Studies of Technetium Complexes. Part 6.[1] The Preparation, Characterisation, and Electron Spin Resonance Spectra of Salts of Tetrachloro- and Tetrabromo-nitridotechnetate(VI): Crystal Structure of Tetraphenylarsonium Tetrachloronitridotechnetate(VI)*

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The air-stable compounds R[$TcNCl_4$] and R[$TcNBr_4$] (R = [$AsPh_4$]$^+$ or [$NBu^n{}_4$]$^+$) have been prepared by the reaction of [NH_4][TcO_4] with NaN_3 in the presence of concentrated HCl or of HBr. The e.s.r. spectra of [$TcNCl_4$]$^-$ and [$TcNBr_4$]$^-$ are typical of ions with a $4d^1$ electronic configuration and the unpaired electron in an orbital with substantial $4d_{xy}$ character. The crystal structure of [$AsPh_4$][$TcNCl_4$] has been determined by single-crystal *X*-ray diffraction methods at 21 °C. Crystals are tetragonal, space group *P*4/*n*, with *a* = 12.707(2), *c* = 7.793(1) Å, and *Z* = 2. Full-matrix least-squares refinement gave a final *R* value of 0.031 for 1 079 independent reflections. The compound is isostructural with the series [$AsPh_4$][$MNCl_4$] (M = Mo, W, Re, Ru, or Os) and with [$AsPh_4$][$MOCl_4$] (M = Mo or Re). The [$TcNCl_4$]$^-$ anion in [$AsPh_4$][$TcNCl_4$] possesses C_{4v} symmetry with Cl–Tc–Cl bond angles of 86.95(1) and 153.33(6)° and N≡Tc–Cl bond angles of 103.34(3)°. The Tc≡N bond distance is 1.581(5) Å and the Tc–Cl distances are 2.3220(9) Å.

The preparation and chemical properties of transition-metal complexes containing metal–nitrogen bonds have attracted much attention in recent years.[2,3] The nitrido-ligand (N^{3-}) is a powerful π-electron donor which may act as a terminal or bridging ligand and which tends to stabilise metals in high oxidation states. Complexes of the type [$M^{VI}NX_4$]$^-$ (X = halide) have been reported for molybdenum, tungsten, rhenium, ruthenium, and osmium.[3] The structures of the tetraphenylarsonium salts of the [$MNCl_4$]$^-$ ions of most of these elements have been determined by *X*-ray crystallography. These complexes, which form an isostructural series, are characterised by short metal–nitrogen bond distances which correspond to M≡N bonds.[4]

The reduction of the pertechnetate anion (TcO_4^-) by hydrazine hydrochloride in the presence of triphenylphosphine and dithiocarbamate ligands has been reported to give the five-co-ordinate nitrido-complexes [$TcCl_2(PPh_3)_2N$] and [$Tc(S_2CNEt_2)_2N$] respectively.[5,6] We now report the preparation, by use of azide ion, of the tetraphenylarsonium and tetrabutylammonium salts of tetrachloro- and tetrabromo-nitridotechnetate(VI), R[$TcNX_4$] (R = [$AsPh_4$]$^+$ or [$NBu^n{}_4$]$^+$, X = Cl or Br). As the structures of only two complexes containing the Tc≡N group are known, [$Tc(S_2CNEt_2)_2N$] and [$Tc(NCS)_2(CH_3CN)(PPh_3)_2N$],[6,7] and in order to compare the properties of the [$TcNCl_4$]$^-$ ion with those of the [$MNCl_4$]$^-$ ions of other transition metals, we have determined the *X*-ray crystal structure of tetraphenylarsonium tetrachloronitridotechnetate(VI), [$AsPh_4$][$TcNCl_4$].

Whilst there have been several e.s.r. studies of tetrahalogeno-oxometal complexes where the metal ion has the d^1 electron configuration, the e.s.r. spectra of the corresponding tetrahalogenonitrido-complexes have received comparatively little attention. The present study affords the opportunity to compare, in a qualitative fashion, the e.s.r. parameters of a $4d^1$ tetrahalogenonitrido-complex with other nitrido- or tetrahalogeno-oxo-complexes. Although e.s.r. spectra due to Tc^{VI} have been reported previously,[8] this is also the first report of the e.s.r. spectrum of Tc^{VI} where the parameters are characteristic of the unpaired electron being largely in a metal orbital instead of being highly delocalised.

Most of the technetium-99m radiopharmaceuticals currently in use are prepared by the reduction of pertechnetate by tin(II) in the presence of a chelating agent. In many cases this results in radiopharmaceuticals containing the Tc=O moiety.[9] The use of [$^{99m}TcNX_4$]$^-$ to prepare new radiopharmaceuticals based on the Tc≡N group has been investigated and the results will be reported elsewhere.

Experimental

Ammonium [^{99}Tc]pertechnetate (34.5 mg Tc per cm^3 in 0.1 mol dm^{-3} NH_4OH solution) was supplied by Amersham International plc. I.r. spectra were determined for KBr discs on a Perkin-Elmer 197 spectrophotometer and optical spectra on a Beckman Acta CII spectrophotometer. E.s.r. spectra were recorded at 120 K on a Varian E-12 spectrometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

Tetraphenylarsonium Tetrachloronitridotechnetate(VI).—Ammonium pertechnetate (63 mg, 0.35 mmol) was mixed with concentrated hydrochloric acid (32% w/w, 20 cm^3). Sodium azide (200 mg, 3.1 mmol) dissolved in water (0.5 cm^3) was then carefully added. The mixture turned orange with the evolution of gas and was heated under reflux for 20 min. Addition of tetraphenylarsonium chloride (160 mg, 0.38 mmol) dissolved in water (2 cm^3) gave an orange precipitate which was collected by filtration, washed with concentrated hydrochloric acid and then with diethyl ether. Yield 210 mg (94% based on Tc). The complex was recrystallised from benzene–acetonitrile (1 : 1 v/v) to give orange-red needles, m.p. 272—274 °C (Found: C, 45.4; H, 3.35; Cl, 22.3; N, 2.40. $C_{24}H_{20}AsCl_4NTc$ requires C, 45.2; H, 3.15; Cl, 22.2; N, 2.20%). The i.r. spectrum showed peaks at 1 482s, 1 441vs, 1 437vs, 1 084vs, 1 076s, 997s, 742vs, 688vs, and 680vs cm^{-1}. Optical spectrum (CH_3CN): 463 (ε = 180), 404 (473), and 297 nm (158 m^2 mol^{-1}).

Tetra-n-butylammonium Tetrachloronitridotechnetate(VI).—Addition of tetra-n-butylammonium hydroxide (0.42 mmol) to the orange-red hydrochloric acid solution described above

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* *Supplementary data available* (No. SUP 56030, 4 pp.): thermal parameters, non-bonded contact distances. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. E.s.r. spectral parameters for $[TcNCl_4]^-$, $[TcNBr_4]^-$, and $[ReNCl_4]^-$ anions

Anion	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}/cm^{-1}$	$A_{\perp}/cm^{-1}$	Q/cm^{-1}	Ref.
$[TcNCl_4]^-$	2.008 ±0.002	2.000 ±0.002	0.0293 ±0.0001	0.0134 ±0.0001	0.000 35 ±0.000 15	*a*
$[TcNBr_4]^-$	2.147 ±0.002	2.034 ±0.002	0.0248 ±0.0002	0.0120 ±0.0002	not resolved	*a*
$[ReNCl_4]^{-\,b}$	1.918	1.947	0.077	0.0391	0.0047	27
$[ReNCl_4]^{-\,c}$	1.909	1.934	0.077	0.0382	0.0016	27

[a] This paper. [b] Single crystal. [c] Acetonitrile solution.

gave an orange precipitate. Yield 165 mg (95% based on Tc). The solid was dissolved in acetonitrile (3 cm^3) and diethyl ether (20 cm^3) was then added. On cooling, orange crystals slowly formed and were collected by filtration, m.p. 181—182 °C (Found: C, 38.65; H, 7.10; Cl, 28.9; N, 5.55. $C_{16}H_{36}Cl_4N_2Tc$ requires C, 38.65; H, 7.30; Cl, 28.5; N, 5.65%). The i.r. spectrum showed peaks at 2 965vs, 2 948s, 2 878s, 1 470vs, 1 080s, and 736m cm^{-1}. Optical spectrum (CH_3CN): 463 (ε = 181), 404 (472), and 297 nm (155 m^2 mol^{-1}).

Tetraphenylarsonium Tetrabromonitridotechnetate(VI).—When concentrated hydrobromic acid (47—49% w/w) was used in place of hydrochloric acid, refluxing for 15 min resulted in a deep violet solution. Addition of tetraphenylarsonium chloride (160 mg, 0.38 mmol) to the cooled solution gave a deep blue precipitate which was collected by filtration, washed with concentrated hydrobromic acid and then diethyl ether. Yield 255 mg (90% based on Tc). Recrystallisation from acetonitrile gave blue-black crystals, m.p. 293—295 °C (decomp.) (Found: C, 35.55; H, 2.65; Br, 40.0; N, 1.85. $C_{24}H_{20}AsBr_4NTc$ requires C, 35.35; H, 2.45; Br, 39.2; N, 1.70%). The i.r. spectrum showed peaks at 1 482s, 1 440vs, 1 436vs, 1 084vs, 1 074s, 977s, 742vs, 688vs, and 680vs cm^{-1}. Optical spectrum (CH_3CN): 610 (ε = 327), 561 (246), 509 (301), 405 (68), and 295 nm (561 m^2 mol^{-1}).

Tetra-n-butylammonium Tetrabromonitridotechnetate(VI).—Addition of tetra-n-butylammonium bromide (125 mg, 0.39 mmol) to the cooled hydrobromic acid solution described above gave a blue precipitate. Yield 220 mg (93% based on Tc). The complex was purified by dissolution in acetonitrile and precipitation with diethyl ether to give brilliant blue crystals, m.p. 202—203 °C (Found: C, 28.75; H, 4.55; Br, 47.5; N, 4.15. $C_{16}H_{36}Br_4N_2Tc$ requires C, 28.45; H, 5.40; Br, 47.4; N, 4.15%). The i.r. spectrum showed peaks at 2 962vs, 2 945vs, 2 875vs, 1 468vs, 1 077s, and 735m cm^{-1}. Optical spectrum (CH_3CN): 611 (ε = 343), 561 (254), 509 (310), 405 (68), and 295 nm (555 m^2 mol^{-1}).

E.S.R. Spectroscopy.—A 2.5 × 10^{-3} mol dm^{-3} solution of $[AsPh_4][TcNCl_4]$ in acetone was orange in colour and when frozen to 120 K gave the e.s.r. spectrum shown in Figure 1. The spectrum could be described in terms of the axially symmetric spin Hamiltonian (1) where $S = \frac{1}{2}$, $I = \frac{9}{2}$, and the

$$\mathcal{H} = g_{\parallel}\beta B_zS_z + g_{\perp}\beta(B_xS_x + B_yS_y) + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) + Q[I^2{}_z - I(I + 1)/3] \quad (1)$$

other symbols have their usual meanings. The spectrum was simulated on a Data General S-140 computer by use of the programs described by De Bolfo *et al.*,[10] which employ the second-order perturbation-theory expressions for the magnetic fields and transition probabilities.[11] The parameters giving the best fit to the experimental spectrum are given in Table 1 and a simulated spectrum is also shown in Figure 1. The best fit was obtained when the quadrupole interaction was included in the spin Hamiltonian. Unlike the case of $[AsPh_4]_2[Tc(NO)(NCS)_5]$ reported previously,[12] forbidden transitions ($\Delta m = \pm 1$) were not observed. These forbidden transitions are calculated to be *ca.* 2% of the intensity of the $\Delta m = 0$ transition, but their most intense features occur at fields where the absorptions due to the allowed transitions are also the strongest. A noteworthy aspect of the experimental spectrum is that whilst the features arising from molecules oriented with their magnetic symmetry axis perpendicular to the magnetic field could be fitted with a Gaussian lineshape, the features arising from molecules with the symmetry axis parallel to the magnetic field were best fitted with a Lorentzian lineshape. Lorentzian lineshapes are usually associated with homogeneous broadening which may arise from lifetime-broadening effects such as spin–lattice relaxation, whilst Gaussian lineshapes arise from inhomogeneous broadening such as that due to the unresolved superhyperfine structure.[13] One may then ascribe the parallel linewidth to the natural linewidth, and the perpendicular linewidth to unresolved superhyperfine structure from the four Cl nuclei.

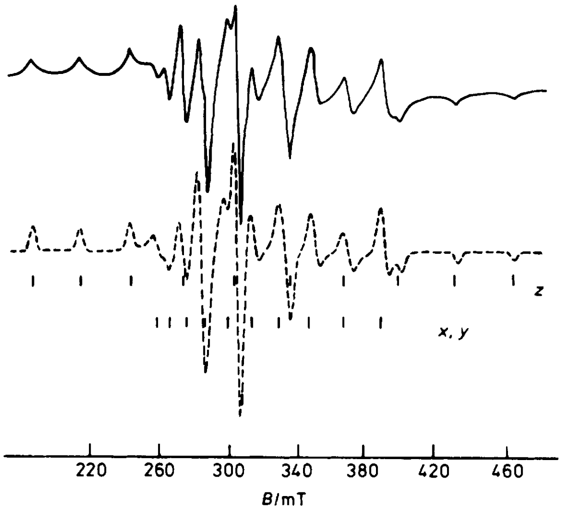

Figure 1. E.s.r. spectrum of $[AsPh_4][TcNCl_4]$ (1.0 × 10^{-3} mol dm^{-3}) in acetone at 120 K and a microwave frequency of 9 139 MHz (solid line). The broken line is a computer-simulated spectrum for $\Delta m = 0$ using a Gaussian lineshape with widths 1.1 mT in the parallel direction and 2.2 mT in the perpendicular direction. The stick spectra relate to the parallel (*z*-axis) and perpendicular (*xy*-plane) directions

The e.s.r. spectra of $[AsPh_4][TcNCl_4]$ and $[NBu^n{}_4][TcNCl_4]$ in frozen acetonitrile solution at 120 K were not as well resolved. They could be fitted with *g* and *A* values similar to

Table 2. Final atomic positional co-ordinates for $[AsPh_4][TcNCl_4]$

Atom	X/a	Y/b	Z/c
Tc	0.25	0.25	0.120 73(6)
N	0.25	0.25	−0.082 1(7)
Cl(1)	0.341 5(1)	0.402 5(1)	0.189 5(1)
As	0.25	0.75	0
C(1)	0.368 6(2)	0.737 3(2)	0.148 0(4)
C(2)	0.443 5(2)	0.660 5(3)	0.119 5(4)
C(3)	0.525 5(3)	0.649 4(3)	0.235 1(5)
C(4)	0.530 6(3)	0.713 8(3)	0.376 7(5)
C(5)	0.457 0(3)	0.790 5(3)	0.403 9(5)
C(6)	0.374 5(3)	0.803 1(3)	0.289 6(4)
H(2)	0.446(3)	0.613(3)	0.019(5)
H(3)	0.576(3)	0.595(3)	0.217(5)
H(4)	0.588(4)	0.702(3)	0.449(6)
H(5)	0.460(3)	0.835(3)	0.509(5)
H(6)	0.318(3)	0.854(3)	0.316(5)

those of $[AsPh_4][TcNCl_4]$ in acetone, although only an upper limit of 0.0005 cm^{-1} could be set for Q because of the larger linewidth.

Solutions of $[AsPh_4][TcNBr_4]$ and $[NBu^n{}_4][TcNBr_4]$ in acetone or acetonitrile had an intense blue colour. The best resolved spectrum at 120 K was that of $[AsPh_4][TcNBr_4]$ in acetonitrile, which was simulated with the parameters given in Table 1. As for $[AsPh_4][TcNCl_4]$ the parallel lineshapes appeared to be Lorentzian and the perpendicular lineshapes Gaussian, and it should be noted that the Br nuclei have a substantially larger magnetic moment than do Cl nuclei. The $[TcNBr_4]^-$ spectra were less well resolved than those of the $[TcNCl_4]^-$ species, and this broadening is probably due to solute aggregation in frozen solution. However, none of the spectra shows evidence for the formation of discrete dimeric or polynuclear species.

Crystallography.—Single crystals of $[AsPh_4][TcNCl_4]$ suitable for X-ray diffraction studies were grown by slow evaporation at room temperature of an acetonitrile–benzene (1 : 1 v/v) solution. The crystals were assumed to be tetragonal, of space group $P4/n$ as is found for the isostructural series $[AsPh_4][MNCl_4]$ with M = Mo, W, Re, Ru, or Os. This was confirmed by the systematic absences observed during data collection on a diffractometer. Unit-cell parameters, together with their estimated standard deviations (e.s.d.s), were derived by a least-squares analysis [14] of the setting angles, determined on a diffractometer at 21 °C with Cu-K_α radiation (λ = 1.5418 Å), for 13 angularly well separated reflections each with 2θ greater than 40°.

Crystal data.—$C_{24}H_{20}AsCl_4NTc$, M = 638.07, tetragonal, a = 12.707(2), c = 7.793(1) Å, U = 1 258.3 Å^3, Z = 2, D_c = 1.684 Mg m^{-3}, $F(000)$ = 630, space group $P4/n$, μ(Cu-K_α) = 9.732 mm^{-1}.[15]

Intensity data were recorded at 20 ± 1 °C on an automatic Siemens AED diffractometer with nickel-filtered Cu-K_α radiation. The crystal had 17 well defined faces of type (100), (010), (001), (110), and (111), and the average 'diameter' of the crystal was 0.25 mm. The crystal was aligned with the c axis approximately parallel to the diffractometer φ axis. Intensities were measured by the 'five-values' θ—2θ scan procedure detailed by Hoppe,[16] with a 2θ scan rate of 10° min^{-1}. A reference reflection, monitored every 20 reflections, showed no significant variation in intensity during data collection. A unique octant of data was collected within the limit $(\sin\theta)/\lambda \leqslant 0.609$ Å^{-1}, together with a second octant of data within $(\sin\theta)/\lambda \leqslant 0.497$ Å^{-1}. Altogether, 1 974 distinct (not systematically absent) reflections were obtained. The intensities of equivalent reflections, after absorption corrections, were in excellent agreement, and these were combined to yield 1 173 unique reflections. Of these, 1 079 reflections were considered observed $[I > 2\sigma(I)]$ and were used for the structure analysis. The integrated intensities were corrected for Lorentz and polarisation effects, and for absorption.[15]

Structure Refinement.—The structure was solved by reference to the isostructural $[AsPh_4][OsNCl_4]$,[17] together with Fourier-difference syntheses. Atomic co-ordinates are in terms of a unit cell in space group $P4/n$ with the origin at $\bar{1}$, and are related to those of $[AsPh_4][OsNCl_4]$ by the transformation (x, 0.5 − y, z). Full-matrix least-squares refinement, with data uncorrected for absorption and with isotropic thermal parameters assigned to all (non-hydrogen) atoms, converged (1 079 data, 34 variables) with a reliability index R, defined as $\Sigma\Delta F/\Sigma|F_o|$ where $\Delta F = ||F_o| - |F_c||$, of 0.108. The function minimised was $\Sigma w(\Delta F)^2$, where $w = [\sigma^2(F_o) + 0.0001F_o{}^2]^{-1}$ is the weight assigned to the $|F_o|$ values. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, and refinement converged (72 variables) with R 0.053. The positions of all five hydrogen atoms were evident on a Fourier-difference map, and these atoms were included in the scattering model with variable co-ordinates and individual isotropic thermal parameters. Refinement (92 variables) converged with R 0.048. After absorption corrections had been applied to the intensity data, with transmission factors ranging between 0.15 and 0.32, the same refinement converged with R 0.045.

An analysis of $|F_o|$ and $|F_c|$ values at this stage indicated the presence of a significant extinction effect. An empirical isotropic extinction parameter was included in the model,[18] and refinement [93 variables (N_v), 1 079 data (N_o)], converged with R 0.031, R' {defined as $[\Sigma w(\Delta F)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$} 0.033, and χ {defined as $[\Sigma w(\Delta F)^2/(N_o - N_v)]^{\frac{1}{2}}$} 2.18. The maximum parameter shift-to-error ratio at convergence was 0.09 : 1. The largest peaks on a final difference synthesis were of heights 0.48 and −0.82 e Å^{-3}.

Final atomic positional co-ordinates, with e.s.d.s in parentheses, are listed in Table 2.

Neutral-atom scattering-factor curves for C, N, and Cl were taken from ref. 19, those for neutral As and Tc from ref. 20, and that for H from ref. 21. Real and imaginary anomalous dispersion corrections were applied to the non-hydrogen atoms.[15] The structure determination and refinement were performed with the SHELX 76 program system [18] on the Commonwealth Department of Health IBM 370/168 computer.

Results and Discussion

The most generally useful method for the preparation of transition-metal halogenonitrido-complexes is the reaction of azides, in particular halogen azides, with the metal halides followed by decomposition of the metal azide halides. Nitrido-complexes of the structure $MNCl_3$ (M = Mo, W, or Re) have been prepared by this method and converted into the $[AsPh_4][MNCl_4]$ salts by reaction with $AsPh_4Cl$.[3] In some cases salts of $[MNX_4]^-$ ions have been prepared in the presence of aqueous hydrohalogenic acids. The reaction of ruthenium tetraoxide with sodium azide in the presence of hydrochloric and of hydrobromic acids has been used to prepare the $[AsPh_4][RuNX_4]$ (X = Cl or Br) complexes and the reaction of potassium osmate with hydrochloric acid and sodium azide has been reported to give $[AsPh_4][OsNCl_4]$ on precipitation with $AsPh_4Cl$.[22]

We have now achieved the facile preparation of $[AsPh_4][TcNX_4]$ and $[NBu^n_4][TcNX_4]$ (X = Cl or Br) complexes in excellent yield by the reaction of ammonium pertechnetate in concentrated hydrochloric or hydrobromic acid with sodium azide and precipitation by the organic cations. The structures of these complexes were assigned on the basis of the microanalytical and e.s.r. data, and the presence of sharp absorption bands at 1 074—1 080 cm^{-1} in the solid-state i.r. spectra. Absorption in the region 1 000—1 100 cm^{-1} is characteristic of terminal $M{\equiv}N$ groups.[3] There were no absorptions bands in the region 1 900—2 500 cm^{-1}, confirming the absence of co-ordinated azido-groups. The crystal structure of $[AsPh_4][TcNCl_4]$ has been determined by *X*-ray diffraction analysis.

Reduction of pertechnetate by concentrated hydrochloric or hydrobromic acids at room temperature gives the technetium(V) oxo-complexes $[TcOX_4]^-$ (X = Cl or Br) which are further reduced to the technetium(IV) complexes $[TcX_6]^{2-}$ on heating with the corresponding acid.[23] We find that the addition of sodium azide to pertechnetate in concentrated hydrobromic acid at room temperature results in the formation of a deep violet colour and the evolution of gas. The reaction with hydrochloric acid results in an orange solution. Both reaction mixtures were refluxed to ensure completion of reaction and to destroy the excess of azide ion.

Since the decomposition of a metal azido-complex to form the nitrido-complex results in a +2 change in the oxidation state of the metal,[24] it is probable that a technetium(IV) intermediate is involved in the formation of the $[TcNX_4]^-$ ions. The stability of the $[TcNX_4]^-$ ions to the reaction conditions is surprising and indicates a remarkable resistance of the $Tc{\equiv}N$ bond to acid hydrolysis. All of the tetrahalogenonitridotechnetate salts were stable in the air. This behaviour may be contrasted with that of $[AsPh_4][MoNCl_4]$ which has been reported to be extremely sensitive to hydrolysis and to react in moist air to form $[AsPh_4][MoOCl_4]$.[25] The $[TcNX_4]^-$ ions are, apart from the tetraoxotechnetate(VI) anion, the only examples of technetium(VI) anions to be prepared in solution. The violet $[NMe_4]_2[TcO_4]$ is reported to be extremely sensitive to oxygen and to atmospheric moisture which cause rapid oxidation and disproportionation.[26]

E.S.R. Spectra.—The only previously published e.s.r. spectrum of a technetium(VI) complex is by Kirmse *et al.*[8] for $[Tc^{VI}(abt)_3]$ [abt = 2-aminobenzenethiolate(2−)], where the spectrum could be fitted by an anisotropic g value close to the free-spin value g_e, and a small anisotropic splitting of magnitude 0.001 cm^{-1} or less. In contrast, in the present case, although the g values are close to g_e, the hyperfine splittings are much larger and are consistent with the values expected from a consideration of the magnetic moment of the ^{99}Tc nucleus and the values observed for the $[ReNCl_4]^-$ anion as given in Table 1.

The g and A values of both $[TcNCl_4]^-$ and $[TcNBr_4]^-$ are not affected by changes in either the cation or the solvent. In the case of $[ReNCl_4]^-$, Q was reduced by a factor of three in acetonitrile solution when compared with its value in dilute solution in a crystalline host lattice, although the values of g and A were only slightly affected.[27]

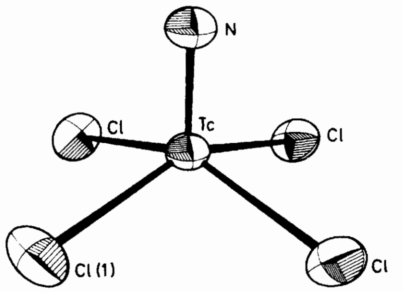

Figure 2. An ORTEP drawing of the $[TcNCl_4]^-$ anion in $[AsPh_4][TcNCl_4]$. The thermal ellipsoids are drawn at the 30% probability level

The g and A values for $[TcNCl_4]^-$ and $[TcNBr_4]^-$ show trends which are consistent with those observed for the analogous anion $[ReNCl_4]^-$ and the d^1 transition metal halogeno-oxo-anions such as $[CrOCl_4]^-$ and $[MoOCl_4]^-$.[28] In these complexes the unpaired electron is in an orbital of b_2 symmetry, *i.e.* primarily a metal d_{xy} orbital. However, the predictions of simple theory, that $g_\parallel < g_\perp < g_e$ (where g_e is the free-electron g value), are generally not fulfilled because the excited-state molecular orbitals of b_1 and e symmetry make such a large contribution that situations may even arise where $g_\parallel > g_\perp > g_e$.[29] The magnitude of these contributions is determined by the admixture coefficients of the metal orbitals and the ligand σ and π orbitals, the metal and ligand spin–orbit coupling coefficients, and the electronic transition (*d–d*) energies. Recent SCF-MS-Xα calculations by Sunil *et al.*[28,30] have shown that the observed g and A values of a series of vanadium, chromium, and molybdenum tetrahalogeno-oxo- and pentahalogeno-oxo-complexes may be satisfactorily explained in this way. Such calculations have also given values of the molecular-orbital coefficients which are in reasonable agreement with those derived by restricted Hartree–Fock calculations and by empirical means. Although detailed calculations have not been performed in the present case, some general deductions may be made.

A comparison of the g and A values of $[TcNCl_4]^-$ and $[TcNBr_4]^-$ shows the expected increase in g and the decrease in A arising from the much larger spin–orbit coupling constant of the Br^- ion (2 000 cm^{-1}) when compared with that of the Cl^- ion (500 cm^{-1}). However, the colour change from orange to blue indicates a decrease in *d–d* transition energies which also contributes to the increase in g values.

It is a little surprising that the value of $g_\perp$ is so close to g_e. Whilst there are a number of contributions to $g_\parallel$, the orbitals affecting $g_\perp$ are primarily those of e symmetry.[31] The large contribution to $g_\perp$ from these orbitals could then be taken to imply strong Tc–N π bonding, which would be consistent with the higher stretching frequencies of $Tc{\equiv}N$ bonds observed here (1 080—1 074 cm^{-1}) relative to those of Tc=O (1 020—996 cm^{-1}) in $[TcOX_4]^-$ (X = Cl, Br, or I).[32,33] Similar conclusions have been drawn for the nitrido-complexes of rhenium [27] and osmium.[34]

Crystallography.—The geometry and atom numbering of the $[TcNCl_4]^-$ anion in $[AsPh_4][TcNCl_4]$ are shown in Figure 2. Interatomic bond distances and angles, with e.s.d.s derived from the refinement, are given in Table 3. There are no interionic contacts for $[TcNCl_4]^-$ of less than the sums of the appropriate van der Waals radii.

The structure consists of discrete $[AsPh_4]^+$ and $[TcNCl_4]^-$ ions. The $[TcNCl_4]^-$ ions possess ideal C_{4v} symmetry and the compound $[AsPh_4][TcNCl_4]$ is isostructural with the series $[AsPh_4][MNCl_4]$ (M = Mo, W, Re, Ru, or Os) [4] and with

Table 3. Interatomic bond distances (Å) and selected bond angles (°) in [AsPh$_4$][TcNCl$_4$]. Roman numeral superscripts refer to the following co-ordinate transformations: I $0.5 - y, x, z$; II $0.5 - x, 0.5 - y, z$; III $0.5 - x, 1.5 - y, z$; IV $-0.5 + y, 1 - x, -z$

Tc–N	1.581(5)	C(3)–C(4)	1.376(6)
Tc–Cl(1)	2.322 0(9)	C(4)–C(5)	1.367(6)
As–C(1)	1.905(3)	C(5)–C(6)	1.385(4)
C(1)–C(2)	1.381(4)	C(6)–C(1)	1.387(4)
C(2)–C(3)	1.384(4)		

N–Tc–Cl(1)	103.34(3)	C(2)–C(1)–C(6)	121.1(3)
Cl(1)–Tc–Cl(1$^{\mathrm{I}}$)	86.95(1)	C(1)–C(2)–C(3)	119.0(3)
Cl(1)–Tc–Cl(1$^{\mathrm{II}}$)	153.33(6)	C(2)–C(3)–C(4)	119.8(4)
C(1)–As–C(1$^{\mathrm{III}}$)	105.5(2)	C(3)–C(4)–C(5)	121.1(3)
C(1)–As–C(1$^{\mathrm{IV}}$)	111.5(1)	C(4)–C(5)–C(6)	120.1(4)
As–C(1)–C(2)	120.5(2)	C(5)–C(6)–C(1)	118.8(3)
As–C(1)–C(6)	118.2(2)		

[AsPh$_4$][MOCl$_4$] (M = Mo or Re).[35,36] The parameters of the [AsPh$_4$]$^+$ ion in the [AsPh$_4$][TcNCl$_4$] structure are as expected and need not be discussed further.

A comparison of the metal–nitrogen and metal–chlorine bond distances and bond angles of the isostructural [AsPh$_4$][MNCl$_4$] (M = Mo, Tc, Re, Ru, or Os) compounds is presented in Table 4. All of the metal–nitrogen bonds are short, corresponding to triple bonds. There is a trend to longer M≡N bonds in going from the second to the third transition series. Except for [AsPh$_4$][MoNCl$_4$] there is little variation in the M–Cl bond distances and the N≡M–Cl bond angles.

The Tc$^{\mathrm{VI}}$≡N bond distance in [AsPh$_4$][TcNCl$_4$] is 0.038(11) Å shorter than the Re$^{\mathrm{VI}}$≡N bond distance in [AsPh$_4$][ReNCl$_4$].[4] This value is comparable with the difference [0.052(10) Å] in the M$^{\mathrm{V}}$≡N bond distances of [Tc(S$_2$CNEt$_2$)$_2$N] [1.604(6) Å][6] and the isostructural rhenium analogue [Re(S$_2$CNEt$_2$)$_2$N] [1.656(8) Å].[37] The only other Tc≡N bond distance which has been determined is 1.629(4) Å in [Tc(NCS)$_2$(CH$_3$CN)(PPh$_3$)$_2$N].[7] While it is reasonable to compare M≡N bond distances in isostructural analogues, it should be noted that in other cases M≡N distances may be sensitive to steric factors. Thus the 1.602(9) Å Re$^{\mathrm{V}}$≡N bond distance in the five-co-ordinated [ReCl$_2$(PPh$_3$)$_2$N][38] is increased to 1.788(11) Å in the six-co-ordinated *mer*-[ReCl$_2$(PEt$_2$Ph)$_3$N] which contains an additional bulky phosphine ligand.[39]

The Cl(1)–Tc–Cl(1$^{\mathrm{I}}$) and Cl(1)–Tc–Cl(1$^{\mathrm{II}}$) angles of 86.95(1) and 153.33(6)° respectively in the [TcNCl$_4$]$^-$ ion are essentially the same as the corresponding angles [86.88(3) and 153.0(1)°] in the [ReNCl$_4$]$^-$ ion.[4]

It is of particular interest to compare the geometry of [TcNCl$_4$]$^-$ with that of the [TcOCl$_4$]$^-$ ion. In [AsPh$_4$][TcNCl$_4$] the N≡Tc–Cl angles are 103.34(3)° and the Tc atom lies 0.54 Å above the plane of the four chlorine atoms. The Tc=O bond distance in [N(PPh$_3$)$_2$][TcOCl$_4$] is short [1.610(4) Å] and the two pairs of O=Tc–Cl bond angles have average values of 103.2 and 110.4°.[40] The Tc atom in the [TcOCl$_4$]$^-$ ion lies 0.66 Å above the S_4-ruffled 'square base.' The Cl–M–Cl angles between adjacent chlorine atoms are 86.95(1)° for [AsPh$_4$][TcNCl$_4$] while those of [N(PPh$_3$)$_2$][TcOCl$_4$] range from 85.1(1) to 85.8(1)°. This shows that the steric requirements of the oxo- and nitrido-ligands, manifested in the repulsion of the basal ligands from the Tc=O or Tc≡N bond, are similar in these square-pyramidal complexes.

The [TcOCl$_4$]$^-$ ion in [N(PPh$_3$)$_2$][TcOCl$_4$] possesses only approximate C_{2v} symmetry with Cl(1)–Tc–Cl(3) and Cl(2)–Tc–Cl(4) angles of 139.2(1) and 153.7(1)° respectively.[40] The authors state that since no interionic contacts are significantly less than the pertinent sum of the van der Waals radii it is not clear that crystal-packing forces may be invoked to explain the distortion of [TcOCl$_4$]$^-$ from idealised C_{4v} symmetry but that this is, of course, possible.[40] However, the [ReOCl$_4$]$^-$ ion in [AsPh$_4$][ReOCl$_4$][36] and the [MoOCl$_4$]$^-$ ion in [AsPh$_4$][MoOCl$_4$][35] possess C_{4v} symmetry and it has been reported that the vibrational spectra of [NBu$^n_4$][TcOX$_4$] (X = Cl, Br, or I) indicate C_{4v} symmetry for the [TcOX$_4$]$^-$ ions in these compounds.[32,33] It is thus likely that the distortion of the [TcOCl$_4$]$^-$ ion in [N(PPh$_3$)$_2$][TcOCl$_4$] is a consequence of the effect of the large [N(PPh$_3$)$_2$]$^+$ cation in the crystal.

Table 4. Comparison of bond distances (Å) and N≡M–Cl bond angles (°) in [MNCl$_4$]$^-$ complexes with C_{4v} symmetry

Complex	M≡N	M–Cl	N≡M–Cl	Ref.
[AsPh$_4$][MoNCl$_4$]	1.66(4)	2.345(5)	101.5(2)	25
[AsPh$_4$][TcNCl$_4$]	1.581(5)	2.322(1)	103.34(3)	*a*
[AsPh$_4$][RuNCl$_4$]	1.570(7)	2.310(1)	104.58(4)	*b*
[AsPh$_4$][ReNCl$_4$]	1.619(10)	2.322(2)	103.49(6)	4
[AsPh$_4$][OsNCl$_4$]	1.604(10)	2.310(2)	104.53(5)	17

[a] This paper. [b] F. L. Phillips and A. C. Skapski, *Acta Crystallogr., Sect. B*, 1975, **31**, 2667.

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