An Electron Spin Resonance and Optical Study of the Behaviour of $Cs_2[TcNCl_5]$ in Hydrochloric Acid Solutions*

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Optical spectroscopy, magnetic susceptibility, and e.s.r. have been used to study the behaviour of $Cs_2[TcNCl_5]$ in aqueous HCl solutions. In 5.6 mol dm^{-3} HCl the predominant species is the $[TcNCl_4]^-$ anion ($\lambda_{max.}$ 398 nm, ε 440 m^2 mol^{-1}) possibly with H_2O weakly bound *trans* to the N atom. Addition of 1 volume of H_2O to $Cs_2[TcNCl_5]$ followed by 2 volumes of 5 mol dm^{-3} HCl gives a deep blue species ($\lambda_{max.}$ 558 nm, ε 393 m^2 mol^{-1}), which is converted to $[TcNCl_4]^-$ on standing. $Cs_2[TcNCl_5]$ dissolved in 0.5 mol dm^{-3} HCl gives a pink solution ($\lambda_{max.}$ 540 nm, ε 215 m^2 mol^{-1}) which is stable over several days. The magnetic susceptibility and e.s.r. measurements indicate that the blue and pink species are diamagnetic. Possible structures of the diamagnetic species are discussed by analogy to the behaviour of $[MOX_5]^{n-}$ in solutions of varying acidity.

The behaviour of the tetrahalogeno- and pentahalogeno-nitridotechnetate(VI) ions in solution is of interest both from the practical viewpoint in development of new radiopharmaceuticals and general chemical interest as a comparison with analogous oxo-species of both technetium(V) and other ions. In a recent e.s.r. spectral study of the equilibrium $[TcNCl_4]^- + Cl^- \rightleftharpoons [TcNCl_5]^{2-}$, we showed that the tetrahalogeno species was strongly favoured in non-aqueous solutions, with the position *trans* to the nitrido ligand either occupied by a solvent molecule or in the case of concentrated hydrochloric acid solutions, by a water molecule.[1] This behaviour may be compared with that observed by other authors for solutions of the oxotechnetium system, where an equilibrium between pentachloro- and tetrachloro-oxotechnetate(V) species could be detected.[2] These results may also be compared with those of studies of the oxomolybdenum(V) complexes, where the $[MoOCl_5]^{2-}$ ion is the predominant species in certain circumstances.[3,4] A related topic of chemical interest is the behaviour of these ions in aqueous solutions at low acid concentrations. Haight[5] and Hare *et al.*,[6] using e.s.r., magnetic susceptibility, and optical spectroscopy demonstrated that a complex equilibrium exists between monomeric, paramagnetic dimer, and diamagnetic dimer species depending on the molarity of the aqueous hydrochloric acid solution. An analogous e.s.r. and magnetic susceptibility study by Dowsing and Gibson[7] of the behaviour of $[MoOBr_5]^{2-}$ in aqueous hydrobromic acid solutions gave evidence for equilibria between two monomeric species and a paramagnetic dimer.

In the present paper we report an electron spin resonance, magnetic susceptibility, and optical spectroscopic study of the behaviour of the $[TcNCl_4]^-$ ion, derived from $Cs_2[TcNCl_5]$, in aqueous hydrochloric acid solutions.

Experimental

U.v.-visible spectra were recorded on a Beckman Acta CII spectrophotometer. $Cs_2[TcNCl_5]$ was prepared as described previously.[8]

E.s.r. spectra were recorded in the temperature range 100—300 K using a Bruker ESR-200D-SRC spectrometer and associated equipment. Spectra of monomeric species were simulated using a Data General MV-8000 computer as described previously.[9] The spectra of dimeric species were simulated using the program GNDIMER on the above computer. GNDIMER has been described in detail elsewhere and can take into account the effects of both dipole–dipole and exchange interactions.[10]

The relative intensities of the spectra in frozen solutions at 130 K were compared using the peak-to-peak height of the highest field perpendicular peak of the derivative spectrum.

The paramagnetic susceptibility of $Cs_2[TcNCl_5]$ solutions at 295 K was determined by the shift of the absorption line of the methyl protons in the n.m.r. spectrum of t-butyl alcohol as described by Evans.[11] A reference solution of 2% t-butyl alcohol in HCl in a 2.2-mm (outside diameter) tube was placed inside a 4.1-mm (inside diameter) n.m.r. sample tube containing $Cs_2[TcNCl_5]$ dissolved in HCl of the same concentration as the reference solution and containing 2% of t-butyl alcohol. The shift in the peak position due to the paramagnetism of the $Cs_2[TcNCl_5]$ solution was measured by a Varian 360A n.m.r. spectrometer. The magnetic moment was calculated by the procedure described by Steigman *et al.*[12]

Results

Optical Spectroscopy of $Cs_2[TcNCl_5]$ *Solutions.*—All spectroscopic measurements were performed at a Tc concentration of 4×10^{-4} mol dm^{-3}. At hydrochloric acid concentrations of 3.33 mol dm^{-3} and greater, $Cs_2[TcNCl_5]$ dissolves to give an orange-yellow solution ($\lambda_{max.}$ 398 nm, ε 440 m^2 mol^{-1}) characteristic of the $[TcNCl_4]^-$ anion (Figure 1). In contrast, dissolution of $Cs_2[TcNCl_5]$ in 0.500 mol dm^{-3} HCl gives a pink solution ($\lambda_{max.}$ 540 nm, ε 215 m^2 mol^{-1}) which partially fades only slowly over a period of several days at room temperature. At intermediate hydrochloric acid concentrations an equilibrium between the yellow and pink species is established. In 1.25 mol dm^{-3} HCl the solution is initially yellow and turns to pink over a period of several hours. At equilibrium the mixture contains *ca.* 66% of the pink species. Well defined isosbestic points at λ 458 and 355 nm indicate that only the two species are present in the mixture.

Addition of water to solid $Cs_2[TcNCl_5]$ (to [Tc] = 2×10^{-3} mol dm^{-3}) gave a yellow solution which very rapidly turned brownish red. After a few seconds a brown precipitate began to form. The brown precipitate does not contain chloride. This was shown by the absence of a white precipitate when the collected and washed brown precipitate was dissolved in dilute nitric acid and silver nitrate solution added.

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* *Non-S.I. unit employed:* B.M. = 9.274×10^{-24} J T^{-1}.

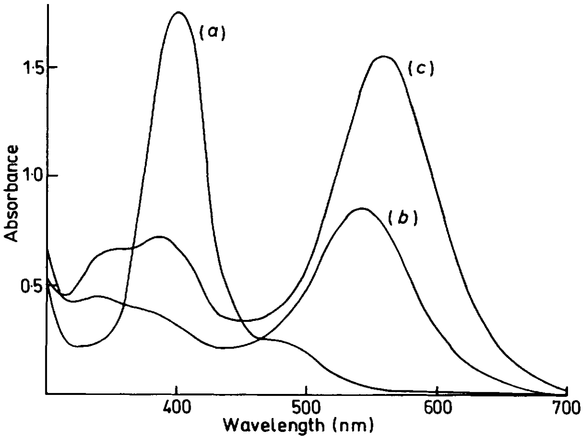


Figure 1. Optical spectra of $Cs_2[TcNCl_5]$ (*a*) in 5.6 mol dm^{-3} HCl, (*b*) in 0.5 mol dm^{-3} HCl, and (*c*) in 3.33 mol dm^{-3} HCl, prepared by the addition of 1 volume of H_2O to $Cs_2[TcNCl_5]$ followed by the addition of 2 volumes of 5 mol dm^{-3} HCl. All $Cs_2[TcNCl_5]$ concentrations were 0.4×10^{-3} mol dm^{-3} and (*b*) and (*c*) were recorded within 5 min of preparation

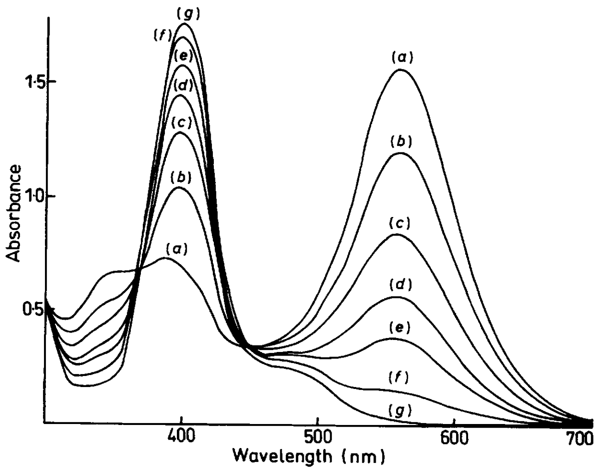


Figure 2. Optical spectra of $Cs_2[TcNCl_5]$ (0.4×10^{-3} mol dm^{-3}) in 3.33 mol dm^{-3} HCl, prepared by the addition of 1 volume of H_2O to $Cs_2[TcNCl_5]$ followed by the addition of 2 volumes of 5 mol dm^{-3} HCl. (*a*) Initial, (*b*) after 15 min, (*c*) 30 min, (*d*) 45 min, (*e*) 60 min, (*f*) 90 min, and (*g*) 150 min

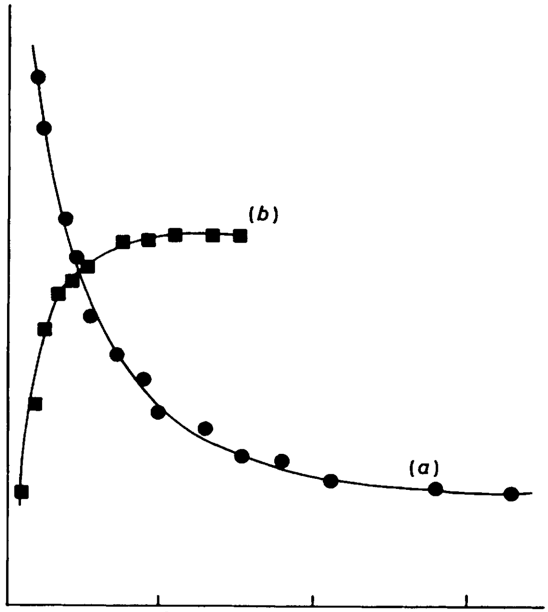


Figure 3. (*a*) Decrease in e.s.r. signal intensity at room temperature after addition of 1 mol dm^{-3} HCl to $Cs_2[TcNCl_5]$. Final [Tc] = 2×10^{-3} mol dm^{-3}. (*b*) Increase in e.s.r. signal intensity at room temperature of a solution prepared by the addition of 1 volume of H_2O to $Cs_2[TcNCl_5]$ followed by the addition of 2 volumes of 5 mol dm^{-3} HCl. Final HCl concentration = 3.33 mol dm^{-3}, [Tc] = 2×10^{-3} mol dm^{-3}

The addition of HCl to the brown precipitate resulted in its dissolution to give the pink solution. Further addition of HCl resulted in an intense blue solution which converted to the yellow colour characteristic of the $[TcNCl_4]^-$ anion on standing over a period of 1 h. The rate of change from deep blue to yellow occurred more rapidly on further addition of HCl and was also greatly accelerated by heating.

The deep blue colour is most conveniently produced by the addition of $Cs_2[TcNCl_5]$ to 1 volume of water immediately followed by 2 volumes of 5 mol dm^{-3} HCl. The optical spectrum of the blue solution at [Tc] = 4×10^{-4} mol dm^{-3} and in 3.33 mol dm^{-3} HCl shows $\lambda_{max.}$ at 558 nm (ε 393 m^2 mol^{-1}) (Figure 1). The conversion of the blue colour to the yellow $[TcNCl_4]^-$ species is shown in Figure 2. The presence of the well defined isosbestic points at λ 445 and 368 nm is evidence for the presence of a single blue species which converts to $[TcNCl_4]^-$. It is noted that when the yellow solutions prepared by dissolving $Cs_2[TcNCl_5]$ in HCl are converted to the pink solution on standing or by the addition of water, the formation of the blue intermediate does not occur.

Magnetic Susceptibility.—The magnetic susceptibility studies were performed on *ca*. 0.05 mol dm^{-3} $Cs_2[TcNCl_5]$ solutions. At these concentrations the colour of the solutions differed to those of the more dilute solutions at the same acidity. The $Cs_2[TcNCl_5]$ solutions in 2 mol dm^{-3} and 1 mol dm^{-3} HCl remained a deep blue on standing, while the solution in 3.33 mol dm^{-3} HCl was brown-yellow. In 5.6 mol dm^{-3} HCl the $Cs_2[TcNCl_5]$ solution was an intense orange-yellow.

The magnetic susceptibility of $Cs_2[TcNCl_5]$ in 5.6 mol dm^{-3} HCl corresponded to a magnetic moment of 1.61 B.M. per Tc atom. In 3.33 mol dm^{-3} HCl the magnetic moment was 1.60 B.M. immediately after dissolution and no change was detectable over a period of 30 min. A magnetic moment of 1.35 B.M. was measured at 5 min after the addition of $Cs_2[TcNCl_5]$ to 2 mol dm^{-3} HCl. The magnetic moment decreased to approximately 0.8 B.M. after 17 min. Further decreases in magnetic moment were indicated by the coalescence of the two peaks but the separation could not be measured with any accuracy after 30 min. No broadening of the t-butyl alcohol peak was detectable for a solution of $Cs_2[TcNCl_5]$ in 1 mol dm^{-3} HCl.

E.S.R. Spectroscopy.—(a) *E.s.r. spectra of solutions at room temperature*. The e.s.r. spectrum of a 0.05 mol dm^{-3} solution of $Cs_2[TcNCl_5]$ in 3.33 mol dm^{-3} HCl showed the 10 lines typical of a Tc^{VI} complex tumbling in solution.The *g* and *A* values were consistent with those measured for frozen solutions of Cs_2-$[TcNCl_5]$ in 11.3 mol dm^{-3} HCl. The e.s.r. spectral intensity did not change over a period of 1 h.

In contrast, a 0.05 mol dm^{-3} solution of $Cs_2[TcNCl_5]$ in 2.0 mol dm^{-3} HCl showed a decrease in spectral intensity to approximately two thirds of the initial value over a period of 1 h.

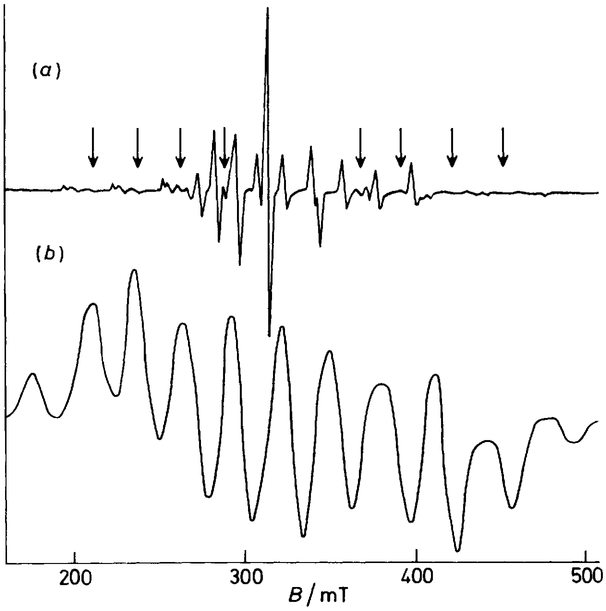


Figure 4. (*a*) E.s.r. spectrum of $Cs_2[TcNCl_5]$ (1.0×10^{-2} mol dm^{-3}) in 3.33 mol dm^{-3} HCl, prepared by the addition of 1 volume of H_2O followed by 2 volumes of 5 mol dm^{-3} HCl and frozen and recorded 30 min after preparation. Temperature 130 K, microwave frequency 9.521 GHz, microwave power 20 mW, 100-kHz modulation amplitude 0.4 mT, spectrometer gain 4.0×10^4, scan rate 0.8 mT s^{-1}, and time constant 0.05 s. The signal intensity of the type A spectrum (see text) is 4% of that expected from a solution of $Cs_2[TcNCl_5]$ in 11.3 mol dm^{-3} HCl of the same concentration. The arrows indicate the resonances referred to in the text which may be indicative of dimeric species. (*b*) Simulated spectrum for a dimeric species, with a Tc $\cdots$ Tc distance of 0.37 nm, the Tc $\cdots$ Tc direction perpendicular to the Tc≡N bond directions and other parameters as for the monomeric $[TcNCl_4]^-$ anion

Over this period the colour of the solution changed from yellow-brown to a deep blue. A more rapid decrease in spectral intensity was observed for a solution of $Cs_2[TcNCl_5]$ in 1 mol dm^{-3} HCl. The spectrum also showed evidence for the existence of more than one species, as the two highest field resonances were broader than expected. The solution remained an intense blue colour during the measurements.

Similar behaviour was exhibited by a less concentrated solution (2×10^{-3} mol dm^{-3}) in 1 mol dm^{-3} HCl, which exhibited more clear-cut evidence for the existence of two species. The rate of decrease of the signal intensity was similar to that of the more concentrated solution described above, and is shown in Figure 3.

The addition of HCl to give an acid concentration of 3.33 mol dm^{-3} to $Cs_2[TcNCl_5]$ (2×10^{-3} mol dm^{-3}) in water resulted in the appearance of an e.s.r. signal which increased in intensity with time. The intensity increased by a factor of three over the period of 5 min after addition of acid (the earliest time after mixing at which the spectrum could be recorded) to 1 h (Figure 3). The brown colour of the aqueous solution changed to deep purple and finally to yellow. Only one species appeared to be present in this solution, with identical spectral parameters to those of the $[TcNCl_4]^-$ anion in 11.3 mol dm^{-3} HCl.

(b) *E.s.r. spectra of frozen solutions.* In the first series of experiments, $Cs_2[TcNCl_5]$ was dissolved in HCl solutions of various concentrations (0.5—5.6 mol dm^{-3}) such that the final Tc concentration was 2×10^{-3} mol dm^{-3}. The solutions were transferred directly to the e.s.r. sample tubes and frozen immediately. In all cases the most prominent e.s.r. signals closely resembled those observed in 11.3 mol dm^{-3} HCl. For convenience, these spectra will be referred to as type A. Whilst the spectra of solutions of low acidity (0.5 mol dm^{-3} in HCl) showed evidence for more than one species by virtue of the splitting of the 'parallel' peaks, the 'perpendicular' spectra did not show any splittings. The e.s.r. spectral intensity decreased when the HCl concentration was reduced below *ca.* 5 mol dm^{-3}, with a 1 mol dm^{-3} HCl solution showing only two thirds of the intensity of the 11.3 mol dm^{-3} solution and a 0.5 mol dm^{-3} HCl solution only *ca.* one eighth. A similar decrease in the e.s.r. spectral intensity with decreasing solution acidity was observed at higher technetium concentrations.

Similarly, no e.s.r. signals were observed from the frozen suspension of the brown $Cs_2[TcNCl_5]$ hydrolysis product in water or solutions of $Cs_2[TcNCl_5]$ in 0.1 mol dm^{-3} NaOH. However, the addition of 11.3 mol dm^{-3} HCl to both preparations to give solutions 5.6 mol dm^{-3} in HCl resulted, after the solutions were allowed to stand until a yellow colour developed, in the reappearance of the type A signal with an intensity corresponding to more than 95% of the Tc concentration. The process occurred *via* a series of intermediate species as shown by the colour changes in the solution on the addition of HCl from a brown or yellow to pink and then to deep blue and finally to the yellow colour of the $[TcNCl_4]^-$ anion.

The time dependence of the signal intensity of the type A species in frozen solution showed similar behaviour to that observed in the room temperature solutions in the acidity range 0.5—3.33 mol dm^{-3} HCl. Addition of HCl to aqueous solutions of low acidity resulted in an increase in the signal with time and conversely the addition of water to the more acid solutions of $Cs_2[TcNCl_5]$ resulted in a decrease.

Changes in signal intensity and colour could also be induced by the addition of chloride ion in the form of lithium chloride. Addition of an aqueous solution of LiCl (12 mol dm^{-3}) to $Cs_2[TcNCl_5]$ gave an e.s.r. spectrum in frozen solution at 130 K which was of type A and accounted for *ca.* 90% of the Tc concentration. The progressive addition of water to this solution resulted in a decrease of the type A signal intensity. For example, dilution (1:1) with water to give 6 mol dm^{-3} Cl^- resulted in a blue solution which exhibited the type A signal at *ca.* 20% of its original intensity. No other signals were observed. Further dilution with water (1:4) to a chloride concentration of 2.4 mol dm^{-3} gave a solution which exhibited no e.s.r. signals. However, in all cases, addition of concentrated HCl resulted in the restoration of e.s.r. signals of type A corresponding in intensity to most of the Tc present in the solution.

Whilst the principal spectra observed in all these solutions were of type A, other weak resonances appeared at various times in solutions of acidities in the range 0.5—3.3 mol dm^{-3} in HCl (Figure 4). The complex series of lines observed in some cases could not be explained by attributing them to the presence of species whose spectra were similar in appearance to type A. It is tempting to attribute these resonances to those which might arise from dimeric species, where two Tc^{VI} ions are coupled by exchange and dipolar interactions. The line positions are best reproduced using computer simulations based on the program GNDIMER, where the Tc^{VI} ions are *ca.* 3.5—3.8 Å apart and the Tc≡N directions are perpendicular to the Tc–Tc direction. Whilst this explanation is attractive in terms of the chemical considerations discussed below, the inability to identify with certainty resonances at around 0.16 T which arise from the 'forbidden' or $\Delta M = \pm 2$ transitions casts doubt on this interpretation. However, it must be noted that these $\Delta M = \pm 2$ transitions are expected to be one twentieth or less of the intensity of the main $\Delta M = \pm 1$ lines, and hence very difficult to detect.

Discussion

The optical spectra establish the existence of three species in solutions of $Cs_2[TcNCl_5]$ in HCl. At high concentrations of

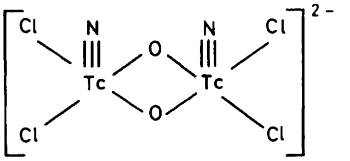
HCl (>*ca.* 3 mol dm^{-3}, depending on the initial $Cs_2[TcNCl_5]$ concentration) the predominant species is the $[TcNCl_4]^-$ anion, characterized by an orange-yellow colour ($\lambda_{max.}$ 398 nm) and the e.s.r. spectrum described previously.[1,9] We have also previously shown that in 11.3 mol dm^{-3} HCl the equilibrium $[TcNCl_4]^- + Cl \rightleftharpoons [TcNCl_5]^{2-}$ is strongly in the direction of the $[TcNCl_4]^-$ anion, with the sixth co-ordination position either vacant or occupied by a water molecule.[1] The magnetic moment of 0.05 mol dm^{-3} $Cs_2[TcNCl_5]$ in 5.6 mol dm^{-3} HCl of 1.61 B.M. per Tc atom is consistent with a monomeric species containing one unpaired electron.

The decreases in magnetic moment and in the e.s.r. signal intensity due to the $[TcNCl_4]^-$ anion at lower HCl concentrations is evidence for the formation of species where the Tc ions are coupled by strong antiferromagnetic exchange interactions. It must be noted that in the dilute HCl solutions and in the brown precipitate the Tc≡N bond and the hexavalent state of the technetium ion remain intact. This is shown by the restoration of the full e.s.r. signal intensity on addition of concentrated HCl.

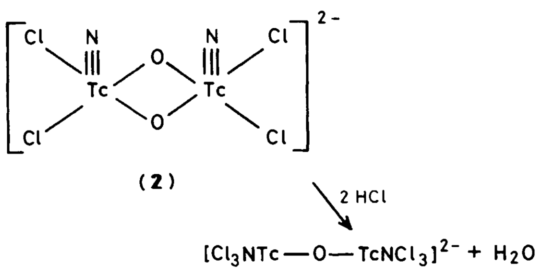
Thus the brown precipitate is most probably a polymeric species based on the Tc≡N core linked by oxo bridges and containing hydroxy groups. The structures of the deep blue and pink species appear to be smaller soluble units with the oxo bridges and hydroxy groups partially replaced by chloride ions. Possible structures for dimeric species containing oxygen bridges are (**1**) and (**2**). Structure (**2**) may be regarded as the more 'condensed' species and thus would be expected to be favoured at the lower HCl concentration, *i.e.* the pink species. The deep blue colour is presumably due to species (**1**). This contention is supported by the formation of the blue colour when concentrated HCl is added to the pink solutions, equation (1).

$[Cl_3NTc{-}O{-}TcNCl_3]^{2-}$

(**1**)



(**2**)

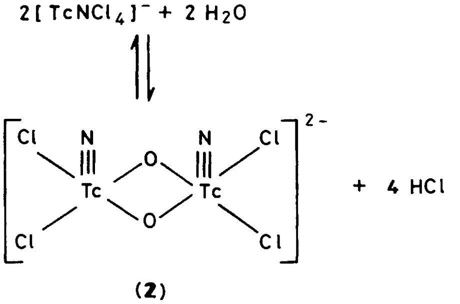


$[Cl_3NTc{-}O{-}TcNCl_3]^{2-} + H_2O$ (1)

The species (**1**) is unstable in 3.33 mol dm^{-3} HCl (Figure 2) and is readily split by HCl to form the monomeric $[TcNCl_4]^-$, equation (2).

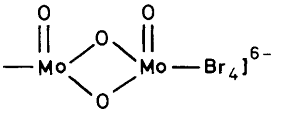
$$\underset{(\mathbf{1})}{[Cl_3NTc{-}O{-}TcNCl_3]^{2-}} \xrightarrow{2\,HCl} 2\,[TcNCl_4]^- + H_2O \quad (2)$$

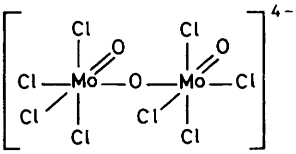
When $Cs_2[TcNCl_5]$ is dissolved in 1.25 mol dm^{-3} HCl ([Tc] = 0.4 × 10^{-3} mol dm^{-3}) an equilibrium arises between $[TcNCl_4]^-$ and the pink species, equation (3). There is no evidence for the presence of the deep blue species as an intermediate. In 0.5 mol dm^{-3} HCl the equilibrium is essentially completely in the direction of the pink species (**2**).

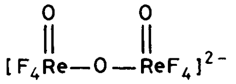


(3)

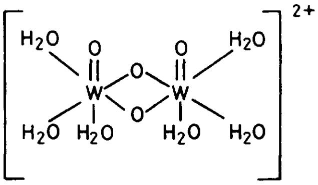
Similar behaviour has been observed in solutions of $[MoOCl_5]^{2-}$,[4-6] $[MoOBr_5]^{2-}$,[7] and $[ReOF_5]^-$.[13] Dimers of the types shown below have been proposed. The formation of the aqua ion (**3**) by hydrolysis of $[WOCl_5]^{2-}$ in 2.0 mol dm^{-3} toluene-*p*-sulphonic acid solution has been established.[14]







$[F_4Re(=O){-}O{-}ReF_4(=O)]^{2-}$



(**3**)

A NTc–O–TcN dimer can have the oxygen bridging either *cis* or *trans* to the nitrido ligand.

We favour the *cis*-bonded dimer (**1**) on the basis that the $[TcNCl_4]^-$ anion shows no evidence for strong co-ordination in the sixth position (*i.e.* *trans* to the nitrido ligand) in solution. It is possible that some of the weaker e.s.r. signals observed at hydrochloric acid concentrations of between 0.5 and 3 mol dm^{-3} are due to species of this type, present in smaller amounts than those giving rise to the main e.s.r. signals. However, it is unlikely that the nitrido nitrogen atom is involved in the hydrolysis process, since this would result in its irreversible loss as an ammonium ion. This enables a clear distinction to be drawn between the reactions which occur in the hydrolysis of the $[TcNCl_4]^-$ anion and those which occur in the seemingly analogous systems such as $[MoOCl_5]^{2-}$ and $[MoOBr_5]^{2-}$, where the 'yl' oxygen plays an important role.[4]

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