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Preparation of the technetium(VI) aquanitrido complexes $(NEt_4)[TcNX_4(OH_2)]$ (X = Cl or Br). Crystal structures of $(NEt_4)[TcNBr_4(OH_2)]$ and $Cs_2[TcNCl_5]$

John Baldas, Silvano F. Colmanet and Geoffrey A. Williams

Australian Radiation Laboratory, Lower Plenty Road, Yallambie, Vic. 3085 (Australia)

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Abstract

Addition of NEt_4X to a conc. HX solution of $[TcNX_4(OH_2)]^-$ (X = Cl or Br) yields crystals of $(NEt_4)[TcNX_4(OH_2)]$ (X = Cl (**1**) or Br (**2**)). Complex **2** crystallises in the orthorhombic space group *Pnma* with $a = 11.366(1)$, $b = 12.930(2)$, $c = 11.540(1)$ Å and $Z = 4$. Refinement with 1434 data measured with Cu Kα radiation converged with $R = 0.047$. The complex anion has distorted octahedral geometry with a water molecule *trans* to the nitrido ligand (Tc≡N 1.599(9) and Tc–OH_2 2.443(7) Å). Crystals of $Cs_2[TcNCl_5]$ (**3**) belong to the cubic space group $Fm\bar{3}m$ with $a = 10.211(1)$ Å and $Z = 4$. The ligands of the complex anion are statistically disordered over six octahedral sites as required by the cubic space group. Refinement based on 78 data measured with Cu Kα radiation, and with a fixed Tc≡N distance of 1.6 Å, converged with $R = 0.034$. In this model Tc is displaced 0.401(3) Å from the plane of the *cis* ligands towards the nitrido ligand with $Tc–Cl_{cis} = 2.373(5)$, $Tc–Cl_{trans} = 2.740(5)$ Å.

Introduction

The strong *trans* influence of the nitrido ligand results in the majority of $Tc^{VI}N$ and $Tc^{V}N$ complexes adopting five-coordinate square-pyramidal geometries with the N^{3-} ligand in the apical position and the *trans* position vacant [1]. In six-coordinate TcN complexes the bond length of technetium to the *trans* ligand is abnormally long, viz. Tc–$NCCH_3$ 2.491(4) Å in *trans,trans*-$[TcN(NCS)_2(PPh_3)_2(CH_3CN)]\cdot\frac{1}{2}CH_3CN$ [2], Tc–$NCCH_3$ 2.64(1) Å in $(NEt_4)_2$*trans*-$[TcN(NCS)_4(CH_3CN)]$ [3], Tc–OH_2 2.559(9) Å in $(AsPh_4)_2$*trans*-$[TcN(CN)_4(OH_2)]\cdot 5H_2O$ [4], and Tc–Cl 2.663(2) and 2.732(1) Å in the tetraphenylborate salts of $[TcN(tad)Cl]^+$ and $[TcN(en)_2Cl]^+$, respectively (tad = 1,5,8,12-tetraazadodecane, en = ethylenediamine) [5].

The isoelectronic oxo ligand (O^{2-}) is generally considered to have a lesser *trans* influence as shown by the generally shorter *trans* OTc–L distances [6, 7]. We have undertaken a programme to compare the structural effects of the $Tc^{V}O^{3+}$ core with both the isoelectronic $Tc^{V}N^{2+}$ core and the $Tc^{VI}N^{3+}$ core in the same coordination environments. Crystal structures have been reported for the pairs $(AsPh_4)_2[TcN(L\text{-}L)_2]/(AsPh_4)[TcO(L\text{-}L)_2]$ (L-L = dithiooxalate [8], 1,2-dicyanoethenedithiolate [9, 10]), and $(AsPh_4)[TcNCl_4]/(AsPh_4)[TcOCl_4]$ [11, 12]. Comparisons of these square-pyramidal pairs [9] indicate that the Tc≡N bond is shorter than the Tc=O bond by *c.* 0.01–0.06 Å in cases of identical coordination environments, that other Tc–ligand bond distances are greater in the nitrido complexes, and that displacements of Tc from the basal planes are greater in the oxo complexes by *c.* 0.11–0.15 Å [9].

Aqua complexes of the type $[MOX_4(OH_2)]^-$ (X = halogen) have been prepared for a number of transition metals and have been extensively studied crystallographically [13, 14]. The corresponding nitrido complexes have previously been prepared in the case of $[OsNX_4(OH_2)]^-$ (X = Cl or Br) [15]. Recently, Mantegazzi *et al.* [16] have reported a structure determination for $(NEt_4)[TcOBr_4(OH_2)]$ and we now report the preparation of $(NEt_4)[TcNX_4(OH_2)]$ (X = Cl (**1**) or Br (**2**)) and the X-ray structure determination of the bromo complex. This enables the first comparison of the TcN and TcO cores in identical six-coordinate environments.

We also report the structure of the disordered cubic salt $Cs_2[TcNCl_5]$ (**3**), a further example in which a Tc–Cl bond *trans* to the nitrido ligand is considerably lengthened. It is of interest to compare this $Tc^{VI}N$ complex with the isostructural $Cs_2[Tc^{V}OCl_5]$ for which an EXAFS study has been reported [17].

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Experimental

Ammonium pertechnetate was obtained from Amersham International plc. Infrared spectra (4000–600 cm^{-1}) were determined in KBr discs on a Perkin-Elmer 197 spectrophotometer. Technetium analyses were performed by liquid scintillation counting after decolourisation of the solutions by the addition of H_2O_2. Other analyses were performed by Chemical and Micro Analytical Services, Melbourne. The preparation of $Cs_2[TcNCl_5]$ has been described previously [18].

Preparation of (NEt$_4$)[TcNCl$_4$(OH$_2$)] (1)

The acetonitrile extract prepared from the reaction of NH_4TcO_4 (26 mg, 0.14 mmol)/NaN_3/HCl [18] was dissolved in 2 cm^3 of 36% HCl and NEt_4Cl (50 mg, 0.3 mmol in 1 cm^3 HCl) added. The orange solution was reduced in volume on a rotary evaporator, absolute ethanol was added and the orange crystals were collected by filtration, washed with a little cold ethanol and dried in an evacuated desiccator over solid KOH. A dried and sealed sample was submitted for microanalysis and the results indicated that dehydration had occurred to give $(NEt_4)[TcNCl_4]$. *Anal.* Found: C, 24.76; H, 5.66; N, 7.26; Tc, 25.33. Calc. $C_8H_{20}Cl_4N_2Tc$: C, 24.96; H, 5.24; N, 7.28; Tc, 25.69%. The oxygen analysis performed several days later, and presumably after the sample had been exposed to the atmosphere, gave 4.54%; $C_8H_{22}Cl_4N_2OTc$ requires 3.97%. The IR spectrum of *1* (exposed to the atmosphere) showed peaks at 3500s, 2998m, 1613vs, 1484vs, 1477vs, 1441vs, 1389s, 1172s, 1065vs(Tc≡N), 995s and 784s cm^{-1}. The IR spectrum of $(NEt_4)[TcNCl_4]$ showed peaks at 2980m, 1459s, 1399m, 1309w, 1183s, 1070s(Tc≡N), 1032m, 1003m and 793m cm^{-1}.

Preparation of (NEt$_4$)[TcNBr$_4$(OH$_2$)] (2)

To a solution of NH_4TcO_4 (52 mg, 0.29 mmol) in 15 cm^3 of cold 47% HBr was added NaN_3 (200 mg in 0.5 cm^3 water) and the mixture refluxed for 10 min. After addition of NEt_4Br (150 mg, 0.71 mmol) the deep-purple solution was placed in a refrigerator (−15 °C) and the blue–black crystals which formed were collected, washed with a little cold HBr and dried under vacuum over solid KOH. Yield 136 mg, 82%. Melting point 332 °C dec. *Anal.* Found: Tc 16.7%. Calc. for $C_8H_{22}Br_4N_2OTc$: Tc, 17.0%. The IR spectrum showed peaks at 3467vs, 1607vs, 1481vs, 1474s, 1440vs, 1387s, 1171s, 1063vs(Tc≡N), 994s and 782s cm^{-1}.

Crystallography

Single crystals of **2** and **3** suitable for X-ray diffraction studies were grown by slow evaporation of conc. HX (X = Br or Cl) solutions of $(NEt_4)[TcNBr_4(OH_2)]$ and $Cs_2[TcNCl_5]$, respectively. Unit cell parameters were obtained by least-squares analyses [19] of the setting angles, determined on a diffractometer at 23 °C with Cu Kα radiation, for 24 (**2**) and 10 (**3**) reflections well separated in reciprocal space.

Intensity data were recorded at 23 ± 1 °C on an automated Siemens AED diffractometer with nickel-filtered Cu Kα radiation. Intensities were measured by a background-peak-background $\theta/2\theta$ scan procedure. Crystal data and conditions for data collections are given in Table 1. The integrated intensities were corrected for Lorentz and polarisation effects and for absorption [20].

Structure determinations and refinements

The sites of all the atoms for **2**, excluding hydrogens, were taken from the isostructural complex $(NEt_4)[MoOBr_4(OH_2)]$ [14]. The technetium, nitrogen and oxygen atoms of the anion are all on the mirror plane with the two bromine atoms located at eightfold general positions. However, the NEt_4^+ cation is disordered with the nitrogen atom located on the mirror plane, two methyl carbons located at general positions, and two methylene carbons each necessarily disordered between two sites. The disorder is such that the four methylene carbon atoms (and *all* hydrogen atoms) of the cation have two different spatial orientations, each equally populated throughout the crystal lattice in order to preserve the symmetry required by the space group. This type of disordered NEt_4^+ cation has been fully described in the structure determination of $(NEt_4)[ReOBr_4(OH_2)]$ [21], and was also observed for $(NEt_4)[TcOBr_4(OH_2)]$ [16]. The methylene carbons were thus included with a site occupancy of 0.5. The hydrogen atoms of the methylene groups were included in the analysis at calculated positions whereas those of the methyl carbons were not.

For **3**, photography and an analysis of equivalences and absences in the diffractometer data suggested that the Laue class of the cubic crystal was $m\bar{3}m$, with possible space group $Fm\bar{3}m$ (No. 225). Several alternative space groups were examined during the structure analysis, but the structure was successfully refined in $Fm\bar{3}m$ making $Cs_2[TcNCl_5]$ isostructural with $Cs_2[MoOBr_5]$ [22]. The structure of the latter was refined with molybdenum at the origin and the five bromine and one oxygen ligands statistically disordered over the six octahedral coordination sites. The oxygen atom was fixed at a position giving Mo=O 1.64 Å, and the average Mo–Br bond distance was 2.492(6) Å. For **3**, attempts to allow the nitrogen atom to refine freely were unsuccessful and so this atom was tied to technetium at a fixed Tc≡N distance

TABLE 1. Crystallographic data and details of intensity data collection and structure refinement for $(NEt_4)[TcNBr_4(OH_2)]$ (2) and $Cs_2[TcNCl_5]$ (3)

	$(NEt_4)[TcNBr_4(OH_2)]$	$Cs_2[TcNCl_5]$
Formula	$C_8H_{22}Br_4N_2OTc$	Cs_2Cl_5NTc
Formula weight, M	580.80	555.99
Crystal dimensions (mm)	0.07×0.43×0.36	0.15×0.18×0.17
Crystal colour	blue-black	red
Crystal system	orthorhombic	cubic
Space group	*Pnma*	$Fm\bar{3}m$
a (Å)	11.366(1)	10.211(1)
b (Å)	12.930(2)	
c (Å)	11.540(1)	
Cell volume (Å^3)	1695.95	1064.64
Molecules/cell, Z	4	4
Density (calc.), D_c (g cm^{-3})	2.274	3.468
$F(000)$	1100	980
μ(Cu Kα) (mm^{-1})	16.95	72.90
Transmission factors	0.036–0.368	0.006–0.058
Wavelength (Å)	1.5418	1.5418
$2\theta_{max}$ (°)	142	142
Data collected	octant	hemisphere
θ scan rate (° min^{-1})	10	2.5
θ scan range (°)	$1.2+0.2\tan\theta$	$1.3+0.3\tan\theta$
Independent data measured	1636	1102
No. unique data	1636	78
Rejection criterion ($I<n\sigma(I)$)	2	0
Terms used for refinement, N_o	1434	78
No. parameters refined, N_v	99	10
Weighting parameter, m ($w=(\sigma^2\|F_o\|+m\|F_o\|^2)^{-1}$)	0.001	0.00002
Extinction coefficient, g	0.0086(3)	0.0018(2)
R	0.047	0.034
R_w	0.058	0.036
χ	1.43	6.23
Residual density (e Å^{-3})	+0.91, −1.82	+0.66, −0.68
Max. Δ/σ for last cycle	0.01	0.002

of 1.600 Å. The basis for this choice was the known Tc≡N distance of 1.581(5) Å in $(AsPh_4)[TcNCl_4]$ [11], having regard to the Os≡N distances of 1.604(10) and 1.614(13) Å in $(AsPh_4)[OsNCl_4]$ [23] and $K_2[OsNCl_5]$ [24], respectively.

Refinement of **3** in a manner similar to that reported for $Cs_2[MoOBr_5]$, with technetium fixed at the origin, converged with $R=0.065$, with high residual electron density (2.5 e Å^{-3}) between technetium and nitrogen, and with unusually high thermal parameters on both these atoms. All these features were improved significantly by refining a model in which technetium was allowed to move away from the origin, having one sixth occupancy of each of six sites displaced a small distance from the origin. This scattering model, with the Tc≡N bond fixed at 1.600 Å, converged with $R=0.034$ and with technetium displaced 0.401(3) Å towards the nitrido ligand from the origin, i.e. from the plane of the *cis* chlorine atoms.

The structures were refined by the full-matrix least-squares method, with anisotropic thermal parameters given to non-hydrogen atoms (except N in $Cs_2[TcNCl_5]$). The R indices are defined as $R=\Sigma\Delta F/\Sigma|F_o|$, $R_w=[\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$, and the 'goodness of fit', χ, as $[\Sigma w(\Delta F)^2/(N_o-N_v)]^{1/2}$ where $\Delta F=||F_o|-|F_c||$, N_o is the number of reflections used in the refinement, and N_v is the number of variables. The function minimised was $\Sigma w(\Delta F)^2$. An empirical isotropic extinction correction was refined [25]. During the refinement of **2** four low-order reflections continuously showed gross discrepancies between F_o and F_c values, and were omitted from the final refinement cycles; viz. (200), (400), (440) and (232). Refinement indices are given in Table 1.

Final atomic positional coordinates for **2**, with estimated standard deviations in parentheses, are given in Table 2. See also 'Supplementary material'. For **3**, technetium, chlorine and nitrogen are at (x,0,0) with $x = 0.0393(3)$, 0.2291(5) and 0.196 respectively, with caesium at ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$). Thermal parameters were $U(1,1)$ 0.019(3), $U(2,2)$ 0.019(2) for technetium, $U(1,1)$ 0.0429(6) for caesium, $U(1,1)$ 0.019(1), $U(2,2)$ 0.043(1) for chlorine, and U_{iso} 0.08(6) Å^2 for nitrogen.

Neutral atom scattering-factor curves for carbon, nitrogen, oxygen and chlorine were taken from ref. 26, that for bromine was from ref. 27, those for technetium and caesium were from ref. 28, and that for hydrogen was from ref. 29. Real and imaginary anomalous dispersion corrections were applied to the non-hydrogen atoms [20]. Structure determination and refinement were performed with the SHELX 76 program system [25]. Figure 1 has been prepared from the output of ORTEP [30].

Results and discussion

The species $[TcNX_4]^-$, $[TcNX_4(OH_2)]^-$ and $[TcNX_5]^{2-}$ (X = Cl or Br) are readily interconverted by the addition or removal of the *trans* ligand. In conc. HX solution the species present is most likely $[TcNX_4(OH_2)]^-$ since ESR studies have shown no evidence for the presence of $[TcNX_5]^{2-}$ [31]. In the case of the oxo analogue (X = Cl) the equilibrium

$$trans\text{-}[TcOCl_4(OH_2)]^- + Cl^- \rightleftharpoons [TcOCl_5]^{2-} + H_2O$$

has been established but found to lie strongly to the left [17]. The product which is isolated from solutions of $[TcNX_4(OH_2)]^-$ is dependent on the nature of the added cation. Large cations such as $AsPh_4^+$ or NBu_4^+ result in the precipitation of R[$TcNX_4$] while small cations such as Cs^+ give $Cs_2[TcNX_5]$. The intermediate-size cation NEt_4^+ has allowed the isolation of $(NEt_4)[TcNX_4(OH_2)]$. The presence of coordinated water was shown by intense δ(H–O–H) peaks at 1613 (X = Cl) and 1607 (X = Br) and strong ν(OH) peaks at 3500 (X = Cl) and 3467 (X = Br) cm^{-1}.

TABLE 2. Atomic positional coordinates, with e.s.d. values in parentheses, for $(NEt_4)[TcNBr_4(OH_2)]$ (**2**)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Tc	0.23296(5)	0.25	0.09279(6)
Br(1)	0.35950(7)	0.11392(7)	0.00043(8)
Br(2)	0.14851(7)	0.11444(6)	0.22555(7)
O	0.3926(6)	0.25	0.2346(6)
N(1)	0.1306(8)	0.25	−0.0023(7)
N(2)	0.7559(6)	0.75	0.3860(6)
C(1)	0.6369(9)	0.6121(7)	0.4970(9)
C(2)	0.8775(9)	0.8863(7)	0.2777(8)
C(3)	0.7553(12)	0.6819(11)	0.4963(11)
C(4)	0.6446(11)	0.6851(10)	0.3775(12)
C(5)	0.8646(10)	0.8179(11)	0.3952(11)
C(6)	0.7569(13)	0.8173(12)	0.2788(12)

C(3)–C(6) have occupancy 0.5.

Crystal structures of $(NEt_4)[TcNBr_4(OH_2)]$ (2) and $Cs_2[TcNCl_5]$ (3)

The crystal structure of **2** consists of discrete NEt_4^+ cations and $[TcNBr_4(OH_2)]^-$ anions. A perspective view of the anion of **2**, including the atom numbering, is shown in Fig. 1, and selected interatomic distances and angles for **2** are given in Table 3.

The technetium(VI) atom in **2** is coordinated by four bromine atoms, one nitrogen and one oxygen (coordinated water) atom to give a distorted octahedron. It was not possible in the analysis to establish the presence of the two hydrogens attached to the water molecule. The bromine atoms occupy the

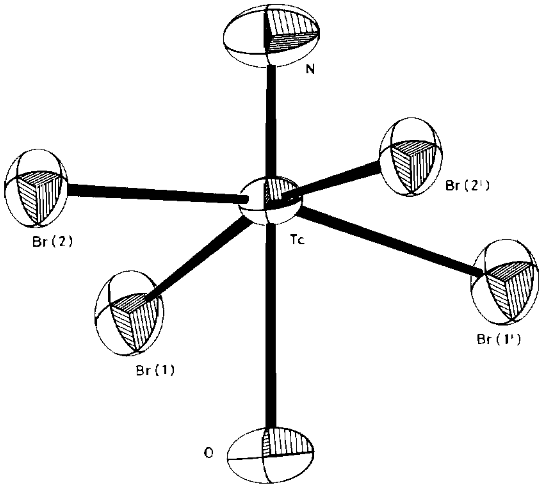

Fig. 1. ORTEP diagram for $(NEt_4)[TcNBr_4(OH_2)]$ (**2**) showing the 50% probability thermal ellipsoids.

TABLE 3. Selected interatomic distances (Å) and angles (°) in the coordination sphere for $[TcNBr_4(OH_2)]^-$ [a]

Tc–N	1.599(9)
Tc–Br(1)	2.510(1)
Tc–Br(2)	2.518(1)
Tc–O	2.443(7)
Br(1)–Tc–N	97.2(2)
Br(1)–Tc–Br(2)	89.37(4)
Br(1)–Tc–Br(1')	89.00(4)
Br(2)–Tc–N	98.0(2)
Br(2)–Tc–Br(1')	164.73(4)
Br(2)–Tc–Br(2')	88.23(4)
O–Tc–N	178.7(3)
O–Tc–Br(1)	81.9(1)
O–Tc–Br(2)	82.9(1)

[a] Primed atoms are related to the corresponding unprimed atoms by the mirror plane.

positions *cis* to the nitrido ligand. The short Tc≡N bond distance of 1.599(9) Å is similar to those observed in $(AsPh_4)[TcNX_4]$, 1.581(5) (X = Cl) and 1.596(6) (X = Br) Å [11, 32]. The very long Tc–O bond distance of 2.443(7) Å for the water molecule in **2** is a manifestation of the strong *trans* influence of the nitrido ligand (one of the strongest π-electron donors known). This distance, and the NM–OH_2 distances of 2.559(9) Å in $(AsPh_4)_2[Tc^VN(CN)_4(OH_2)]\cdot 5H_2O$ [4] and 2.50(3) (X = Cl), 2.42(3) (X = Br) Å, in $K[OsNX_4(OH_2)]\cdot H_2O$ [33, 34], may be compared to the OM–OH_2 distances in $(NEt_4)[Tc^VOBr_4(OH_2)]$, 2.317(9) Å [16], and $(NEt_4)[Mo^VOX_4(OH_2)]$, 2.34(1) (X = Br) and 2.40(1) (X = I) Å [14]. The greater *trans* influence of the nitrido ligand is clearly evident.

The water molecule in **2** is coordinated in an essentially linear arrangement with an N≡Tc–OH_2 angle of 178.7(3)°. The strong *trans* influence of the nitrido ligand also causes the technetium atom to be displaced by 0.334(1) Å from the Br_4 plane with N≡Tc–Br angles of 97.2(2) and 98.0(2)°.

Recently, a study of the TcO^{3+} and TcN^{2+} cores in the same square-pyramidal environments has shown that, although the electronic influence of the nitrido ligand is greater than that of the oxo ligand, there is apparently a larger steric requirement for the latter [9]. A comparison of the structural parameters of the six-coordinate **2** and its oxo analogue $(NEt_4)[TcOBr_4(OH_2)]$ shows similar but smaller differences to those observed in the five-coordinate pair $(AsPh_4)[TcZCl_4]$ (Z = N, O). Thus, the N≡Tc–Br angles in **2** (98.0(2), 97.2(2)°) are smaller than the O=Tc–Br angles in $(NEt_4)[TcOBr_4(OH_2)]$ (99.5(3), 97.6(2)°) and the technetium atom has a lesser displacement (0.33 cf. 0.37 Å) from the Br_4 plane in the nitrido complex. Also the Tc–Br bond lengths of 2.518(1) and 2.510(1) Å in **2** are slightly longer than in $(NEt_4)[TcOBr_4(OH_2)]$, 2.508(1) and 2.505(1) Å, and, as expected, are significantly longer than in the five-coordinate $(AsPh_4)[TcNBr_4]$, 2.4816(5) Å. The Tc^{VI}≡N distance of 1.599(9) Å in **2** and the Tc^V=O distance of 1.618(9) Å in $(NEt_4)[TcOBr_4(OH_2)]$ show a similar trend to the Tc^{VI}≡N and Tc^V=O distances of 1.581(5) and 1.593(8) Å in $(AsPh_4)[TcZCl_4]$.

The crystal structure of **3** consists of discrete Cs^+ cations and $[TcNCl_5]^{2-}$ anions. However, the nitrogen and five chlorine ligand atoms in the anion are equally disordered over six octahedral sites. Similar disorder is to be expected in the salts $Cs_2[TcOX_5]$ (X = Cl, Br) which also crystallise in the cubic system [22]. In the successfully refined model of **3**, the fixed Tc^{VI}≡N bond distance of 1.60 Å compares with a Tc^V=O bond distance of 1.65 Å determined for $[TcOCl_5]^{2-}$ by EXAFS [17]. As expected, the *trans* Tc–Cl distance of 2.740(5) Å in **3** is greater than that of 2.50 Å in the oxo analogue. The *cis* Tc–Cl distances in **3**, 2.373(5) Å, are slightly greater than those of 2.36 Å in the oxo analogue, as found in other comparisons of oxo and nitrido complexes of technetium in identical coordination environments. The N≡Tc–Cl angle is 99.73(8)°. The displacement of technetium from the Cl_4 plane in **3** is 0.401(3) Å and compares with an estimated value of 0.28 Å in $Cs_2[MoOBr_5]$ [22] and a calculated value of 0.26 Å in $K_2[OsNCl_5]$ [24]. This parameter is not available for $[TcOCl_5]^{2-}$ from the EXAFS study.

Infrared spectra

The presence of a *trans* ligand in six-coordinate oxo and nitrido complexes results in a decrease in the M=O or M≡N IR stretching frequencies relative to the five-coordinate complexes. When the *trans* ligand is halide this decrease is considerable, ν(Tc≡N) in $R[TcNX_4]$ (X = Cl, Br; R = $AsPh_4$, $NnBu_4$) is in the range 1080–1074 cm^{-1} [11] and in $Cs_2[TcNX_5]$, 1028–1027 cm^{-1} [31, 18]. For the oxo analogues $(NnBu_4)[TcOX_4]$ (X = Cl or Br) and $Cs_2[MOX_5]$ (M = Tc, X = Cl or Br; M = Mo, X = Cl) the corresponding ν(M=O) absorptions are in the ranges 1020–1011 and 954–950 cm^{-1} [17].

Complex **1** was found to undergo essentially complete dehydration under vacuum at room temperature, to give $(NEt_4)[TcNCl_4]$. This was shown by the disappearance of the intense δ(H–O–H) peak at 1613 cm^{-1} and the ν(OH) peak at 3500 cm^{-1}. Dehydration was also achieved by dissolution of **1** in thionyl chloride and removal of the solvent. Exposure of $(NEt_4)[TcNCl_4]$ to the atmosphere resulted in rapid absorption of water, which was largely complete at one hour and after three hours the IR spectrum was identical with that of **1**. The absorption of water resulted in the decrease of ν(Tc≡N) from 1070 to 1065 cm^{-1}, indicative of weak technetium–water binding. The removal of the water molecule from **1** caused significant changes in the cation peaks, in particular the peaks in the region 1484–1441 cm^{-1} coalesced to a single peak at 1459 cm^{-1}. The bromo complex **2** was unaffected under the drying conditions used for **1**.

Similar behaviour has been reported for $R[MoOX_4(OH_2)]$ complexes. The dried complex $(AsPh_4)[MoOCl_4]$ was found to rapidly absorb water from the atmosphere with a consequent decrease of ν(Mo=O) from 1012 to 981 cm^{-1} [35]. Other reported ν(Mo=O) values for these complexes are 1015 and 985 cm^{-1} [36]. While $(AsPh_4)[MoOCl_4(OH_2)]$ was completely dehydrated under vacuum, the bromo complex was only partially dehydrated under the same conditions, with an increase of ν(Mo=O) from 981 to 1007 cm^{-1} [35]. The M–OH$_2$ distances in R[MoOX$_4$(OH$_2$)] (X=Cl, Br, I) [14, 36] and (NEt$_4$)[TcOBr$_4$(OH$_2$)] [16] lie in the range 2.32–2.40 Å which is significantly shorter than the 2.443(7) Å distance in **2**. Since M–OH$_2$ distances appear to be greater in chloro than in bromo complexes (for example, M–OH$_2$ 2.50(3) (X=Cl), 2.42(3) (X=Br) Å in K[OsNX$_4$(OH$_2$)]·H$_2$O [33, 34], and 2.393(15) Å in (AsPh$_4$)[MoOCl$_4$(OH$_2$)] [36], 2.34(1) Å in (NEt$_4$)[MoOBr$_4$(OH$_2$)] [14]) the small difference in ν(Tc≡N) for **1** and the dehydrated complex is consistent with a long NTc–OH$_2$ bond in **1**. The ν(Tc=O) values for (NEt$_4$)[TcOBr$_4$(OH$_2$)] and [NnBu$_4$][TcOBr$_4$] are 1000 and 1011 [37] (or 1015 [38]) cm^{-1}, respectively.

Supplementary material

Atomic thermal parameters and observed and calculated structure factors for both structures are available from the authors on request.

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