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Magnetic and Electrochemical Properties of Transition Metal Complexes with Multiple Metal-to-Metal Bonds. I. $[Tc_2Cl_8]^{n-}$ and $[Re_2Cl_8]^{n-}$ with n = 2 and 3

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Rotating-disk electrode polarography and cyclic voltammetry have shown that in mixtures of hydrochloric acid and ethanol at 25° the reaction $[Tc_2Cl_8]^{2-} + e^- \rightleftarrows [Tc_2Cl_8]^{3-}$ is quasireversible with $E_{1/2} = 0.140$ V *vs.* sce. $[Tc_2Cl_8]^{2-}$ has a lifetime of >>300 sec under these conditions. In acetonitrile and dichloromethane at 25° the reaction $[Re_2Cl_8]^{2-} + e^- \rightleftarrows [Re_2Cl_8]^{3-}$ is quasireversible with $E_{1/2} = -0.840$ V *vs.* sce. $[Re_2Cl_8]^{3-}$ decomposes with a rate constant $k = 0.5 \pm 0.1$ sec^{-1} in acetonitrile and $k = 0.3 \pm 0.1$ sec^{-1} in dichloromethane. These data explain why earlier attempts to isolate salts of $[Tc_2Cl_8]^{2-}$ and $[Re_2Cl_8]^{3-}$ have failed but suggest that a suitably designed effort to isolate the former might be successful. The $[Tc_2Cl_8]^{2-}$ ion gives no esr signal in frozen solution at 77 K and is probably diamagnetic. $[Tc_2Cl_8]^{3-}$ is paramagnetic. Ammonium and yttrium salts have $\mu_{eff} = 1.78 \pm 0.03$ BM in the temperature range 80–300 K. The frozen-solution esr spectra at X- and Q-band frequencies show the presence of one unpaired electron with hyperfine coupling to two equivalent ^{99}Tc ($I = {}^9/_2$). The spectrum has been analyzed to afford the following parameters: $g_\parallel = 1.912$, $g_\perp = 2.096$, $|A_\parallel| = 166 \times 10^{-4}$ cm^{-1}, and $|A_\perp| = 67.2 \times 10^{-4}$ cm^{-1}. $[Re_2Cl_8]^{2-}$ is diamagnetic. Frozen-solution esr spectra of $[Re_2Cl_8]^{3-}$ could not be obtained because of its short lifetime.

Introduction

The quadruple bond, consisting of one σ, two π, and one δ components, was first recognized in the $[Re_2Cl_8]^{2-}$ ion.[1] Soon after, it was shown[2] that the $[Tc_2Cl_8]^{3-}$ ion is isostructural with $[Re_2Cl_8]^{2-}$. The presence of one more electron beyond the set of eight required to make the quadruple bond was reconciled with the fact that all or at least enough of the δ bonding persists to maintain the eclipsed configuration by assigning this extra electron to an orbital with little or no antibonding character with regard to metal–metal bonding. The suggestion was made that the orbital occupied might be an essentially nonbonding σ-type orbital, but this detail need not be insisted upon.

It was also discovered some time ago that the $[Re_2X_8]^{2-}$ ions with X = Cl, Br, and SCN can all be polarographically reduced, at fairly negative potentials, presumably to yield $[Re_2X_8]^{3-}$ and possibly also $[Re_2X_8]^{4-}$ ions.[3] Finally, the discovery has recently been made that a stable $Re_2Cl_4(PEt_3)_4$ molecule, with an eclipsed structure and a Re–Re bond short enough to be considered a quadruple one, can be isolated. This molecule is related to the $[Re_2Cl_8]^{2-}$ ions by a combination of ligand replacements (4 PEt_3 for 4 Cl^-) *and* two-electron reduction.[4]

In short, evidence has been steadily accumulating that the quadruply bonded M_2L_8 species can accept an additional electron, forming paramagnetic species, and in some cases can accept two additional electrons. There is also one clear case in which a δ-bonding electron can be removed with retention of structural integrity,[5] namely $[Mo_2(SO_4)_4]^{3-} + e^- \rightleftarrows [Mo_2(SO_4)_4]^{4-}$.

It therefore seemed clear that there must be a large number of cases in which valuable information about the electronic structures, bonding, and redox chemistry of complexes with strong metal–metal bonds could be obtained by using electrochemical and electron spin resonance techniques, both separately and in combination. This is the first of a series of reports on such investigations which have recently been carried out in this laboratory. In this paper we shall deal with the $[Tc_2Cl_8]^{3-}$ and $[Tc_2Cl_8]^{2-}$ ions, including the esr spectra of the former, and also with the reduction of the $[Re_2Cl_8]^{2-}$ ion, for which the earlier results[3] require some modification.

With regard to the technetium complexes there is some confusion in the recent Russian literature. One report[6] alleges the existence of the compounds $M_8(Tc_2Cl_8)_3 \cdot nH_2O$, with M = K, n = 4; M = NH_4, n = 2; and M = Cs, n = 2. This formulation is based on chemical analyses and an apparently confused idea that since Z = 3 for the unit cell the presence of "trimeric dimers" is implied. Two of these compounds are isostructural[7] with $(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$.[2] The ideas of Glinkina, *et al.*, in ref 6 were in fact disproved 1 year before their publication by the results in ref 7. Our esr spectra did not show the presence of anything but $[Tc_2Cl_8]^{3-}$ in solutions. Glinkina, *et al.*, also present some incomplete statements about an esr spectrum and some magnetic susceptibilities which appear to be incorrect.

It is our belief that the only authentic $[Tc_2Cl_8]^{n-}$ species known prior to the work reported here is that with n = 3.

Experimental Section

Magnetic Susceptibilities. These were measured on an Alpha-Ainsworth instrument by the Faraday method. Reproducibility and noise level allowed accuracies of approximately ±3% to be obtained. $Hg[Co(NCS)_4]$ was used as a calibrant.[8]

Esr Spectra. X-Band spectra at 77 and 298 K were recorded on a Varian E-6 spectrometer, X-band spectra at 4.2 K on a combined Strand Laboratories Varian instrument, and Q-band spectra at 77 K on a Varian V-4502 spectrometer with a 12-in. magnet. For the X-band spectra the accuracies of the frequencies and the magnetic fields are ±0.5% as given directly from the dials. The Q-band frequencies were measured with a resonant-cavity wavemeter to an accuracy of ±10 MHz. By means of a DPPH standard the magnetic field was calibrated to an accuracy of ±0.1% in the range 11,500–13,500 G. Outside this range the accuracy is ±0.5%.

Electrochemical Reactions. These were investigated with a Beckman Electroscan 30 with accessories. All measurements were performed at 25 ± 1°.

Preparation of $Y[Tc_2Cl_8] \cdot 9H_2O$ and $(NH_4)_3[Tc_2Cl_8] \cdot 2H_2O$. We used a slightly modified version of the literature procedures.[2,9] It was found that if the reduction of hexachlorotechnetate(IV) with zinc in concentrated hydrochloric acid is carried out at 75° instead of 100°,[9] the formation of a black unidentified precipitate (presumably technetium metal) can be almost entirely eliminated. The reduced technetium compounds thereby obtained from ammonium and magnesium hexachlorotechnetate(IV) were black and chocolate brown powders, respectively, in contrast to the earlier results. The black powder containing ammonium ions dissolved in nondeoxygenated, concentrated hydrochloric acid with a blue color with no evidence of red-brown intermediates as reported by Eakins, *et al.*,[9] but not observed by Bratton, *et al.*[2] The brown powder containing magnesium ions dissolved, however, with a brown color as reported previously.[9] Addition of yttrium chloride was followed by very slow oxidation of the brown solution and subsequent precipitation of the final turquoise blue yttrium salt. Bubbling with air completed the reaction in 1 hr at which stage the supernatant liquid was only slightly blue-green. Prolonged oxygenation leads to re-formation of hexachlorotechnetate(IV). The recrystallized ammonium and yttrium salts were black and dark turquoise blue crystalline powders, respectively, and both formed turquoise-blue solutions in concentrated hydrochloric acid. None of the products showed any contamination with yellow hexachlorotechnetate(IV) salts as previously observed.[2] The yields were approximately 40%.

All chemical reactions were carried out in the hot laboratory at Texas A&M Cyclotron Laboratory under permanent radiation control. (^{99}Tc emits β particles with energy 0.29 MeV and has a specific activity of 6.2×10^8 sec^{-1} g^{-1}). During the reduction of the pertechnetate in concentrated hydrochloric acid according to Eakins, *et al.*,[9] small but dangerous amounts of the volatile ditechnetium heptoxide are evolved.

Thanks are due to Mr. L. Shive for preparation of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$, using procedures described elsewhere.[10,11]

Results

Redox Reactions of Technetium Complexes. Electrochemical reactions of $[Tc_2Cl_8]^{3-}$ were studied by rotating-disk electrode polarography and cyclic voltammetry at platinum electrodes in different solvents. For instrumental reasons it was necessary to exclude 12 *M* hydrochloric acid, the solvent in which the complex was originally prepared. In water, ethanol, and acetonitrile the yttrium salt is moderately soluble, but with rapid decomposition, and reproducible electrochemical behavior could not be obtained in these solvents. It was found that a mixture of 10% by volume of 12 *M* aqueous hydrochloric acid in absolute ethanol gave the best compromise between solubility and stability of the yttrium salt. This solvent limited the available potential range of the platinum electrode from −0.15 to +0.90 V *vs.* sce. The rotating-disk electrode polarograms in this range showed a one-wave oxidation. Examples are shown in Figure 1a. At rotation rates between 0.5 and 30 sec^{-1} $i_L\omega^{-1/2}$ was independent of ω, where i_L is the limiting value of the oxidation current and ω is the cyclic frequency of rotation. Plots of E *vs.* log $(i_L - i)/i$ had slopes varying from 80 to 60 mV with variation of rotation rates from 30 to 0.5 sec^{-1}, respectively. The limiting value of 60 ± 1 mV, as expected for a reversible reaction, was reached for rotation rates less than 3 sec^{-1} at potential sweep rates of 2 mV sec^{-1}. This suggested a quasireversible (moderately slow electron transfer) oxidation involving one electron. The limiting value of $E_{1/2}$ was 0.140 V *vs.* sce. No information concerning the stability of the oxidation product was thereby obtained.

Cyclic voltammetry confirmed the presence of a quasireversible reaction and showed that the lifetime of the oxidation product was considerable. Examples are shown in Figure 1b. Potential sweep rates from 200 to 5 mV sec^{-1} were used. The minimum value allowed by convection and diffusion was 5 mV sec^{-1}. The ratios between the anodic and cathodic peak currents, i_p^a/i_p^c, were unity and independent of the sweep rate. The potential separation between the peaks varied from 210 to 70 mV. For a quasireversible reaction the relation between this peak separation and the potential sweep rate was derived by Nicholson[12] in terms of the dimensionless parameter Ψ defined according to

$$\Psi = k_s\left(\pi\frac{nF}{RT}\nu D_{ox}D_{red}\right)^{-1/2} \tag{1}$$

where k_s is the rate constant of charge transfer and ν the potential sweep rate. (For definition of the other symbols see the original paper.[12]) Nicholson also gives a plot of the peak separation as a function of Ψ. For values of $\Psi > 0.5$ corresponding to a peak separation of <105 mV this separation is almost independent of the charge-transfer coefficients α and β, and $\Psi\nu^{1/2}$ was expected to be independent of ν as actually observed within the experimental uncertainties. The values of $\Psi\nu^{1/2}$ were 0.08 ± 0.01 V$^{1/2}$ sec$^{-1/2}$. Since we were not concerned about details of the charge-transfer mechanism itself, we did not try to calculate k_s. This would involve estimates of the charge-transfer coefficients and the diffusion coefficients.

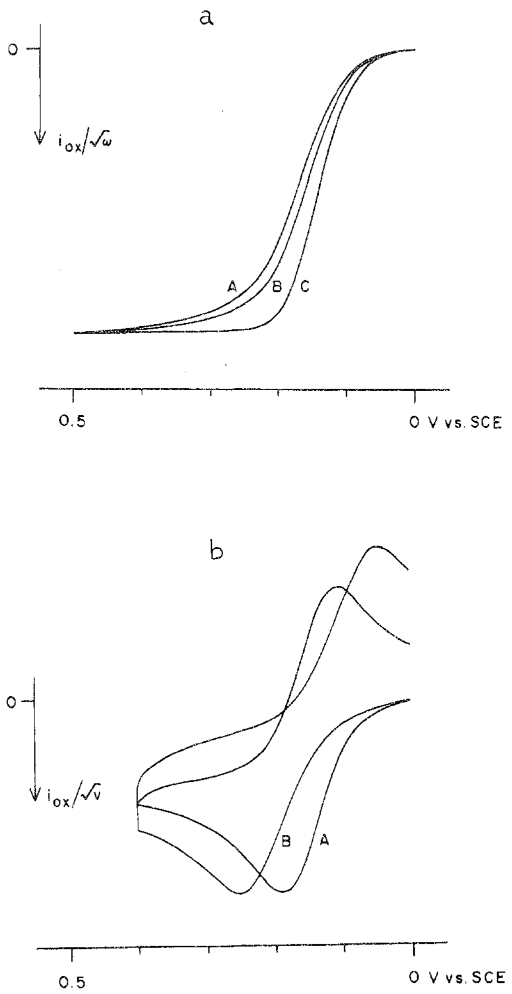

Figure 1. (a) Rotating-disk electrode polarograms of 10^{-4} *M* $Y[Tc_2Cl_8]\cdot 9H_2O$ in 10% v/v 12 *M* aqueous hydrochloric acid in ethanol using a platinum electrode and potential sweep rate of 2 mV sec^{-1}: (A) 30 rotations sec^{-1}; (B) 10 rotations sec^{-1}; (C) 1 rotation sec^{-1}. (b) Cyclic voltammetry in the same solution: (A) 5 mV sec^{-1}; (B) 200 mV sec^{-1}.

The maximum time between the anodic and the corresponding cathodic peak in this series of experiments was 300 sec. Since there was no evidence of decreasing values of i_p^c/i_p^a with decreasing sweep rates, we conclude that the lifetime of the oxidized product is considerably longer than 300 sec.

We feel that these experiments strongly suggest the reaction scheme of eq 2 where X and Y are unidentified decomposition

$$\begin{tikzcd} {[Tc_2Cl_8]^{2-} + e^-} \arrow[r, leftrightharpoons, "E_{1/2} = 0.140\ \mathrm{V}", "vs.\ \mathrm{sce}"'] \arrow[d, "k << 3 \times 10^{-3}\ \mathrm{sec}^{-1}"] & {[Tc_2Cl_8]^{3-}} \arrow[d, "\text{very slow}"] \\ X & Y \end{tikzcd} \qquad (2)$$

products.

Attempts to isolate crystalline salts of $[Tc_2Cl_8]^{2-}$ by evaporation of 5-ml samples approximately 10^{-4} *M* in $[Tc_2Cl_8]^{3-}$ after transfer of charge corresponding to approximately 50% oxidation failed.

Redox Reactions of the Rhenium Complexes. An earlier study[3] of the polarographic reduction of $[Re_2X_8]^{2-}$ with X = Cl, Br, and NSC showed two-wave one-electron reductions for X = Cl and NCS with $E_{1/2}$ at −0.82 and −1.44 V *vs.* sce at a dropping mercury electrode in acetonitrile solutions, 0.5 *M* in tetrabutylammonium perchlorate. At platinum, gold, and carbon electrodes, we were unable to find more than one reduction wave for $[Re_2Cl_8]^{2-}$ in 0.1 *M* tetrabutylammonium

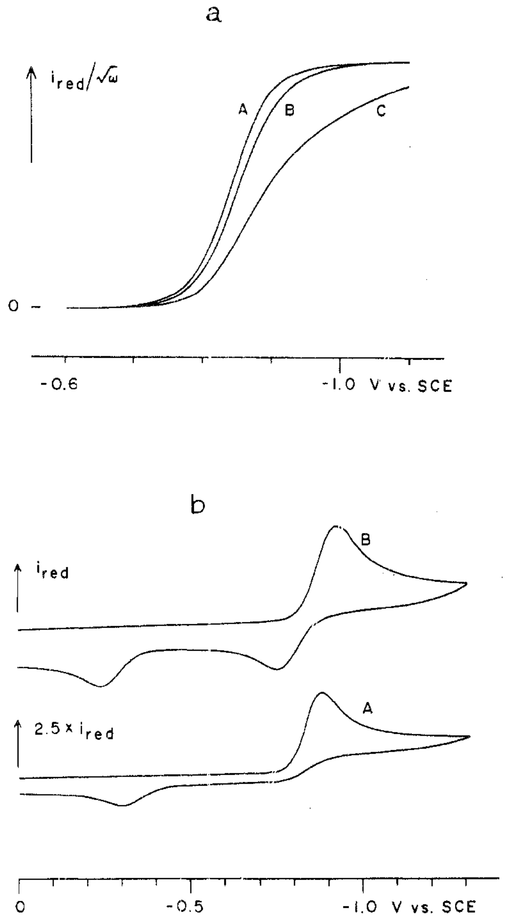

Figure 2. (a) Rotating-disk electrode polarograms of 10^{-4} *M* [$(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in 0.1 *M* tetrabutylammonium perchlorate solution in acetonitrile using a platinum electrode and potential sweep rate of −2 mV sec^{-1}: (A) 30 rotations sec^{-1}; (B) 10 rotations sec^{-1}; (C) 1 rotation sec^{-1}. (b) Cyclic voltammetry in the same solution: (A) 20 mV sec^{-1}; (B) 200 mV sec^{-1}.

perchlorate in anhydrous acetonitrile. The potential range covered was −2 to +2 V *vs.* sce.[13]

The rotating-disk electrode polarograms were recorded as for the technetium complex. Examples are shown in Figure 2a. In the same range of ω, $i_L\omega^{-1/2}$ was independent of ω. The values of the slopes of plots of *E vs.* log $(i_L - i)/i$ reached a limiting value of 60 ± 1 mV at rotation rates 2 sec^{-1} at sweep rates of 2 mV sec^{-1}. The limiting value of $E_{1/2}$ was −0.840 V *vs.* sce. Oxidation processes were observed at potentials ≥1.25 V. Since this is in a range where oxidation of Cl^- was observed to take place, this will not be discussed further.

Cyclic voltammetry confirmed the presence of a quasi-reversible reduction and showed that the lifetime of the reduced product was short. Potential sweep rates from 500 to 5 mV sec^{-1} were used. Examples are shown in Figure 2b. The values of i_p^a/i_p^c varied from 1 to 0, respectively. The quantity $i_p^c\nu^{-1/2}$ was independent of ν. In the range of sweep rates from 200 to 50 mV sec^{-1}, where it is possible to estimate charge-transfer parameters, we found $\Psi\nu^{1/2}$ = 0.09 ± 0.01 $V^{1/2}$ $sec^{-1/2}$, determined as for the technetium complex. The variation of i_p^a/i_p^c is ascribed to a rapid and irreversible decomposition of the reduced product. The rate constant for this reaction was estimated from the variation of i_p^a/i_p^c as a function of the time required to scan from $E_{1/2}$ to the switching potential.[14] A value of k = 0.5 ± 0.1 sec^{-1} was found.

We interpret these experiments in terms of the reaction scheme of eq 3. As seen from Figure 2b the decomposition product Y is short-lived and electroactive and shows an oxidation peak at −0.3 V *vs.* sce.

$$\begin{tikzcd}[Re_2Cl_8]^{2-} + e^- \arrow[r, shift left, "E_{1/2} = -0.840\text{ V}"] \arrow[d, "\text{very slow}"] & {[Re_2Cl_8]^{3-}} \arrow[l, shift left, "\textit{vs. sce}"] \arrow[d, "k = 0.5 \pm 0.1\ sec^{-1}"] \\ X & Y\end{tikzcd} \qquad (3)$$

Several attempts were made to find experimental conditions where $[Re_2Cl_8]^{3-}$ salts were more stable. The following solvents were tried: (a) 0.1 *M* tetraethylammonium chloride in acetonitrile, (b) 0.1 *M* tetraethylammonium chloride in dichloromethane, and (c) 0.1 *M* tetrabutylammonium perchlorate in dichloromethane. In the chloride-containing media (a) and (b), a multitude of overlapping reactions was found. In (c) we found almost the same behavior as discussed in detail above. $\Psi\nu^{1/2}$ = 0.02 ± 0.01 $V^{1/2}$ $sec^{-1/2}$ was found but determined for values of Ψ where the charge-transfer coefficients have some importance for the peak separation. Since diffusion coefficients are also unknown, this value of $\Psi\nu^{1/2}$ does not necessarily imply that the charge-transfer process is slower in this medium than in acetonitrile. The value of k = 0.3 ± 0.1 sec^{-1} found is not significantly different from the value (0.5 ± 0.1 sec^{-1}) in acetonitrile solution. Experiments at reduced temperatures will probably be more successful.

Concluding Remarks on the Redox Reactions. In terms of the reaction schemes, eq 2 and 3, it is now clear why $[Tc_2Cl_8]^{2-}$ and $[Re_2Cl_8]^{3-}$ have remained undetected during the preparation of the fairly stable salts of $[Tc_2Cl_8]^{3-}$ and $[Re_2Cl_8]^{2-}$. The value of $E_{1/2}$ of eq 2 shows that $[Tc_2Cl_8]^{2-}$ is almost nonexistent in mixtures of zinc and hydrochloric acid, provided $E_{1/2}$ does not change dramatically with the solvent. It should, however, be possible to reoxidize $[Tc_2Cl_8]^{3-}$ under mild conditions without obtaining hexachlorotechnetate(IV), known to be the end product from oxidation with oxygen.[2]

Chemical reductions[3] of $[Re_2Cl_8]^{2-}$ may previously have given $[Re_2Cl_8]^{3-}$ which, however, remained unnoticed because of the short lifetime.

The difference in redox potentials for the technetium and rhenium systems is in agreement with the general tendency of the higher oxidation states to be more stable for the heavier transition metals in a given group.

Magnetic Properties of $[Tc_2Cl_8]^{3-}$. Static Susceptibility. Measurements on powdered samples of $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$ and $Y[Tc_2Cl_8]\cdot 9H_2O$ in the temperature range 80–300 K showed Curie law dependence of the susceptibilities corresponding to μ_{eff} = 1.78 ± 0.03 BM for both samples after correction for diamagnetism (−305 × 10^{-6} and −368 × 10^{-6} cgsu per formula weight unit, respectively). In an earlier report[2] the ammonium salt contaminated with ammonium hexachlorotechnetate(IV) was found to have μ_{eff} = 2.0 ± 0.2 BM not including corrections for diamagnetism. (With this correction μ_{eff} = 2.2 ± 0.2 BM). This corresponds to the presence of 13% of an impurity with μ_{eff} = 3.87 BM. Assuming the ground state to be a spin doublet our value of μ_{eff} corresponds to an average *g* factor g_{av} = 2.06 ± 0.03, in agreement with the average value obtained from the esr spectra.

Esr Spectra. No diamagnetic crystalline lattices suitable for magnetic dilution of $[Tc_2Cl_8]^{3-}$ are known. Only liquid and frozen solutions were therefore amenable to recording of spectra. No esr spectra of liquid solutions could be observed. As solvents for the frozen-solution spectra we found mixtures of aqueous hydrochloric acid and ethanol most suitable. The resolution and intensity of the spectra obtained from approximately 10^{-3} *M* solutions at 77 K were very sensitive to the ratio of these mixtures. A 10% v/v solution of 12 *M* aqueous hydrochloric acid in absolute ethanol was found most satisfactory, although a broad background signal is also observed. This solvent was also used for the electrochemical investigations. Higher concentration of acid led to excessive

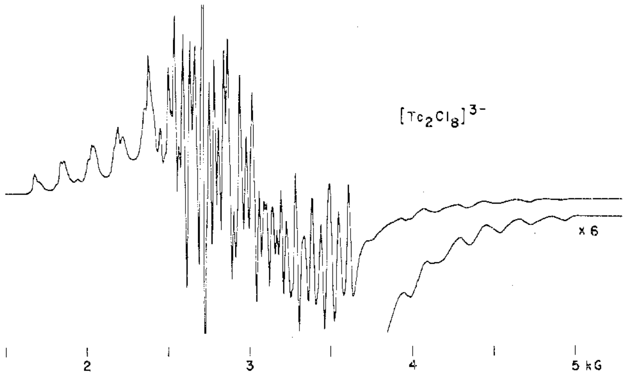

Figure 3. Frozen-solution esr spectrum of 10^{-3} *M* $Y[Tc_2Cl_8]\cdot 9H_2O$ in a mixture of 10% v/v 12 *M* aqueous hydrochloric acid and ethanol at 77 K; microwave frequency 9.186 GHz.

line broadening, probably due to freezing out and accompanying clustering effects in such strongly hydrogen-bonded media. Lower concentrations reduced the solubility of the technetium salts at room temperature and increased the rate of decomposition. In solution, $[Tc_2Cl_8]^{3-}$ is slowly oxidized to hexachlorotechnetate(IV).[2] We found that this reaction does not give rise to extra lines in the spectrum at 77 K. This agreed with our observation that the esr spectrum of $[TcCl_6]^{2-}$ in the same solvent at 4.2 K disappears completely by heating to 77 K. This result is unexpected for a system with a $^4A_2$ ground state in octahedral symmetry, with high-energy excited states and with a free-ion value of the spin–orbit coupling constant ζ = 1300 cm^{-1} but is in agreement with earlier observations for $[TcCl_6]^{2-}$ in a $K_2[PtCl_6]$ lattice.[15] We therefore conclude that all the lines observed come from $[Tc_2Cl_8]^{3-}$.

The X- and Q-band spectra are shown in Figures 3 and 4, respectively. The ammonium and yttrium salts had identical spectra. The X-band spectrum is qualitatively as expected for an axially symmetric $S = {}^1/_2$ system with anisotropic **g** tensor and anisotropic hyperfine coupling to two equivalent nuclei with $I = {}^9/_2$. (The technetium was isotopically pure ^{99}Tc with $I = {}^9/_2$, $\mu_n = +5.6572$, and $Q = +0.3$). The broad bands in the range 1700–4950 G form a series of 19 almost equidistant parallel orientation lines. The 12 outer lines, although slightly split, have intensity ratios crudely resembling 1:2...8:9:8...2:1 as expected for the similar isotropic case in the high-frequency limit. The 7 lines not observed are buried in a multitude of perpendicular and probably intermediate orientation lines in the range 2400–3700 G with a poorly defined lower limit.

The Q-band spectrum has a smaller number of lines. Some of these can easily be classified as weak parallel orientation lines having approximately the same splitting as found for the 19-line set in the X-band spectrum and intense perpendicular and intermediate orientation lines having characteristic splittings comparable to that found for the corresponding lines around 3500 G in the X-band spectrum.

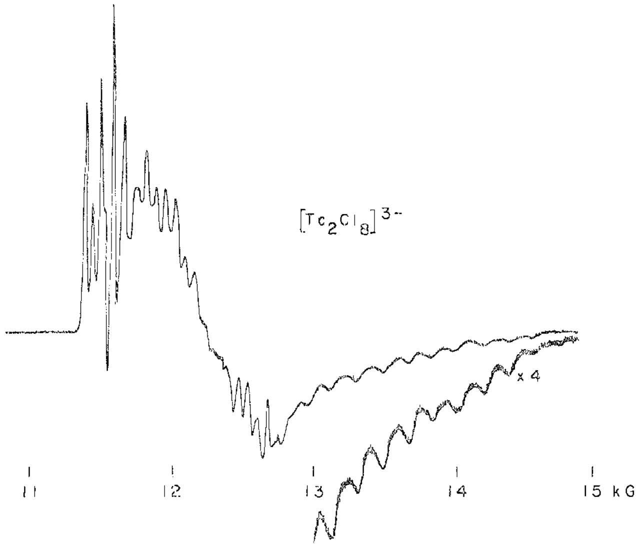

Figure 4. Frozen-solution esr spectrum of $Y[Tc_2Cl_8]\cdot 9H_2O$ under the same conditions as in Figure 3; microwave frequency 35.56 GHz. No lines could be detected below 11,000 G and above 14,765 G.

Interpretation of the Esr Spectra. The simplest spin Hamiltonian that may be expected to account for the spectra is

$$\mathcal{H} = \mu[g_{\|}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + A_{\|}S_z(I^1{}_z + I^2{}_z) + A_{\perp}[S_x(I^1{}_x + I^2{}_x) + S_y(I^1{}_y + I^2{}_y)] \quad (4)$$

with $S = {}^1/_2$ and $I^1 = I^2 = {}^9/_2$. The corresponding energy matrix is of the size 200 × 200. If the basis functions are chosen according to the scheme $|SM_SJM_J\rangle$ where $J = I^1 + I^2$, the matrix is simplified into sets of smaller matrices corresponding to J = 0, 1, ..., 9. This matrix was diagonalized approximately by using second-order perturbation theory in a way equivalent to the method used by Bleaney.[16] We considered only spin-allowed transitions of the type $\Delta M_S = \pm 1$, $\Delta J = 0$; $\Delta M_J = 0$. The resonance field positions of these are given as

$$H(J,M_J,\theta) = \left[\nu + KM_J - \frac{A_{\|}{}^2(A_{\perp}{}^2 + K^2)}{4\nu K^2}[J(J+1) - M_J{}^2] - \frac{1}{2\nu}\left(\frac{A_{\|}{}^2 - A_{\perp}{}^2}{K}\right)^2 M_J{}^2 \sin^2\theta \cos^2\theta\right] \Big/ g\mu \quad (5)$$

where

$$g = (g_{\|}{}^2 \cos^2\theta + g_{\perp}{}^2 \sin^2\theta)^{1/2} \quad (6)$$

and

$$K = (A_{\|}{}^2 g_{\|}{}^2 \cos^2\theta + A_{\perp}{}^2 g_{\perp}{}^2 \sin^2\theta)^{1/2}/g \quad (7)$$

ν is the frequency of the spectrometer, and θ is the angle between the *z* axis and the applied magnetic field. The transition probability was assumed to be proportional to

$$P(\theta) = g_{\perp}{}^2(g_{\|}{}^2/g^2 + 1) \quad (8)$$

Computer-simulated spectra were obtained by summing first-derivative lorentzian functions $F(H,\theta)$, centered at field positions according to eq 5–7 and having intensities according to eq 8, over all J and M_J values and integrating over all field orientations. The total shape function is of the form

$$G(H) = \sum_{\theta}\sum_{J}\sum_{M_J} P(\theta)F(H,\theta)(\sin\theta)\Delta\theta \quad (9)$$

The validity of eq 5 is based on the assumption $JA << g\mu H$, a requirement that is obviously not completely fulfilled at X-band frequencies.

Preliminary values of $A_{\|}$ and $A_{\perp}$ were obtained from the splittings in the Q-band spectrum. Disregarding the second-order shifts (third term in eq 5) the values of $g_{\|}$ and $g_{\perp}$ were estimated from the positions of lines no. 10 counted from the high-field and low-field limits of the spectrum, respectively. The simulated spectrum with these parameters had limited resemblence to the experimental spectrum and showed that the first intense low-field line did not correspond to $\theta = \pi/2$ but to $\theta \approx 0.4\pi$ where $\partial H(9,-9,\theta)/\partial\theta = 0$ according to eq 5, corresponding to a minimum for $H(9,-9,\theta)$. The second low-field line is $H(9,-9,\pi/2)$. This assignment gave a better set of parameters leading to a simulated spectrum that accounts for the positions of all the lines in the experimental spectrum. In order to explain the absence of a negative peak at the first low-field intermediate orientation line, we had to assume the presence of an undetected parallel orientation line at 14,955

Table I. Spin Hamiltonian Parameters for $[Tc_2Cl_8]^{3-}$

$g_\parallel$	$g_\perp$	$10^4 \lvert A_\parallel \rvert$, cm^{-1}	$10^4 \lvert A_\perp \rvert$, cm^{-1}	g_{av}
1.912	2.096	166	67.2	2.035

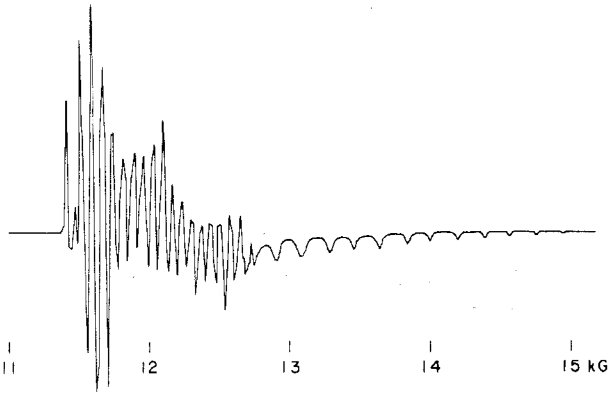

Figure 5. Computer-simulated esr spectrum, with $S = {}^1/_2$, $I^1 = I^2 = {}^9/_2$, $g_\parallel = 1.912$, $g_\perp = 2.096$, $A_\parallel = 166 \times 10^{-4}$ cm^{-1}, and $A_\perp = 67.2 \times 10^{-4}$ cm^{-1}. First-derivative lorentzian functions with half-widths of 25 G were added for every step of 0.1° in the polar angle θ.

G. Such a line will have approximately half of the intensity of the last high-field line observed at 14,765 G and will therefore remain buried in noise. Computer simulation also showed that it was unreasonable to assume that more than one line was missing. A comparison with the X-band spectrum which clearly shows the position of this $H(9,9,0)$ line confirms that such an assumption is impossible. The validity of this argument is based on the fact that the second-order diagonalization of the energy matrix is reasonably accurate at fields around 5,000 G for the final spin Hamiltonian parameters as tabulated in Table I. (The second-order correction to $H(9,9,0)$ is only 10% of the correction to $H(9,0.0)$.) The computer-simulated spectrum for these parameters is shown in Figure 5. The most prominent difference between this and the experimental spectrum is the presence of the broad background in the latter. This could be reproduced neither by assuming larger lorentzian line widths nor by assuming these line widths to depend on θ according to

$$B(\theta) = (B_\parallel^2 \cos^2 \theta + B_\perp^2 \sin^2 \theta)^{1/2} \qquad (10)$$

This background is ascribed to nonideal magnetic dilution.

The X-band spectrum of a compound with the parameters in Table I is expected to have a large number of lines, mainly because the second-order corrections in eq 5 depend strongly on J at this low frequency. Furthermore "spin-forbidden" lines are expected especially at low fields, quadrupole effects will probably be important, and hyperfine coupling from the ligand nuclei may perhaps contribute, for example, to the splitting observed in the $H(9,-9,0)$ line. In order to solve these problems more accurate diagonalizations of a more complete energy matrix are required.

All attempts to observe esr spectra of liquid solutions in the temperature range −50 to +25° failed. The isotropic contribution to the hyperfine coupling constants are therefore not directly observable. The signs of these also remain undetermined, of course.

The g factors and their relation to the molecular structure[2] and the energies and symmetries of the excited states will be discussed in a later publication.

Magnetic Properties of $[Tc_2Cl_8]^{2-}$, $[Re_2Cl_8]^{2-}$, and $[Re_2Cl_8]^{3-}$. Electrolytic generation of $[Tc_2Cl_8]^{2-}$ at a rotating-disk platinum electrode at +0.30 V *vs.* sce and under the same conditions as used for the electrochemical investigations did not give rise to extra peaks in the esr spectrum after transfer of charge that would correspond to oxidation of 25% of the $[Tc_2Cl_8]^{3-}$. We suppose therefore that $[Tc_2Cl_8]^{2-}$ is diamagnetic as expected for a system like this with an even number of electrons. This conclusion is not unequivocal, however, as large zero-field splittings, for example, in a possible triplet ground state could be responsible for the absence of an esr signal.

$[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ is diamagnetic at 300 K according to Faraday measurements.

$[Re_2Cl_8]^{3-}$ could not at room temperature be generated in sufficient concentration to allow detection of an esr signal in frozen solution from the expected spin-doublet ground state.

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Registry No. $[Tc_2Cl_8]^{3-}$, 53260-19-8; $[Tc_2Cl_8]^{2-}$, 53229-24-6; $[Re_2Cl_8]^{2-}$, 19584-24-8; $[Re_2Cl_8]^{3-}$, 53260-18-7.

References and Notes

(1) F. A. Cotton, *et al.*, *Science*, **145**, 1035 (1964); F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).
(2) F. A. Cotton and W. K. Bratton, *J. Amer. Chem. Soc.*, **87**, 921 (1965); W. K. Bratton and F. A. Cotton, *Inorg. Chem.*, **9**, 789 (1970).
(3) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 1257 (1967).
(4) F. A. Cotton, B. A. Frenz, J. R. Ebner, and R. A. Walton, *J. Chem. Soc., Chem. Commun.*, 4 (1974).
(5) F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Amer. Chem. Soc.*, **95**, 4431 (1973).
(6) M. I. Glinkina, A. F. Kuzina, and V. I. Spitzyn, *Russ. J. Inorg. Chem.*, **18**, 210 (1973).
(7) P. A. Koz'min and G. N. Novitskaya, *Russ. J. Inorg. Chem.*, **17**, 1652 (1972).
(8) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
(9) J. D. Eakins, D. G. Humphreys, and C. E. Mellish, *J. Chem. Soc.*, 6012 (1963).
(10) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, **6**, 929 (1967).
(11) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 330 (1965).
(12) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).
(13) The previously reported[3] occurrence of two reduction waves for $[Re_2Cl_8]^{2-}$ must be considered in error, although the reason is not entirely clear. We have found that $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ which is not recrystallized immediately prior to use shows two waves with $E_{1/2}$ of −0.18 and −0.84 V *vs.* sce. The current for the −0.18-V wave appears to be a function of purity, disappearing entirely in freshly recrystallized material. The fact that the two waves previously observed, and reported, had equal diffusion currents was evidently fortuitous, and, unfortunately then, led to the reasonable conclusion that both waves were genuine. The difference between the previous $E_{1/2}$ (−1.44 V) and the present value (−0.84 V) for the genuine wave is more difficult to explain with certainty. There are several factors which might account for it. The previous work was done with a two-electrode dropping mercury circuit, in which potential errors due to an ir drop in the cell can occur; there might be a specific influence of mercury for this system; the previous circuitry could simply have been misstandardized.
(14) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(15) S. Manniv, J. Bronstein, and W. Low, *Phys. Rev.*, **187**, 403 (1969).
(16) B. Bleaney, *Phil. Mag.*, **42**, 441 (1951).