt)Br_2(4\text{-nitropyridine})_2]$ [25], 1.90(1) Å in $[\{TcO(salpd)\}_2]$-O [salpd = *N,N'*-propane-1,3-diylbis(salicylidene iminate)] [26], 1.96 Å (determined by EXAFS) in $[TcO(OH)(dmpe)_2](CF_3SO_3)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) [27] and 2.069(6) Å in $(AsPh_4)_2[TcO(ox)_2(Hox)]\cdot 3H_2O$ [11]. In $[TcO(OH_2)(acac)_2en]Br_{0.25}Cl_{0.75}$ ((acac)$_2$en = *N,N*-ethylenebis(acetylacetoneiminate)) the *trans* Tc–OH$_2$ bond length is 2.282(2) Å [28]. More pertinent to the present case are the complexes $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ and $[Pt(en)_2][MoO(OH_2)(CN)_4]\cdot 2H_2O$, which have Mo–OH(H) bond lengths of 2.077(7) and 2.271(4) Å, respectively [1]. The exceptionally long Tc–O bond length of 2.559(9) Å for the coordinated water molecule in **1** is no doubt a manifestation of the strong *trans* influence

TABLE 3. Selected interatomic distances (Å) and angles (°) in the coordination sphere for $[TcN(CN)_4(OH_2)]^{2-}$

Tc–N(5)	1.596(10)	Tc–OW(1)	2.559(9)
Tc–C(1)	2.113(16)	Tc–C(2)	2.110(14)
Tc–C(3)	2.093(14)	Tc–C(4)	2.113(14)
C(1)–N(1)	1.136(20)	C(2)–N(2)	1.158(19)
C(3)–N(3)	1.146(18)	C(4)–N(4)	1.117(19)
C(1)–Tc–C(2)	90.5(7)	C(1)–Tc–C(3)	160.1(7)
C(1)–Tc–C(4)	83.5(7)	C(1)–Tc–N(5)	100.0(6)
C(1)–Tc–OW(1)	80.6(6)	C(2)–Tc–C(3)	89.2(7)
C(2)–Tc–C(4)	161.8(7)	C(2)–Tc–N(5)	99.7(6)
C(2)–Tc–OW(1)	78.3(6)	C(3)–Tc–C(4)	90.7(7)
C(3)–Tc–N(5)	99.6(6)	C(3)–Tc–OW(1)	79.9(6)
C(4)–Tc–N(5)	98.3(6)	C(4)–Tc–OW(1)	83.8(6)
N(5)–Tc–OW(1)	177.9(5)	Tc–C(1)–N(1)	170.9(12)
Tc–C(2)–N(2)	178.8(13)	Tc–C(3)–N(3)	178.3(11)
Tc–C(4)–N(4)	178.2(13)		

of the nitrido ligand (one of the strongest π-electron donors known) [7]. This distance may be compared to the Os–OH_2 bond lengths in *trans*-$K[OsNX_4(OH_2)]\cdot H_2O$ (2.50(3) (X = Cl) and 2.42(3) Å (X = Br)) [29, 30] and the very long Tc–$NCCH_3$ bond lengths of 2.491(4) Å in $[Tc^VN(NCS)_2(CH_3CN)(PPh_3)_2]\cdot 0.5CH_3CN$ [31]. The water molecule in **1** is coordinated in an essentially linear arrangement with a N≡Tc–O angle of 177.9(5)°.

The strong *trans* influence of the nitrido ligand also results in the technetium atom in **1** being displaced by 0.35 Å above the plane of the four equatorial cyano ligands. The N≡Tc–CN angles of 98.3(6)–100.0(6)° are similar to those observed in other six-coordinate nitrido technetium complexes, e.g. 91.4(1)–100.4(2)° in $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]\cdot 0.5CH_3CN$ [31], 91.3(2)–104.7(2)° in $[TcNCl_2(Me_2PhP)_3]$ [32] and 95.5(8)–105.2(8)° in $(AsPh_4)_4[Tc_4N_4(O)_2(ox)_6]$ [11]. The Tc–C≡N angles of 171(1)–179(1)° associated with cyano ligands of **1** are close to linearity and are similar to the range of Mo–C≡N angles (171.1(5) to 178.0(4)°) reported for $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ and $[Pt(en)_2][MoO(OH_2)(CN)_4]\cdot 2H_2O$ [1].

The alternatives of C or N bonding of the cyano ligands in **1** were checked by refinement of the isocyanide structure. The *R* indices are not significantly different and each structure gave similar bond distances and angles. However, refinement of the isocyanide structure generally gave higher thermal parameters for the cyano atoms, and for this reason the C-bonded arrangement was chosen as the more consistent. This is as expected and accords with the statement that unidentate cyano ligands always appear to bond through carbon [33]. Nitrogen bonded cyano ligands have, however, been proposed for $K_2[ReN(NC)_4]\cdot H_2O$, where the Re and nitrido nitrogen atoms are arranged in infinite chains with alternating Re≡N···Re bond lengths of 1.53 and 2.44 Å [5]. Other surprising structural features of this rhenium complex are the strongly bent Re–N≡C configuration (136.2°) and the unusually long N≡C bond distance of 1.31 Å. The C≡N bond distances in **1** range from 1.117(19) to 1.158(19) Å and these distances in $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$ and $[Pt(en)_2][MoO(OH_2)(CN)_4]\cdot 2H_2O$ lie in the range 1.130(6) to 1.143(6) Å [1].

ESR Spectra

No signals were observed at 130 K from a polycrystalline powder sample of **1**. Similarly, no signals were observed from solutions of **1** (2.0×10^{-3} mol dm^{-3}) frozen to 130 K in CH_3CN, H_2O, concentrated H_2SO_4 and in concentrated H_2SO_4 after the solution had been heated to produce an orange–brown colour. Addition of solid NaCl to the concentrated H_2SO_4 solution at room temperature resulted in the evolution of HCl gas and a clear solution which also showed no ESR signals. These results confirm that the $[TcN(CN)_4(OH_2)]^{2-}$ anion is diamagnetic with the Tc present as Tc(V).

Solutions of nitridotechnetic(VI) acid, $[TcN(OH)_3]_n$, and of $Cs_2[TcNCl_5]$ in aqueous KCN (10 mg/ml) ([Tc] 2.0×10^{-3} mol dm^{-3}) were yellow and, when frozen to 130 K, both exhibited no ESR signals. On addition of concentrated HCl (1:1 vol./vol.), the solutions turned a deep purple and at 130 K, the $Cs_2[TcNCl_5]$ solution exhibited the ESR signals shown in Fig. 2. These signals may be interpreted as arising from three distinct species, one of which is the $[TcNCl_4]^-$ anion ((a) of Fig. 2). The other two species have values of $A_\parallel$ smaller than that of $[TcNCl_4]^-$ (Table 4) and are presumed to arise from the replacement of some of the equatorial CN^- ligands by Cl^- to give two of the three species, $[TcNCl_3(CN)]^-$, $[TcNCl_2(CN)_2]^-$ or $[TcNCl(CN)_3]^-$. For both solutions the overall ESR spectral intensity corresponded to *c*. 10% of the Tc present.

TABLE 4. ESR spectral parameters of $[TcNCl_3(CN)]^-$, $[TcNCl_2(CN)_2]^-$ and related anions

Species	$g_\parallel$	$g_\perp$	$A_\parallel$ ($\times10^4$ cm^{-1})	$A_\perp$ ($\times10^4$ cm^{-1})	$\beta_2{}^2$
$[TcNCl_4]^-$ [34]^a	2.0075	2.0020	294.8	133.7	0.77
$[TcNCl_3(CN)]^{-b}$	2.013(2)	2.006(5)	277(1)	127(2)	0.73
$[TcNCl_2(CN)_2]^{-b}$	2.018(3)	1.998(5)	261(1)	115(5)	0.73
$[TcNCl_3Br]^-$ [35]	2.046		280		
$[TcNCl_2Br_2]^-$ [35]	2.076		268		
$[TcNBr_4]^-$ [34]^a	2.145	2.032	248.7	120.0	0.79

^{a}In the hydrohalic acid solution. ^{b}This work.

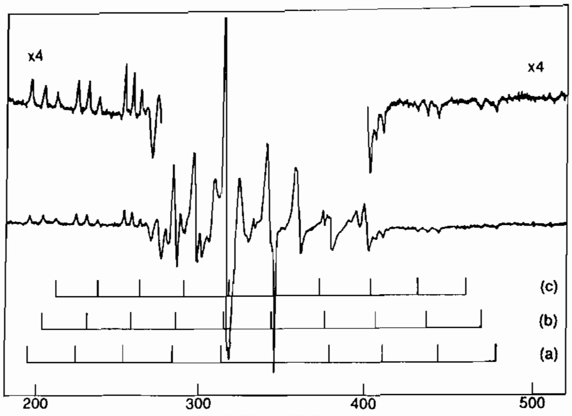

Fig. 2. ESR spectrum at 130 K of $Cs_2[TcNCl_5]$ in an aqueous KCN solution (10 mg/ml) to which concentrated HCl had been added (1:1 vol./vol.) immediately prior to freezing. Final Tc concentration: 1.0×10^{-3} mol dm^{-3}. The positions of the outermost 'parallel' features of the spectra described in the text are indicated on the diagram; (a) $[TcNCl_4]^-$, (b) $[TcNCl_3(CN)]^-$, (c) $[TcNCl_2(CN)_2]^-$. Spectrometer conditions: microwave power, 20 mW; frequency, 9.519 GHz; gain, 8.0×10^4; 100 kHz modulation amplitude, 1.0 mT; time constant, 0.1 s; field scan rate, 0.8 mT s^{-1}.

On standing at room temperature for one hour prior to freezing, the signal intensity due to the species with the smallest value of $A_\parallel$ (spectrum (c) of Fig. 2) was little changed. However, the intensity of the other two signals had increased by a factor of about three. After prolonged standing, only signals due to $[TcNCl_4]^-$ were observed. Over this period of time, the colour changed from an intense purple to a pale orange–yellow. These changes could be accelerated by heating, with the final signal intensity of the solution prepared from $[TcN(OH)_3]_n$ and heated after $1\frac{1}{4}$ h at room temperature corresponding to about 90% of the Tc present and that of the solution prepared from $Cs_2[TcNCl_5]$ and heated after 3 h at room temperature corresponding to about 60% of the Tc.

In the absence of resolved superhyperfine structure, it is not possible to determine directly the number and nature of the ligands coordinating to the Tc≡N core. However, the changes in the values of g and A, particularly $g_\parallel$ and $A_\parallel$, are related to the changes in the coordinating ligands [36]. In the present case, the changes in $g_\parallel$ and $A_\parallel$ (as shown in Table 4) are consistent with the coordination of one and two CN^- groups, respectively, i.e. species (b) of Fig. 2 may be formulated as $[TcNCl_3(CN)]^-$ and species (c) as $[TcNCl_2(CN)_2]^-$. Thus, the Tc(V) ion is oxidised to Tc(VI) only at the stage where two CN^- ligands are replaced, and $[TcNCl_2(CN)_2]^-$ is the first paramagnetic ion formed. It is not possible to determine from the ESR spectra whether the two CN^- ligands are *cis* or *trans*.

If we write the molecular orbital of the unpaired electron as

$$\phi(B_2) = \beta_2|d_{xy}\rangle - \beta_2'|\phi_L\rangle$$

where the metal orbital is described as $|d_{xy}\rangle$ and $|\phi_L\rangle$ represents a linear combination of the p-orbitals of the equatorial ligands, then $\beta_2{}^2$ is a measure of the electron density on the Tc ion. Following the approach outlined previously by Baldas *et al.* [14] (see also McGarvey [37]), we calculate the values of $\beta_2{}^2$ given in Table 4, which clearly demonstrate the decrease in electron density on Tc in the cyano complexes. This result is consistent with the higher Tc≡N stretching frequency (1100 cm^{-1}) in **1** compared to those of $(AsPh_4)[TcNCl_4]$ and $(AsPh_4)[TcNBr_4]$ (1076 and 1074 cm^{-1}) [10].

Supplementary Material

Anisotropic thermal parameters, hydrogen atom coordinates, short intermolecular contacts, listings of observed and calculated structure amplitudes and the crystal packing diagram are available from the authors on request. A stereodrawing of the complex and a perspective view of the cation in the complex are also available.

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