An Electron Spin Resonance Study of the Equilibrium between Tetrahalogeno- and Pentahalogeno-nitridotechnetate(VI) Ions in Solution

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The e.s.r. spectra of $[AsPh_4][TcNCl_4]$, $Cs_2[TcNCl_5]$, $[AsPh_4][TcNBr_4]$, and $Cs_2[TcNBr_5]$ have been studied in non-aqueous and concentrated aqueous acid solutions. None of the spectra shows evidence for the co-ordination of a fifth halide ligand in the *trans* position, even under circumstances such as a 2 000-fold excess of halide ion, which would be expected to favour the formation of the pentahalogenonitridotechnetate ion. The predominant species in solution is the tetrahalogenonitridotechnetate ion, where the *trans* position may be vacant or occupied by a solvent molecule in the case of the non-aqeuous solvents and by a water molecule in the case of HCl and HBr solutions. This conclusion may be contrasted with the behaviour of a number of tetra- and penta-halogeno-oxometal complexes, where the equilibrium $[MOX_4]^{n-} + X^- \rightleftharpoons [MOX_5]^{(n+1)-}$ is clearly established.

In some recent papers we have reported the preparation and properties of a number of compounds based on the nitridotechnetate(VI), Tc≡N, core.[1–3] The nitrido ligand (N^{3-}) is isoelectronic with the oxo ligand (O^{2-}) and is a powerful π-electron donor which tends to stabilize metals in high oxidation states. A topic of current interest in studies of oxometal complexes is the question of the nature of the equilibrium in solution between tetrahalogeno- and pentahalogeno-oxometal complexes, *i.e.* $[MOX_4]^{n-} + X^- \rightleftharpoons [MOX_5]^{(n+1)-}$, where X = Cl or Br. For example, the equilibrium between the technetium(V) complexes $[TcOCl_4]^-$ and $[TcOCl_5]^{2-}$ has been investigated in 12 mol dm^{-3} HCl and in dichloromethane solutions by Raman spectroscopy.[4] It was found that the former species predominated in both solvents and that water competed for the sixth co-ordination position in 12 mol dm^{-3} HCl, forming $[TcO(OH_2)Cl_4]^-$ rather than $[TcOCl_5]^{2-}$. In the case of the analogous chloro-oxomolybdenum(V) complexes, Boorman *et al.*[5] used electron spin resonance (e.s.r.) spectroscopy to distinguish between the various species formed in aqueous acid and dichloromethane solutions. The e.s.r. spectra of solutions at room temperature exhibited signals with different *g* values which were attributed to $[MoOCl_4]^-$, $[MoO(OH_2)Cl_4]^-$, or $[MoOCl_5]^{2-}$ ions. From the e.s.r. evidence Boorman *et al.*[5] concluded that the predominant species in concentrated hydrochloric acid was $[MoOCl_4(OH_2)]^-$ rather than $[MoOCl_5]^{2-}$. However the opposite conclusion has been reached by Kim and Murmann[6] on the basis of kinetic ^{18}O-exchange measurements.

Whilst the technetium(V) ion is not expected to give a readily detectable e.s.r. signal, the technetium(VI) ion, such as arises in complexes of the form $[TcNCl_4]^-$ or $[TcNBr_4]^-$, gives well resolved spectra.[1] It therefore seemed appropriate to use e.s.r. spectroscopy to examine the behaviour in solution of tetra- and penta-halogenonitridotechnetium(VI) complexes and to compare this behaviour with that of oxotechnetium(V) and other related oxo- and nitrido-metal complexes.

Experimental

Ammonium [^{99}Tc]pertechnetate (58 mg cm^{-3} in 0.1 mol dm^{-3} NH_4OH solution) was obtained from Amersham International plc. The i.r. spectrum was determined in a KBr disc on a Perkin-Elmer 197 spectrophotometer and the microanalysis was performed by the Australian Microanalytical Service, Melbourne. E.s.r. spectra were recorded in the temperature range 100—300 K using a Bruker ESR-200D-SRC spectrometer and associated equipment.

The compounds $[AsPh_4][TcNCl_4]$, $[AsPh_4][TcNBr_4]$, and $Cs_2[TcNCl_5]$ were prepared as described previously.[1,3] Solvents were of analytical grade and were used without further purification.

Caesium Pentabromo(nitrido)technetate(VI).—Ammonium pertechnetate (58 mg, 0.32 mmol) was mixed with concentrated HBr (47%, 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 was heated under reflux for 10 min and the deep violet-black solution allowed to cool. Caesium bromide (200 mg, 0.94 mmol) dissolved in the minimum amount of water was added and the solution filtered. The solution was reduced in volume on a rotary evaporator, heated to dissolve the precipitate, and allowed to stand. The blue-black precipitate which slowly formed was collected by filtration, washed with a little concentrated HBr, and dried under vacuum. M.p. > 360 °C (Found: Br, 45.2; N, 2.1. Br_5Cs_2NTc requires Br, 51.3; N, 1.80%). The i.r. spectrum showed a single peak at 1 028 cm^{-1} (Tc≡N).

E.S.R. Spectroscopy.—The spectra were simulated on Data General S-140 and MV-8000 computers using the programs described previously which employ second-order perturbation theory expressions for the magnetic fields and transition probabilities.[7] The spin Hamiltonian used to represent the spectra was of the form shown in (1), where $S = \frac{1}{2}$, $I = \frac{9}{2}$, the

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

other symbols have their usual meaning, and the form of $\mathcal{H}_{\text{shf}}$, which represents the superhyperfine interactions due to the ligand nuclei, will be discussed below. Apart from $\mathcal{H}_{\text{shf}}$, which may in general have orthorhombic symmetry, the spin Hamiltonian [equation (1)] has axial symmetry.

In principle the superhyperfine structure arising from each of the six possible co-ordinating ligands needs to be considered independently. In practice this usually reduces to a consideration of the superhyperfine interaction due to the four halide ions co-ordinated equatorially, *i.e.* approximately perpendicular to the Tc≡N direction in the present case. The symmetry of the interaction from a given equatorial ligand is orthorhombic, with the component along the metal–ligand bond direction being different to that perpendicular to this direction in the equatorial plane, and both being different to that perpendicular to this plane, *i.e.* in the same direction as the Tc≡N direction. The labelling of the co-ordinate system for the four equatorial ligands is shown in Figure 1.

The usual treatment of superhyperfine interactions in systems of this type is to consider the ligands as forming two pairs of magnetically equivalent nuclei.[8] The terms in the spin Hamiltonian take the forms shown in (2a) and (2b) for the ligands

$$a_xS_xI'_x + a_yS_yI'_y + a_zS_zI'_z \qquad (2a)$$

$$a_yS_xI'_x + a_xS_yI'_y + a_zS_zI'_z \qquad (2b)$$

along the X axis and the Y axis respectively. The largest component is along the bond direction and is taken to be a_x. There is no *a priori* reason why $a_y = a_z$ must hold. The effect of these terms is to add to the expressions for the resonance magnetic fields terms of the form (3), where m'_x and m'_y are the

$$m'_x(a_x^2g_\perp^2 \sin^2\theta\cos^2\varphi + a_y^2g_\perp^2\sin^2\theta\sin^2\varphi + a_z^2g_\parallel^2\cos^2\theta)^{\frac{1}{2}} + m'_y(a_y^2g_\perp^2\sin^2\theta\cos^2\varphi + a_x^2g_\perp^2 \sin^2\theta\sin^2\varphi + a_z^2g_\parallel^2\cos^2\theta)^{\frac{1}{2}} \qquad (3)$$

sums of the magnetic superhyperfine quantum numbers of the ligand nuclei along the X and Y axes respectively. For both Cl and Br ligands $I = \frac{3}{2}$, so that m'_x and m'_y take on the values −3, −2, −1, 0, 1, 2, and 3. Thus each pair of ligand nuclei gives a seven-line spectrum where the relative intensity of the lines is in the ratio 1:2:3:4:3:2:1. The combination of the two pairs gives a very complex spectrum.

A special case, applicable to the present circumstances, arises when a_x is much greater than both a_y and a_z and both the latter are less than the linewidth. Along both the X and Y axes the spectrum will consist of seven equally spaced lines, with a splitting of a_x and relative intensity 1:2:3:4:3:2:1. In the case of powders and frozen solutions the perpendicular spectrum will have this appearance because the resonance fields vary only slowly with angle around $\theta = \frac{\pi}{2}$ and $\varphi = 0$ or $\frac{\pi}{2}$. However, the overall intensity of the perpendicular spectrum relative to that of the parallel spectrum will be markedly less than that expected if the seven-line spectrum was due only to a single pair of ligand nuclei.

A second special case occurs when $a_x = a_y$, *i.e.* the superhyperfine interaction for each ligand is isotropic in the X–Y plane. Here the spectrum will exhibit 13 lines, with a splitting of $a_x(= a_y)$ and relative intensity 1:4:10:20:31:40:44:40:31:20:10:4:1. This special case is the only one where a 13-line spectrum could in principle be observed from powders or frozen solutions of the chemical systems studied in this paper. Whilst a 13-line spectrum does occur for $a_x \neq a_y$ when $\varphi = \frac{\pi}{4}$, the variation of the resonance field with angle is so rapid that the spectra due to molecules with this orientation are smeared out in powders or frozen solutions. We also note that at $\theta = \frac{\pi}{2}$ and $\varphi = \frac{\pi}{4}$ the splitting will be $(a_x^2 + a_y^2)^{\frac{1}{2}}/\sqrt{2}$ rather than $(a_x + a_y)/2$.

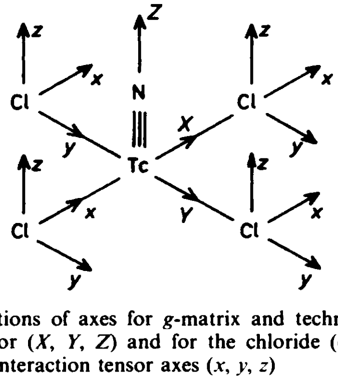

Figure 1. Directions of axes for *g*-matrix and technetium hyperfine interaction tensor (X, Y, Z) and for the chloride (or bromide) ion superhyperfine interaction tensor axes (x, y, z)

Results

E.S.R. Spectroscopy of $[AsPh_4][TcNCl_4]$ *and* $Cs_2[TcNCl_5]$ *Solutions.*—(*a*) *In acetone.* The e.s.r. spectrum of a solution (1.0×10^{-3} mol dm^{-3}) of $[AsPh_4][TcNCl_4]$ at *ca.* 120 K was similar to that described previously for this solvent.[1] The spectral parameters, obtained using the spin Hamiltonian of equation (1) without inclusion of the superhyperfine terms due to the Cl^- ligands, are given in Table 1 and are in agreement with those reported previously.[1]

(*b*) *In acetonitrile.* The e.s.r. spectrum of a solution (1.0×10^{-3} mol dm^{-3}) of $[AsPh_4][TcNCl_4]$ at 120 K was similar to that in acetone. The spectral parameters are given in Table 1 and show small differences when compared with those obtained from acetone solutions.

(*c*) *In dichloromethane.* The e.s.r. spectrum of a 1.0×10^{-3} mol dm^{-3} solution of $[AsPh_4][TcNCl_4]$ in dichloromethane gave a spectrum at 120 K similar to that described above. Addition of $[AsPh_4]Cl$ to this solution to a concentration of 2.0×10^{-2} mol dm^{-3} resulted in a much better resolved spectrum and enabled the weak resonances due to the nuclear forbidden transitions ($\Delta m = \pm 1$) at around 295.5 and 307.0 mT to be detected. These transitions arise because of the presence of the nuclear quadrupole interaction term in the spin Hamiltonian of equation (1). A spectrum with an identical appearance but with a slightly smaller linewidth was obtained for a 5.0×10^{-3} mol dm^{-3} solution of $[AsPh_4][TcNCl_4]$ in dichloromethane which contained 0.5 mol dm^{-3} $[AsPh_4]Cl$. The parameters obtained by computer simulation of the spectrum are given in Table 1. All three solutions gave identical spin-Hamiltonian parameters and are only differentiated by variations in the linewidth. The central region of the spectrum, including the forbidden transitions, is shown in Figure 2. The magnitude of the quadrupole interaction parameter, Q, was determined from the spectrum of the $\Delta m = 0$ transitions. The position of the $\Delta m = \pm 1$ resonances was largely independent of Q for $Q \leqslant 0.0005$ cm^{-1}, and a comparison of the relative intensities of the $\Delta m = 0$ and $\Delta m = \pm 1$ transitions gave a value for Q less than that obtained from the line positions. Linewidth differences between allowed and forbidden transitions and errors introduced by the perturbation theory treatment used here may contribute to this discrepancy.

There was no evidence for resolved superhyperfine splitting due to the Cl^- ligands. A computer simulation including the superhyperfine interaction terms gave an upper limit of 7×10^{-4} cm^{-1} for the magnitude of the largest component of the

Table 1. E.s.r. spectral parameters for $[AsPh_4][TcNCl_4]$ and $Cs_2[TcNCl_5]$ in frozen solution at 120 K. All hyperfine and quadrupole interaction parameters are given in units of $\times 10^4$ cm^{-1}

Solvent	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	Q
	(±0.0005)		(±0.2)	(±0.5)	(±0.5)
Acetone	2.0075	2.0005	292.5	132.0	4.5
Acetonitrile	2.0085	2.0005	294.0	133.7	4.0
Dichloromethane	2.0085	2.0005	293.0	132.7	4.0
Dimethyl sulphoxide	2.0065	2.0005	293.5	132.5	4.5
Hydrochloric acid	2.0075	2.0020	294.8	133.7	4.0

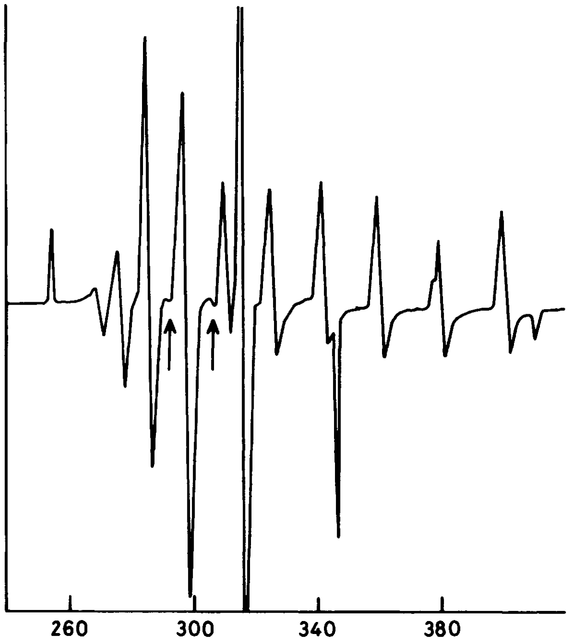

Figure 2. E.s.r. spectrum of $[AsPh_4][TcNCl_4]$ (5.0×10^{-3} mol dm^{-3}) in CH_2Cl_2 after addition of 0.5 mol dm^{-3} $[AsPh_4]Cl$. Temperature 120 K; microwave frequency 9.521 GHz; microwave power 5 mW; 100-kHz modulation amplitude 0.2 mT. The positions of the $\Delta m = \pm 1$ transitions referred to in the text are indicated by arrows. The two lowest-field and two highest-field 'parallel' lines, at 192.6, 225.2, 444.3, and 478.0 mT, are not shown. (The complete spectrum, less well resolved, and the appropriate computer simulation, are shown in ref. 1, Figure 1)

superhyperfine tensor, and an upper limit of 1×10^{-4} cm^{-1} for the component parallel to the Tc≡N direction.

(*d*) *In dimethyl sulphoxide.* The e.s.r. spectra of 1.0×10^{-3} mol dm^{-3} solutions of both $[AsPh_4][TcNCl_4]$ and $Cs_2[TcNCl_5]$ were identical to within experimental error, and could be simulated with the parameters given in Table 1. The forbidden transitions were not observed in these solutions. Some improvement in spectral resolution was obtained on dilution to 0.5×10^{-3} mol dm^{-3}, although the forbidden transitions were still not resolved. The best resolution, resulting in the observation of the forbidden transitions, was obtained with a solution of $[AsPh_4][TcNCl_4]$ in dimethyl sulphoxide (1.0×10^{-3} mol dm^{-3}) to which 1.8 mol dm^{-3} of LiCl had been added. Apart from a smaller linewidth this spectrum was identical to the others obtained from dimethyl sulphoxide solution. Once again there was no direct evidence for Cl^- superhyperfine structure in either the parallel or the perpendicular regions of the spectrum. A computer simulation which included the superhyperfine interaction terms indicated that the appropriate linewidths of the perpendicular spectrum were obtained with an interaction of 0.0004 ± 0.0002 cm^{-1} along the Tc–Cl bond direction.

(*e*) *In concentrated hydrochloric acid.* The e.s.r. spectrum of $Cs_2[TcNCl_5]$ in concentrated HCl at solute concentrations of between 1.0×10^{-3} and 0.5×10^{-3} mol dm^{-3} was well resolved with clear evidence for the presence of $\Delta m = \pm 1$ transitions. The spectrum could be fitted with the parameters given in Table 1. Once again, there was no evidence for the presence of Cl superhyperfine structure, even though the linewidths were smaller than in the other solvents. An upper limit of 5×10^{-4} cm^{-1} was found for the magnitude of the largest component of the Cl^- superhyperfine tensor by computer simulation.

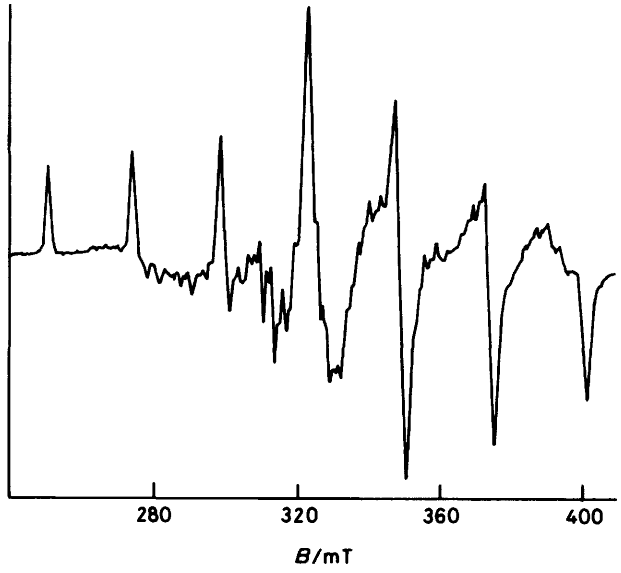

Figure 3. E.s.r. spectrum of $[AsPh_4][TcNBr_4]$ (1.0×10^{-3} mol dm^{-3}) in acetone after addition of 2.3 mol dm^{-3} of LiBr. Temperature 130 K; microwave frequency 9.521 GHz; microwave power 50 mW; 100-kHz modulation amplitude 0.5 mT. The 'parallel' lines at 204.3, 227.2, and 427.5 mT are not shown

E.S.R. Spectroscopy of $[AsPh_4][TcNBr_4]$ *and* $Cs_2[TcNBr_5]$ *Solutions.*—(*a*) *In acetone.* The e.s.r. spectrum of a 1.0×10^{-3} mol dm^{-3} solution of $[AsPh_4][TcNBr_4]$ in acetone at room temperature showed 10 approximately equally spaced lines centred around $g = 2.070$ and an average of *ca.* 17 mT apart. There was no evidence for any superhyperfine structure, and the spectrum is typical of that expected for a technetium(VI) complex tumbling in solution.

The spectrum of this solution, frozen to 130 K, was better resolved than that reported previously.[1] The most striking feature of this spectrum was the relatively high intensity of the lines associated with the parallel features of the spectrum, *i.e.* those features arising from the spectrum of those molecules where the magnetic field was close to the direction of $g_{\parallel}$, taken as being along the symmetry axis (the Tc≡N bond direction). In the place of the perpendicular features there appeared a series of relatively weak lines spaced in an apparently regular fashion. As shown in Figure 3, the addition of 2.3 mol dm^{-3} of LiBr to this solution prior to freezing resulted in a much improved resolution of the spectrum.

This improved resolution enabled a computer simulation of the spectrum to proceed on the basis that these lines arose from the interaction of the unpaired electron with the nuclei of the Br^- ligands. The most satisfactory agreement with experiment was obtained assuming interaction with two pairs of two magnetically equivalent Br^- ligands arranged equatorially around the Tc≡N bond. In Figure 4 a representative portion of the experimental spectrum is compared with the simulated spectrum. Although the simulation reproduced most of the features of the experimental spectrum, it did not reproduce some of the weaker and broader resonances observed in this field range. Since there is no other evidence for the presence of a second species (*e.g.* a three- or five-co-ordinated Br^- species), the most likely explanation of the additional resonances arises from the fact that the bromine nucleus has a substantial quadrupole moment and that the bromine superhyperfine

Table 2. E.s.r. spectral parameters for $[AsPh_4][TcNBr_4]$ and $Cs_2[TcNBr_5]$ at room temperature and in frozen solution at 120 K. All hyperfine and quadrupole interaction parameters are given in units of $\times 10^4$ cm^{-1}

Solvent	$g_{\parallel}$ ($\pm$0.001)	$g_{\perp}$ ($\pm$0.002)	$A_{\parallel}$ ($\pm$0.2)	$A_{\perp}$ ($\pm$0.5)	Q ($\pm$1)	a_x ($\pm$2)	a_y ($\pm$2)	a_z ($\pm$1)
Room temperature								
Acetonitrile and acetone	$g_{av.}$ = 2.070 ($\pm$0.001)		$A_{av.}$ = 162.0 ($\pm$0.2)				$a_{av.} < 15$	
Frozen solution								
Acetone	2.145	2.032	246.7	119.5	4	29	<5	<1
Acetonitrile	2.145	2.032	246.7	119.5	4	29	<5	<1
Dibromomethane	2.145	2.032	247.5	119.5	4	29	<5	<1
Hydrobromic acid	2.145	2.032	248.7	120.0	4	29	<5	<1

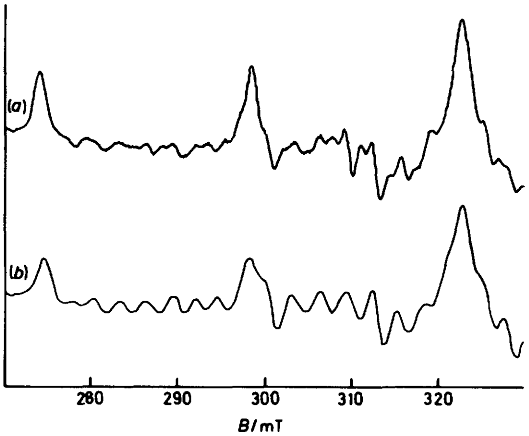

Figure 4. E.s.r. spectrum of $[AsPh_4][TcNBr_4]$ (1.0×10^{-3} mol dm^{-3}) in acetone after addition of 2.3 mol dm^{-3} of LiBr. Conditions as in Figure 3. (*a*) Experimental spectrum, (*b*) simulated spectrum using the parameters given in Table 2 and a Gaussian lineshape with an isotropic peak-to-peak derivative linewidth of 0.8 mT. The experimental spectrum shows the additional lines referred to in the text. Their overlap with the lines of the main spectrum causes some shifts to occur in the positions of the latter

interactions are of a similar order of magnitude to that of the perpendicular technetium hyperfine interaction. Both of these are likely to result in considerable mixing of the nuclear spin states, rendering the usual $\Delta m = 0$ selection rule invalid. Hence, transitions other than the $\Delta m_{Tc} = 0$ and $\Delta m_{Br} = 0$ transitions included in the computations may have very considerable intensity. If all effects are to be taken into account, a matrix of dimension $(10 \times 4 \times 4 \times 4 \times 4) \times (10 \times 4 \times 4 \times 4 \times 4)$ would appear to be required for each orientation. This task would not be justified by any additional information obtained.

The spectral parameters obtained from the simulations are given in Table 2. The spectrum of the acetone solution without added LiBr could be fitted with the same parameters but with a larger linewidth.

(*b*) *In acetonitrile.* The spectrum of a 1.0×10^{-3} mol dm^{-3} solution of $[AsPh_4][TcNBr_4]$ in acetonitrile at room temperature gave a 10-line spectrum with a similar appearance to that obtained in acetone. A solution of $[AsPh_4][TcNBr_4]$ at a concentration of 1.0×10^{-3} mol dm^{-3} in acetonitrile, frozen to 130 K, gave a spectrum with an overall appearance similar to that in acetone. The spectrum was simulated as described above and the parameters are given in Table 2.

(*c*) *In dibromomethane.* The e.s.r. spectrum at 120 K of a solution of $[AsPh_4][TcNBr_4]$ (1.0×10^{-3} mol dm^{-3}) which contained 0.5 mol dm^{-3} $[NEt_4]Br$ was very similar to the spectra in acetone and acetonitrile described above. The spectrum was better resolved than in acetonitrile, but not as well resolved as that of the acetone solution after addition of LiBr. The spin-Hamiltonian parameters are given in Table 2 and are similar to those of the other solutions.

(*d*) *In concentrated hydrobromic acid.* Solutions of $Cs_2[TcNBr_5]$ in concentrated HBr at concentrations of 1.0×10^{-3} and 0.66×10^{-3} mol dm^{-3} at 120 K gave well resolved spectra with an appearance similar to that described above for the acetone solutions of $[AsPh_4][TcNBr_4]$ after addition of LiBr. The more dilute solutions gave the best resolved spectra. The resonances in the perpendicular region of the spectrum are explained in the same way as for the acetone solution. There was no evidence for the existence of a species involving a fifth bromine ligand. Spectra from solutions of $Cs_2[TcNBr_5]$ were fitted with the parameters given in Table 2.

Discussion

The precipitation of $[MOX_4]^-$ and $[MNX_4]^-$ salts by large organic cations and of $[MOX_5]^{2-}$ and $[MNX_5]^{2-}$ salts (X = Cl or Br) by alkali-metal cations is characteristic of transition-metal oxo- and nitrido-halogeno-complexes.[4,9] In the solid-state i.r. spectrum the presence of a fifth halogen atom *trans* to the oxo- or nitrido-group results in a lowering of the wavenumber for M=O or M≡N. Thus for $[AsPh_4][TcNCl_4]$ and $[AsPh_4][TcNBr_4]$ the Tc≡N stretch occurs at 1 076 and 1 074 cm^{-1} respectively,[1] and is lowered to 1 027 and 1 028 cm^{-1} for $Cs_2[TcNCl_5]$[3] and $Cs_2[TcNBr_5]$. E.s.r. spectroscopy provided a convenient method for the investigation of the $[TcNX_4]^- + X^- \rightleftharpoons [TcNX_5]^{2-}$ (X = Cl or Br) equilibrium in solution and the effect of addition of excess of halide ion in a variety of solvents.

Although no superhyperfine structure was observed for the chloro ligand systems, it was clearly observed for the bromine complexes. These spectra were simulated by assuming co-ordination of the technetium ion with four Br^- ligands, as described above. Models involving alternative configurations, *e.g.* five Br^- ligands with the fifth Br^- ion the same as the other four or different, did not give as good agreement with experiment, both as regards line position and intensity. There was no evidence for superhyperfine interactions with either nitrogen (expected to be quite small) or with a Br^- ion or other ligands co-ordinated in the position *trans* to the N atom. Furthermore, simulations using the model described above, namely two pairs of two equivalent Br^- ions along X and Y directions, gave better agreement with experiment than models assuming four equivalent Br^- ions and an isotropic interaction in the equatorial plane. The simulations also showed that the bromine superhyperfine interaction in the equatorial plane but perpendicular to the Tc–Br bond direction was small, an upper estimate being

Table 3. E.s.r. spectral parameters of some tetrahalogeno- and pentahalogeno-oxo or -nitrido metal complexes. The units of $A_{\parallel}$ and $A_{\perp}$ are $\times$ 10^4 cm^{-1}

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	Ref.
$[MoOCl_4]^-$	1.967	1.950	72.8	35.5 (estimated)	*a*
$[MoOCl_5]^{2-}$	1.970	1.938	74.6	30.5	10
$ReOCl_4$ (in dioxane)	1.968	1.720	630	320	*b*
$[ReOCl_5]^-$ (in dioxane)	1.975	1.740	609	305	*b*
$[AsPh_4][ReNCl_4]$ (single crystal)	1.918	1.947	770	391	*c*
$[ReNCl_4]^-$ (in acetonitrile)	1.909	1.934	770	382	*c*

[a] C. D. Garner, L. H. Hill, F. E. Mabbs, D. L. McFadden, and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1977, 853. [b] A. H. Al-Mowali and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 1975, 50. [c] G. M. Lack and J. F. Gibson, *J. Mol. Struct.*, 1978, **46**, 299.

5×10^{-4} cm^{-1}. Larger interactions resulted in too great a broadening of the spectral features to be acceptable.

Thus, the chloronitridotechnetate(VI) and bromonitridotechnetate(VI) anions show many spectral features in common with their halogeno-oxometal equivalents where the metal ion is chromium, molybdenum, or rhenium. We should note that resolved superhyperfine structure due to a fifth halogen ligand has been observed on the features associated with $g_{\parallel}$ for the $[CrOF_5]^{2-}$ and $[ReOF_5]^-$ complexes.[10,11] However, it does not appear to have been observed for other systems particularly where chlorine or bromine are the halogens. The model for the superhyperfine interaction in the bromine complexes, namely that of two equivalent pairs of two, is the same as that used for some of the oxometal complexes, where the conclusions reached from studies of powders or frozen solutions have been confirmed by studies of single crystals.[8a,c]

It is perhaps surprising that none of the spectra observed here shows direct evidence for the simultaneous existence of a second species. Thus there is no direct evidence for the existence of the equilibrium $[TcNX_4]^- + X^- \rightleftharpoons [TcNX_5]^{2-}$ in solution, even in circumstances, such as the presence of a large excess of halide ion, which are expected to favour its establishment. In contrast the equilibrium $[TcOCl_4]^- + Cl^- \rightleftharpoons [TcOCl_5]^{2-}$ in dichloromethane has been studied by Thomas *et al.*[4] and there have been a number of studies of the equilibrium $[MoOCl_4]^- + Cl^- \rightleftharpoons [MoOCl_5]^{2-}$ by e.s.r. spectroscopy and other techniques.[5,6] The co-existence of species attributed to $[CrOCl_4]^-$ and $[CrOCl_5]^{2-}$ in dichloromethane has also been reported.[12]

The absence of signals due to a second species even under circumstances favouring its formation, the observation that the e.s.r. spectral parameters of both $[AsPh_4][TcNCl_4]$ and $Cs_2[TcNCl_5]$ in the same solvent (dimethyl sulphoxide) are identical, and the known stability of the $[TcNCl_4]^-$ ion[1] all point to the conclusion that the formation of the tetrahalogeno species is very strongly favoured over that of the pentahalogeno species in solution. It is unlikely that the e.s.r. spectral parameters of the $[TcNCl_5]^{2-}$ ion would be so close to those of the $[TcNCl_4]^-$ ion as to be unresolved in our experiments. E.s.r. spectral studies have been able to distinguish clearly between the different species formed in solution for a number of the oxometal complexes referred to above.[5] As shown in Table 3, the differences between the *g* and *A* values of five- and six-coordinated complexes are significantly larger than those reported here.

Thus, we propose that the $[TcNX_5]^{2-}$ ion dissociates in solution with the fifth halide being displaced and its position either left vacant or occupied by a solvent molecule with only weak bonding between the solvent and the technetium atom. This is consistent with the stronger π bonding between the nitrogen and technetium atoms and hence a stronger *trans* effect than occurs in the oxotechnetium complexes. In aqueous acid solutions the solvent molecule is water, thus forming a species of the form $[TcN(OH_2)X_4]^-$ analogous to the species $[MoO(OH_2)Cl_4]^-$,[5] $[TcO(OH_2)Cl_4]^-$,[4] and $[OsN(OH_2)Cl_4]^-$,[13] formed in hydrochloric acid. The differences between the e.s.r. spectral parameters of the $[TcNCl_4]^-$ ion in the non-aqueous solvents imply the coordination of solvent molecules. However, the differences between the e.s.r. spectral parameters of the $[TcNBr_4]^-$ ion in the non-aqueous solvents are smaller, indicating that the *trans* position may be unoccupied. This is presumably due to the larger steric effect of the bromide ligands.

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Received 22nd *September* 1986; *Paper* 6/1876