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Chemistry of *trans*-Aquonitrosyltetraamminetechnetium(I) and Related Studies

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Attempts to reduce Tc(VII) or Tc(IV) in strongly acidic solutions containing noncomplexing anions indicate that reduction to Tc(II) is possible, but the species of lower oxidation state are unstable and there is no assurance that they are mononuclear. This instability contrasts markedly with that of a compound reported by Eakins et al.[2] as containing $[Tc(NH_2OH)_2(NH_3)_3H_2O]^{2+}$. Structure determination by Radonovich and Hoard on the chloride salt of the cation shows it to be *trans*-$[Tc(NH_3)_4(H_2O)NO]^{2+}$, rather than that formulated by Eakins. The nitrosyl ion shows a stretch in the ir spectrum at 1680 cm^{-1}, the low frequency indicating great stabilization by $Tc^{I}\rightarrow(NO)^{I}$ back-bonding. The species is remarkably inert to substitution, as is the nitrosyl group to nucleophilic attack. At low pH, the *trans*-$[Tc(NH_3)_4(H_2O)NO]^{3+/2+}$ couple is reversible, E_f against NHE being 0.80 V. The ion of higher oxidation state undergoes substitution more readily than does that of charge 2+ and is unstable at higher pH. The values of pK_a for the 2+ and 3+ species have been measured as 7.3 and ca. 2.0, respectively. Modification of the Eakins method of preparation leads to other derivatives but of these only $[Tc(1,10\text{-phen})_2(NH_3)NO]^{2+}$ has been at all well characterized.

Introduction

A large amount of interesting chemistry depends on the propensity which Ru(II), when most of the ligands in combination with it are saturated, has for back-bonding with an unsaturated one.[1] It was felt that Tc(II) in a similar state of combination would show the effects of back-bonding to an even greater degree than does Ru(II), and the original motivation for the work to be described was to prepare Tc(II) as a mononuclear complex having only saturated ligands associated with it. This part of the work led to failure even when very powerful reducing agents were used in water solution and will be reported on only very briefly. Our attention then turned to the investigation of a compound, reported[2] as having the composition $[Tc(NH_2OH)_2(NH_3)_3H_2O]Cl_2$ (the cation is hereafter referred to as the pink ion or complex). If correctly formulated, this compound would in fact be an example of what we originally sought to prepare. The great stability of the compound was however in marked contrast to the instability our own experiments led us to assign to mononuclear Tc(II) in combination with saturated ligands. The major part of this report deals with characterizing the pink complex and developing its chemistry further.

Experimental Section

Materials. All stock solutions and aqueous reaction media were made up using doubly distilled water.

Argon as obtained from Liquid Carbonic was 97.95% pure. To remove oxygen, the gas was passed through two bubbling towers containing Cr(II). All-glass lines were used to convey it to reaction vessels.

Bio-Rad Ag50W-X2, 200–400 mesh cation-exchange resin was cleaned following the procedure described by Deutsch.[3]

Deuterium oxide (99.84 mol %) was purchased from Bio-Rad.

Nitric oxide and dinitrogen were used as delivered from lecture bottles supplied by Matheson Co.

Trifluoromethanesulfonic acid as obtained from 3M Co. was redistilled and then diluted to 6 M for storage. Trifluoroacetic acid as purchased from Matheson Coleman and Bell and tetrafluoroboric acid as purchased from J.T. Baker were used without further purification.

Pyrazine, 2,2′-bipyridine, and 1,10-phenanthroline purchased from Aldrich were used without further purification. Pyridine was stored over molecular sieve. Isonicotinamide was purified by recrystallization from water.

Hydroxylamine hydrochloride and hydrazine hydrate (99–100%) were used as purchased from Matheson Coleman and Bell.

The reducing agents Cr^{2+}, V^{2+}, and Eu^{2+} were generated from Cr^{3+}, VO^{2+}, and Eu^{3+} as trifluoromethanesulfonate salts in trifluoromethanesulfonic acid using amalgamated zinc. The solution of $Cr^{3+}(aq)$ was generated from CrO_3 dissolved in trifluoromethanesulfonic acid solution using H_2O_2 as reducing agent.[4] The solution containing VO^{2+} was prepared as described by Deutsch.[3] Europium(III) in solution was prepared by dissolving a known quantity of Eu_2O_3 (99.9% purity supplied by Grace Chemical Co.) in an excess of acid in aqueous solution.

Technetium-99, a weak β emitter with a half-life of 2.12×10^5 years[5] was purchased from Oak Ridge National Laboratory, in two lots, one as solid ammonium pertechnetate and the other as a solution of the salt in 0.08 M acid. The salt $(NH_4)_2TcCl_6$ was prepared by a slight variation of the method of Nelson et al.[6] and the hexaiodo salt by the method of Dalziel et al.[7] The preparation of the pink compound of Eakins et al.[2] worked precisely as described by them. In addition to following the procedure outlined by them for obtaining a solid, a cation-exchange column was used to isolate a pink band. This band was eluted by 1 M HCl, the solution containing it was evaporated to dryness, and the solid was recrystallized from water and absolute ethanol. When the solid was dissolved in water and the resultant solution allowed to evaporate at room temperature, a crystalline product formed. Some of the crystals proved to be suitable for structural determination by x-ray diffraction. Eakins et al.[2] described the preparation only of the chloride salt of the pink complex. The bromide and tetrafluoroborate salts were prepared by dissolving the chloride in water, capturing the pink complex on a cation-exchange resin, eluting it with 1 M trifluoromethanesulfonic acid, and precipitating it by adding solid NaBr or concentrated HBF_4. For the trifluoroacetate salt, 1 M trifluoroacetic acid was used as eluent, and the solid was obtained by rotary evaporation. In each case the solid was recrystallized from water and absolute ethanol.

The description of a number of other preparations which are not such obvious extensions of established procedures are deferred to the Results section.

Apparatus and Methods. Provision was made so that, when necessary, operations, including ion-exchange separations, were carried out under inert atmospheres.

Uv and visible spectra were recorded on Cary 14 or 15 spectrophotometers. Infrared spectra were taken on a Perkin-Elmer Model 621 spectrophotometer covering the range 250–4000 cm^{-1}, samples being pelleted in KBr.

The cyclic voltammetry apparatus was built by Glenn Tom. The reference electrode was saturated calomel and the indicator electrode

Table I. Microanalyses of Compounds Containing the Pink Complex

Compd	% Tc		% C		% H		% N		% halide	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
trans-$[(NH_3)_4Tc(NO)(OH_2)]Cl_2$	34.6	35	0.0	0.0	4.90	4.78	24.5	24.6	24.8	24.7
trans-$[(NH_3)_4Tc(NO)(OH_2)]Br_2$	26.4	27	0.0	0.0	3.73	3.79	18.7	18.6	42.7	42.6
trans-$[(NH_3)_4Tc(NO)(OH_2)](F_3C_2O_2)_2$	22.5	22	10.9	10.7	3.17	3.31	15.9	15.7	25.9	25.8
trans-$[(NH_3)_4Tc(NO)(OH_2)](BF_4)_2$	25.6	25	0.0	0.0	3.60	3.73	18.1	18.0		

either platinum or a hanging mercury drop. The solutions were ca. 2.5×10^{-3} M in complex and at least 0.1 M in supporting electrolyte. The formal potentials, E_f, as reported are understood to be reduction potentials. They were taken as the mean of the anodic and cathodic peaks and are referred to the NHE. The cell used for potentiometric titrations was H shaped, the two compartments being connected by a fine glass frit, provision being made for deaerating the solutions from below. The sample cell was fitted with a Pt electrode and in the reference compartment a SCE was used. Titrant was delivered through a Teflon needle from a micrometer syringe. Potentials were measured using a Beckman Expandometric pH meter, standardized with a Weston cell. To make allowance for liquid junction potentials, Fe^{2+}(aq) was titrated with Ce(IV) in a reaction medium of the same composition. The difference between E_f as measured and $E°$ as recorded was applied also to the Tc system. If activity coefficients were identical for the couples, this would in effect give $E°$ for the unknown one.

The pH measurements were made using a Metrohm combination microglass electrode on a Beckman Expandometric pH meter or a Metrohm 101 pH meter. NBS buffers purchased from Beckman Instruments were used to standardize the pH meters. The technetium complexes were dissolved in water and titrated with standard sodium hydroxide solution, and the pK_a was determined from a plot of pH vs. extent of neutralization.

Magnetic susceptibility measurements were made on the Ventron Corp. Model 7600 system. Though there was provision for varying the temperature over the range −140 to +25 °C, as will be seen, the measurements were so irreproducible that no additional information was gained from studying the susceptibility as function of temperature. To calibrate the apparatus, $CoHg(NCS)_4$ was used as standard. Diamagnetic corrections were taken from published tables.[8]

Analyses for C, H, N, and halides, but not Tc, were performed by the Stanford Microanalytical Laboratory. Compounds were analyzed for Tc by two different methods.

1. The sample, whether an aliquot of a liquid sample or a weighed amount of solid, was made basic with sodium hydroxide, and 30% hydrogen peroxide was added to oxidize all technetium species to pertechnetate. The solution was boiled to remove excess peroxide and made acidic. If metal cations were present, they were replaced by protons using cation exchange (TcO_4^- comes through with water) and the resulting solution was diluted to a known volume. The optical densities at 287 and 244 nm were determined and the concentration of TcO_4^- was calculated using extinction coefficients of 2360 and 6220 M^{-1} cm^{-1}, respectively.[9] A number of species including chloride ion interfere, and it was not always convenient to use the spectrophotometric method.

2. A 1-ml aliquot was added to 10 ml of Packard Insta-Gel Emulsifier (for aqueous and organic samples) in a vial. The technetium-99 isomer used has an activity of 3.7×10^4 dpm μg^{-1},[10] but as a solid it is not suitable for direct measurement because of the low energy of the β rays (0.3 MeV). The samples were therefore measured on a Packard Tri-Carb liquid scintillation spectrometer, Model 3375, equipped with computer programmer and an IBM Selectric printout. Counts per minute were compared with known samples prepared from recrystallized NH_4TcO_4 and $(NH_4)_2TcCl_6$. Whenever possible, samples were chosen to give between 10^4 and 10^6 cpm in order to keep the counting error within 1%. However, the inaccuracies in weighing out solid samples between 0.5 and 1.0 mg and in separating ion-exchange fractions resulted in analytical errors occasionally as high as 5%.

Results

A. The Pink Species. Characterization of the Pink Complex. It will simplify the further presentation of the observations if the constitution of the pink complex is dealt with at the outset. The conclusion[2] that Tc is contained in an ion of charge 2+ and that the chloride is present in solution as the free ion was confirmed by cation-exchange techniques. In the absence of proof of the identity of the nitrogen-containing products formed on oxidation, the observations on stoichiometry of the oxidation reaction are not particularly useful. We found moreover (vide infra) that the amount of oxidizing agent consumed, Ce(IV) or MnO_4^-, was dependent on conditions. Eakins et al.[2] did not do elemental analysis on the compound, but their conclusion that the N:Tc ratio is 5:1 was confirmed by analytical work done here. However, their conclusion that NH_2OH is present rests on analytical data that can be accounted for in alternate ways and the infrared spectrum of the pink compound (cf. Figure 1) made it seem certain that the complex in fact does not contain NH_2OH. Metal complexes of this ligand have sharp N–O stretches between 910 and 1035 cm^{-1} [11] and this region of the ir spectrum of the pink compound is free of absorption. There is a rather strong absorption at 1680 cm^{-1} which does not diminish in intensity on deuteration, though the peak nearby at lower frequency is thereby removed. The band at 1680 cm^{-1} is at a high enough energy to suggest the presence of nitrosyl, but in the absence of analysis for oxygen, there is also the possibility that two nitrosyls are present, trans to each other. Apart from the issue of whether the group trans to nitrosyl is HO or H_2O, the ambiguities in the structure of the pink complex were completely removed by the structure determination on the pink compound, using x-ray diffraction, completed by Radonovich and Hoard.[12] In fact, the structural work provides strong evidence that the trans ligand is H_2O rather than OH^-, evidence which is supported by the properties of the ion to be described. As implied in the above, the structural work shows the pink species to be *trans*-aquonitrosyltetraamminetechnetium(I).[13] Bond distances are as follows (Å): N–O, 1.203 (6); Tc–NO, 1.716 (4); $(Tc\text{–}NH_3)_{av}$, 2.163 (5); Tc–OH_2, 2.168 (4). The Tc–N–O bond angle is 178.7 (2)°.

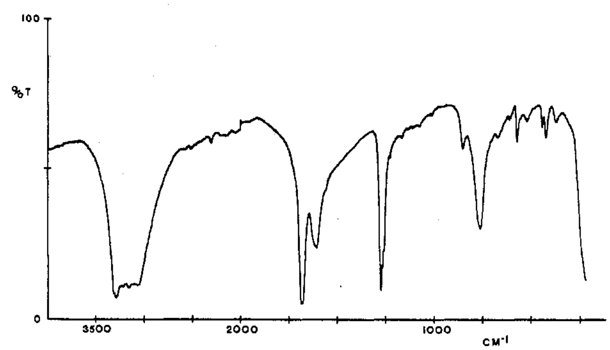

Figure 1. Infrared spectrum of *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_2$.

With this formulation, it being understood that Tc(I) is strongly stabilized by back-donation to $(NO)^I$, the apparent conflict between our conclusions as to the behavior of Tc(II) complexed by saturated ligands and the stability of the pink compound is resolved.

Analytical Results on Preparations Containing the Pink Complex. A summary of the results of elemental analyses on compounds containing the pink species is presented in Table I.

As implied earlier, analytical results based on redox titrations are ambiguous unless a complete determination of the products is made. Our "analytical" results in this connection

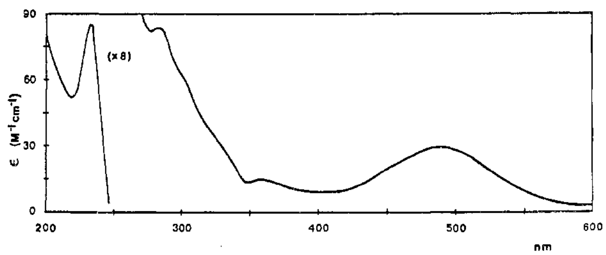

Figure 2. Absorption spectrum of *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_2$ in water.

are reported only in general terms. Eakins et al.[2] observed that 9 equiv of cerium(IV) sulfate is consumed/mol of pink complex when ICl was used as catalyst. We observed only 1 equiv of Ce(IV) to be taken up under like conditions (however, the acid concentration may have been different) and also when Ce(IV) as the perchlorate is used. In 2 M H^+, only 1 equiv of MnO_4^- is consumed/mol of Tc complex, but in 0.01 M H^+, 9 equiv is consumed. For the oxidation $Tc^IN^{III} \rightarrow Tc^{VII}N^V$, 8 equiv/mol is expected. Apparently, there is some induced oxidation (of NH_3 for example) accompanying the processes referred to above.

Visible–Uv Absorption Spectra. The general features of the absorption spectrum of the chloride salt of the pink complex are shown in Figure 2. Band maxima in nm and extinction coefficients (ϵ, M^{-1} cm^{-1}) are as follows: 487 (29), 358 (17), 305 sh, 283 (81), 233 (670). The band maxima and extinction coefficients were not altered on changing the medium from water to 2 M $HClO_4$ or by using the trifluoroacetate salt in place of the chloride.

Magnetic Susceptibility. As mentioned earlier, the molar susceptibility varied from sample to sample, some values being as high as 600 × 10^{-6} cgsu. The majority however showed the material to be diamagnetic (−41, −61, −31, −63 × 10^{-6} cgsu). When a correction is made for the diamagnetic contribution, a slight residual paramagnetism remains which is ascribable to temperature-independent paramagnetism.

Acid Dissociation Constant of the Pink Ion. Titration of a solution of the pink complex using NaOH as titrant yielded for pK_a at $I \approx 0.01$ and at 25 °C the value of 7.3, a value that was reproduced when the titration was repeated after acidification. When the product solution at a pH above the end point is left exposed to air, slow decomposition does take place.

Electrochemistry. A solution of the pink ion in 3 M trifluoromethanesulfonic acid was prepared, using the cation-exchange method. Cyclic voltammograms were run at pH intervals as the acidity was reduced by adding solid sodium acetate. One-electron oxidation of Tc(I) takes place reversibly at high acid concentration, E_f being registered as 0.80 V. The value of E_f does not change with acidity until the pH is raised above 2. Above this, E_f decreases monotonously as the pH increases, but the behavior is no longer reversible. The peak to peak separation in the pH range above 2 and below 5 is ~75 mV and the slope in the plot of pH vs. E_f is 35 mV per pH unit rather than the 59 mV expected for the half-reaction

$$trans\text{-}[Tc(NH_3)_4(NO)OH]^{2+} + H^+ + e^- = trans\text{-}[Tc(NH_3)_4(NO)H_2O]^{2+}$$

Nevertheless, a definite break in the pH vs. E_f profile can be located at pH 2.0 and it is reasonable to conclude that pK_a for the dissociation of *trans*-$[Tc(NH_3)_4(NO)H_2O]^{3+}$ is ca 2.0. The reaction giving rise to irreversibility has not been identified but in view of the rapid decomposition of the higher oxidation state to be reported on presently, the irreversibility is no surprise. At pH's above 5, the cyclic voltammetry traces become very irreversible.

Reactions of the Pink Ion. The solubility of the chloride of the pink complex in water is moderately high and exceeds 0.03 M. In dilute acid, and even in 2 M $HClO_4$ or HCF_3SO_3, the species appears to be indefinitely stable. However, in 2 M HCl or 2 M HBr slow decomposition takes place, and in a period of 2 weeks to 1 month, a green solid appears. The solids show prominent peaks in the ir spectra at 1800–1830 cm^{-1} and appear closely related to the better characterized green oxidation products to be described in the next section. The oxidizing agent responsible for the transformation has not been identified nor has it been shown that light is not responsible.

The pink complex is unstable in basic solution. In 1 M NaOH, the color of the solution darkens even in the absence of O_2. On acidifying and separating the cationic species by ion exchange, some starting material appears, as well as a fraction which, on being separated from liquid by rotary evaporation, shows a prominent ir stretch at 1810 cm^{-1}. This is in the region of a nitrosyl stretch shown by the nitrosyl of technetium(II) (vide infra). The agent causing oxidation has not been identified; conceivably, the coordinated nitrosyl disproportionates in alkaline solution.

Attempts to form new products by substitution on the pink complex with isonicotinamide, CO, SO_2, or HS^- led to failure. Even on refluxing for 20 h with isonicotinamide (0.3 M), no inner-sphere substitution was observed. When NO is bubbled through a solution 0.01 M in complex, a yellow-green color develops, but on passing N_2 through the solution, the pink color is restored.

No reaction was observed when the pink ion in 2 M HCF_3SO_3 was treated with Eu^{2+}, Cr^{2+}, V^{2+}, or Cr^{2+} in the presence of $EDTA^{2-}$ (reducing agents at 0.01 M; time ca $^1/_2$ h), nor was reaction observed when hydrazine or azide ion (at ~1 M) was added to a solution of the pink salt, apart from a slight decomposition ascribable to the increased alkalinity.

B. The Nitrosyl Complex of Tc(II). The electrochemistry of the pink complex showed that the technetium(I) nitrosyl is readily oxidized by a one-electron change. This section deals with the preparation of compounds containing the technetium(II) nitrosyl complex and with some of its properties.

Preparation of *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_3$. A solution of the pink complex in 2 M $HClO_4$ with ClO_4^- as the only anion present was prepared by means of a cation-exchange column. Sufficient cerium(IV) perchlorate was added for one-electron oxidation, whereupon the solution turned green. A green band was separated using a cation-exchange column with 3 M HCl as eluent, and the solution containing the green ion was rotary evaporated to dryness. The yield based on the formula *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_3$ was about 70–80%. Anal. Calcd: Tc, 30.8; N, 21.8; Cl, 33.2; H, 4.40. Found: Tc, 31; N, 21.4; Cl, 32.4; H, 4.5.

The oxidation was performed successfully also with MnO_4^- in acid, but attempts to obtain solids with anions other than Cl^- failed. In fact, the green band could not be eluted with 6 M tetrafluoroboric acids. Trifluoromethanesulfonic acid did elute the green band but more slowly than HCl and crystals were not obtained from the solution.

The green solid which results when the pink salt is left in contact with 2 M HCl (vide supra) contains a Tc:N:Cl atom ratio of 1.0:5.0:2.5–2.8. A residual ir absorption band at 1680 cm^{-1} for the solid shows that some of the original starting material is left, but there is also a band at about 1815 cm^{-1} ascribable to a new material. An absorption band that appears at 312 cm^{-1} can be attributed to a Tc^{II}–Cl^- stretch. When the pink complex is heated in concentrated HCl at 60 °C, the solid eventually dissolves forming a green solution. The green solid which separates on rotary evaporation has a prominent ir band at 1803 cm^{-1}, that at 1680 cm^{-1} having disappeared. Peaks characteristic of coordinated ammonia have disappeared, but a strong peak at 1398 cm^{-1} is present, attributable to

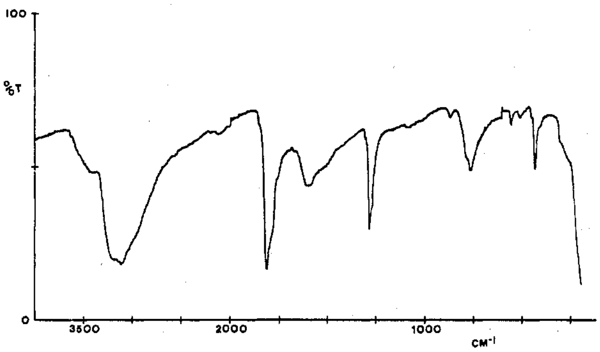

Figure 3. Infrared spectrum of *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_3$.

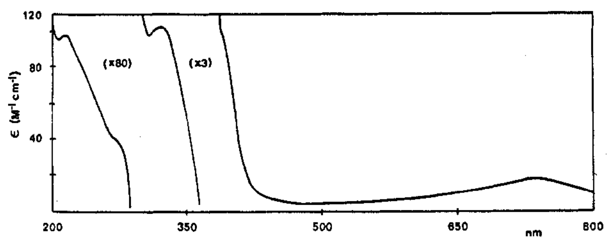

Figure 4. Absorption spectrum of *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_3$ in 0.1 M trifluoromethanesulfonic acid.

NH_4^+. This evidence and elemental analysis suggest the major component of the solid to be $(NH_4)_2[Tc(NO)Cl_5]$.

Characterization of *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_3$. The ir spectrum of the compound is shown in Figure 3. For present purposes, the most interesting of the bands is that at 1830 cm^{-1} which we take as being due to the N–O stretch. The bands at 1610, ~1300, and 830 cm^{-1} are attributable to coordinated ammonia. As before, it is impossible on the basis of present evidence to assign the bands at lower frequencies.

Once the green chloride has been formed, considerable difficulty is experienced in getting it back into solution. The solid is insoluble in acetone, ethanol, ether, dimethylformamide, and dimethyl sulfoxide. It does dissolve in water but produces a pink rather than green solution. It is insoluble in strong acid (1 M or greater HCl, HCF_3SO_3, HCF_3CO_2, $HClO_4$) but it does dissolve, though slowly, in 0.1 M HCF_3SO_3 to form a green solution. The uv–visible spectrum of the solution is shown in Figure 4. Band maxima (nm) and the corresponding extinction coefficients (M^{-1} cm^{-1}) are as follows: 743 (19), 320 (3.0×10^2), 272 sh (6×10^2), 213 (8.0×10^3).

The molar susceptibility of the solid is 1100×10^{-6} cgsu at room temperature. Assuming that the variation with temperature is not anomalous and correcting for diamagnetism lead to a magnetic moment of 1.7 μ_B per Tc. The solid shows electron spin resonance absorption but no fine structure is observable at room temperature or 77 K. The absorption is symmetrical and it corresponds to $g = 2.03$.

Reactions. Observations already cited suggest that the green Tc(II) species is stable in water only at low pH. This instability made it impossible to determine pK_a for $[Tc(NH_3)_4(NO)H_2O]^{3+}$ spectrophotometrically and is presumably responsible for the fact that the cyclic voltammograms for the Tc^{II}–Tc^{I} couple become irreversible at high pH. A cursory investigation of the processes that accompany dissolution in water was made by taking the ir spectrum of the solid formed on rotary evaporation of the solution after it had been kept 1 day. The solid showed ir peaks of about equal intensity at 1680 and 1810 cm^{-1}, peaks at 1398 cm^{-1} ascribable to NH_4^+, and one at 312 cm^{-1}, which, as before, we attribute to Tc^{II}–Cl^- stretch. The latter peak appears prominently when the green ion is left for a protracted period of time in 3 M HCl. The solid which forms appears to be a mixture of *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_3$ and *trans*-$[Tc(NH_3)_4(NO)Cl]Cl_2$; at any rate, five N's are retained in the solid per Tc.

Europium(II) reduces *trans*-$[Tc(NH_3)_4(NO)H_2O]^{3+}$ quantitatively to the pink ion. Though in principle $(NO)^I$ coordinated to Tc^{II} should be more reactive than when it is coordinated to Tc^I, all attempts to exploit this supposed increased reactivity failed. Nucleophilic reagents such as hydrazine etc. simply reduce Tc^{II} to Tc^I, and as we have already seen, the technetium(I) nitrosyl is unreactive to nucleophilic attack.

C. Attempts to Prepare Derivatives of the Pink Ion. Apart from the experiments already mentioned concerned with investigating the reactions of π acid ligands with the pink species, little was done attempting direct substitution of NH_3 by other ligands. Owing to the great substitution inertia of the $(ON)Tc^I$–NH_3 bonds, we felt that a more productive approach would be to vary the Eakins[2] procedure and, at the point that NH_3 is ordinarily added, to add other ligands of interest in its place. These experiments supported our surmise that the bulk of the tetraammine is produced after NH_3 is added but led to only limited success in producing other derivatives.

In one attempt, NaOH was added to the reaction mixture to bring the pH to 7.0. At this point, the solution was brownish purple. It was rotary evaporated to dryness and taken up in water, and ethanol was added which caused a brown precipitate to form. This showed a strong ir peak at 1730 cm^{-1}, significantly different from that of the pink ion. When the solid was redissolved and passed through an ion-exchange column, a small amount of pink ion was eluted, but the brown band did not move even with 12 M HCl or 9 M HCF_3SO_3.

Using ethylenediamine in place of NaOH, again adding enough to bring the pH to 7.0, on subjecting the product solution to ion-exchange separation, as many as five pink cationic products were observed, ranging in charge from 1+ to 4+. Some of these do contain ethylenediamine but in no case could solids be obtained from the separate fractions. Using *n*-propylamine, a brown material similar to that described earlier and a small amount of the pink species were obtained.

With EDTA, some pink complex was produced, and, in addition, several cationic complexes and anionic species of charges 1− and 2− were formed. Examination of solids containing the anionic species by ir spectra showed EDTA to be present and showed prominent peaks at 1730 and 1805 cm^{-1}, presumably due to nitrosyl.

With 2,2′-bipyridine and 1,10-phenanthroline, we did get promising results. These are rather similar for the two kinds of ligands but those for the latter are the less ambiguous and only they will be described here.

A solution of 1,10-phenanthroline in aqueous ethanol was added, as in the cases just described, until the pH became 7.0. The product solution was evaporated and the residue was dissolved in water and placed on a cation-exchange resin. Three fractions were eluted using HCl solutions, the first green and the next two red. The apparent charges carried by the species, as judged from the speed of elution are 2+, 3+, and >>3+, respectively. The major bands were the extremes—these comprise ca. 10 and 88% of the total—and the middle band seems to be an oxidation product of the first.

The solid obtained by evaporating the solution containing the first fraction shows a strong peak in the ir spectrum at 1690 cm^{-1}, small peaks due to ammonia, and peaks characteristic of phenanthroline. Elemental analyses on various preparations showed the Tc:C:N:Cl ratio to be 1.0:12.0:4.9–5.0:2.9–3.0. The absorption spectrum in the visible region for the green solution made by dissolving the salt in water shows maxima at 590 and 467 nm, the corresponding values of the extinction coefficients being 1.5×10^3 and 3.4×10^3. Cyclic voltammetry on a solution of the solid in 2 M HCl shows a reversible redox process, the value of E_f corresponding to it being 0.69 V. The oxidation by Ce(IV) produces a red species, which is restored to the green by Eu^{2+}. The red species is also formed when a solution of the green is left in 2 M $HClO_4$ for 2 days but not when 2 M HCl is the reaction medium.

The solid obtained by rotary evaporation of the solution containing the second fraction has a strong ir peak at 1822 cm^{-1} and a small one at 1690 cm^{-1} (the second presumably arising from partial reduction of red to green), peaks characteristic of NH_4^+ and phenanthroline, and a peak at 340 cm^{-1} which is ascribable to a Tc–Cl^- stretch. The solution has absorption maxima at 555 and 444 nm, with extinction coefficients of the order of 10^3. These absorption characteristics are the same as those of the solution formed by oxidizing the green monophenanthroline species.

The solid resulting from the fraction of highest charge has a strong peak in the ir spectrum at 1712 cm^{-1}, as well as peaks characteristic of phenanthroline. The uv–visible spectrum has bands at 522 nm (ϵ 1.5×10^2), 440 nm (ϵ 3.9×10^3), 415 nm (ϵ 3.5×10^2), and 355 nm (ϵ 2.4×10^2). A solution in 4 M HCl subjected to cyclic voltammetry undergoes oxidation at 1.1 V vs. NHE, but the wave is irreversible. Elemental analyses were reproducible and the Tc:C:N:Cl ratio was found to be 1.0:12:6.0:2.0. All the values were somewhat low but are brought into agreement with a simple formula if four molecules of water of crystallization are assumed to be present.

The apparent high charge is an idiosyncracy of HCl as the eluent. If HCF_3SO_3 or $HClO_4$ solutions are the eluents, the apparent charge is 4+. Gel filtration, using $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{4+}$ to define the elution behavior of a "dimeric" species, indicates that the red ion is monomeric.

Though the species have not been studied exhaustively, it appears that we have characterized $[Tc(NH_3)_2(1,10\text{-phen})(NO)H_2O]^{2+}$ (first fraction), its one-electron oxidation product, and $[Tc(1,10\text{-phen})_2(NH_3)(NO)]^{2+}$ (last fraction). The extra chloride in the solid obtained from the first species is apparently present as HCl of crystallization. The resistance of the bis(phenanthroline) complex to elution from a cation exchange by HCl is not understood. The fact that the ion moves more slowly than an ammine complex of the same charge is not surprising. Elutability is affected by the nature of the ligands as well as the charge on the species.

D. Aquo Ions of Technetium in Lower Oxidation States. Attempts to produce solutions containing Tc in low oxidation states by the reduction of TcO_4^- failed unless the acidity of the reaction solution was very high. At moderate acidity, 1 M or less, TcO_2 forms, but in 4 M HCF_3SO_3, potentiometric titration indicates that reduction below Tc(IV) does occur. Owing to the eventual formation of TcO_2 even under these conditions, the end point is not well defined, but the results suggest that 5 equiv of reducing agent (Eu^{2+}) was consumed/mol of TcO_4^-. The product solution with excess reducing agent when placed on a cation-exchange column shows several species to be present. A striking result is that some Tc(VII) can be stripped from the column. Technetium dioxide, which is the major product, remains in the top of the column. Sometimes a yellow band separated which spread out on the resin and eventually produced TcO_2. With Cr^{2+} as reducing agent, a Tc-containing species is collected with the $Cr(H_2O)_6^{3+}$ fraction. Exposure of this fraction to air resulted in TcO_2 being formed. Some encouraging signs also appeared in attempts to reduce $TcCl_6^{2-}$ in strongly acidic solution with Eu^{2+} and Cr^{2+}, but, again, the species of lower oxidation states are too unstable to survive isolation by ion-exchange techniques. The species in homogeneous solution produced by Eu^{2+} in these experiments was pink, but the pink color at most lasted a few seconds. The fact of reduction is also indicated by the observation that when Cr^{2+} is used as reducing agent, $CrCl^{2+}$ forms, in some cases as much as 1.8 mol/mol of $TcCl_6^{2-}$.

The results suggest that Tc in lower oxidation states can be formed in aqueous, very acidic solution by the action of strong reducing agents, but the species are very unstable. Rapid in situ methods will be required to characterize them, and there is of course no assurance that species of reasonable kinetic stability will prove to be monomeric.

Some experiments were done reducing $TcCl_6^{2-}$, TcI_6^{2-}, and TcO_4^- in 4 M HCF_3SO_3 with Eu^{2+} or Cr^{2+} while N_2 was being passed through. Infrared spectra of the solid formed by rotary evaporation revealed no peaks that might be attributable to a complex of N_2.

Discussion

There is little further to comment on with respect to the attempted reductions of Tc(VII) and Tc(IV) to aquo ions of lower oxidation states except to note that because $CrCl^{2+}$ is formed when Cr^{2+} is added to $TcCl_6^{2-}$ in strongly acidic solution, we can infer that reduction does occur. From the observation that as much as 1.8 mol of $CrCl^{2+}$ is produced/mol of $TcCl_6^{2-}$, we further infer that in fact there is reduction below the 3+ state. Additional work on these reactions, but changing the experimental approach so that fugitive species can be characterized, seems worthwhile.

In the Discussion, as in the experimental work, the major emphasis will be on the properties of the pink species, *trans*-$[Tc(NH_3)_4(NO)H_2O]^{2+}$. The low NO frequency and the relatively long NO bond distance, together with the relatively short Tc–NO[14,15] distance, suggest very strong back-donation from Tc^I to $(NO)^I$. This interaction is manifested also in the chemical properties of the complex. It should be noted that the language used in describing the interaction is dependent on the choice of elements which are to be combined, and it is convenience rather than necessity that leads to the choice Tc^I–$(NO)^I$ in preference to, say, Tc^{II}–NO.

Noteworthy among the chemical properties is the extraordinary resistance of the coordinated NH_3 to aquation. There is no precedent for the remarkable substitution inertia of an ammine complex of formal oxidation state 1+—the Tc^I–NH_3 bond seems to be kinetically stable almost indefinitely in acidic solution. There is little doubt that in such a mixture the failure to react is a result of inertia rather than thermodynamic stability. Delabilizing effects have been observed also for another low-spin d^6 metal ion, namely, Ru(II), where a π acid ligand in place of NH_3 cis or trans to a water molecule decreases the lability of the water.[16] The effect is attributable to the removal of electron density by the π acid ligand from the central ion, making it more difficult to break the metal ion–ligand bond. This effect, it should be emphasized, can operate in both cis and trans positions, and it is observed only for leaving groups such as NH_3 or H_2O which do not depend on $\pi d \rightarrow \pi^*$ donation in binding to the metal ion. When the leaving group is itself a π acid, it is labilized by a strong π acid ligand in the coordination sphere.[16] In the technetium(I) nitrosyl complex under consideration, the situation is quite clear for the ligands cis to $(NO)^I$—they are enormously delabilized by the presence of $(NO)^I$ as compared to that of a saturated ligand such as NH_3. (The half-time for aquation in $Ru(NH_3)_6^{2+}$ is ca. 7×10^{-6} s,[17] and $Tc(NH_3)_6^+$, because of the lower charge on the metal ion, can confidently be expected to be *much* more labile.) This is probably true also of the group trans to $(NO)^I$, but this has not been proven. Of interest also is the relative lability of the ligands cis and trans to the nitrosyl. Since we have not succeeded in substituting the trans ligand (water) by another, we have no measure of relative labilities. It would be hazardous to extrapolate from the behavior of isonicotinamide on Ru^{II} to that of $(NO)^I$ on Tc^I. Nitrosyl is a much stronger π acid than is isonicotinamide, and it may make some special electronic and structural demands in the activated complex which then differentiate strongly between cis and trans ligands.

The indications are that the NH_3 groups are more labile in $[Tc(NH_3)_4(NO)H_2O]^{3+}$ than they are in the pink species—at any rate, in acid, replacement of NH_3 by another group has been observed only when the higher oxidation state is generated. In most instances, in passing from a low-spin d^6 system to a low-spin d^5 system of the same element, rates of substitution decrease, the increase in positive charge on the central metal more than compensating for the decrease in ligand field stabilization. The present example is probably an exception to this general behavior, one which on closer examination does not violate any cherished principles. In the Tc(II) low-spin d^5 system, the electron hole is undoubtedly localized in the d_{xy} orbital—the Tc–N–O axis being chosen as z—and, as a result, there is an especially large loss in ground-state crystal field stabilization energy over that of the various structures that might arise in the course of a substitution reaction.

Thus far we have been concerned with rate behavior. Several instructive comparisons can be made in considering also equilibrium behavior.

The value of pK_a for *trans*-$[Tc(NH_3)_4(NO)H_2O]^{2+}$ has been measured as 7.3. An acidity as great as this for H_2O coordinated to a metal ion in the formal oxidation state of 1+ is unprecedented, and it speaks for a very large drain on the electron density of Tc^I caused by $(NO)^I$. The effect exerted by $(NO)^I$ is in fact greater than that which results from increasing the oxidation state by 1 unit—thus note that pK_a for $[Ru(NH_3)_5(H_2O)]^{2+}$ is >12[18,19] (Tc(I) and Ru(II) are isoelectronic).

The failure of π acids such as CO, isonicotinamide, and SO_2 to substitute for H_2O or NH_3 in the pink ion is quite in line with the idea that $(NO)^I$ is an exceedingly strong π acid. The complexes with the π acids are expected to be unstable at least in an equilibrium sense and, for all that is known, the substitution itself may be very slow. The replacement of H_2O by OH^-, it should be noted, is rapid but undoubtedly does not involve metal–oxygen bond breaking. The Tc^I–$(NO)^I$ unit is expected to have the highest affinity for ligands which are both good σ and π bases, and among these OH^- is a leading candidate. The high affinity of technetium(I) nitrosyl for OH^- has already been commented on in discussing the acidity of the pink ion.

The ease of oxidation of *trans*-$[Tc(NH_3)_4(NO)H_2O]^{2+}$ to *trans*-$[Tc(NH_3)_4(NO)H_2O]^{3+}$ ($E_f = -0.80$ V) is much greater than it is for the isoelectronic process involving Ru(II) → Ru(III) for which $E < -1.1$ V. The tendency Ru(II) has for back-bonding interactions has already been noted but there is no evidence that back-bonding is significant for Ru(III). Thus, there is a large loss in back-bonding stabilization in oxidizing Ru(II) to Ru(III). The comparisons cited suggest that this loss is less for Tc(I) → Tc(II), a conclusion which it would be difficult to arrive at on the basis of a priori arguments.

When NH_3 in the pink species is replaced by π acid ligands such as 1,10-phenanthroline, it is expected that the oxidation of Tc(I) to Tc(II) will become more difficult. This is in fact observed for the species which we formulate as $[Tc(phen)_2(NO)NH_3]^{2+}$, but not for the monophenanthroline complex (for the latter, $E_f = 0.69$ V). We have nothing to offer by way of rationalizing the latter result and the observation in fact raises the suspicion that the green monophenanthroline complex of Tc(I) has been incorrectly formulated.

A point of considerable interest is the relative acidity of *trans*-$[Tc(NH_3)_4(NO)H_2O]^{3+}$ and *trans*-$[Ru(NH_3)_4(NO)H_2O]^{3+}$, because it bears on the question of the extent of back-bonding for the two centers of the same charge and thus on the original intent of this work. Though the Ru(II) species is known from qualitative observations to be quite acidic,[20] no measurements of pK_a for the complex appear to have been published.

A number of observations suggest that redox processes for $Ru^{II}(NO^+) \rightarrow Ru^I(NO^+)$ are remarkably facile (thus note the ready reduction of the Ru(II) complex at high pH and the oxidation of Ru(I) when left in acidic aqueous solution exposed to air). These and other aspects of the work seem worthy of further study. The limitations on experimental procedures imposed by dealing with radioactive material greatly increase the difficulty of the work and make its continuation with present facilities uninviting.

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Registry No. *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_2$, 59188-02-2; *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_3$, 59188-03-3; *trans*-$[(NH_3)_4Tc(NO)(OH_2)]Br_2$, 59188-04-4; *trans*-$[(NH_3)_4Tc(NO)(OH_2)](F_3C_2O_2)_2$, 59188-05-5; *trans*-$[(NH_3)_4Tc(NO)(OH_2)](BF_4)_2$, 59188-00-0; $[Tc(NH_3)_2(1,10\text{-phen})(NO)H_2O]^{2+}$, 59187-98-3; $[Tc(1,10\text{-phen})_2(NH_3)(NO)]^{2+}$, 59188-01-1.

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(14) Comparing *trans*-$[Ru(NH_3)_5(NO)]^{2+}$ [14] and *trans*-$[Tc(NH_3)_4(NO)H_2O]^{2+}$, the Me–NO bond is shorter in the latter case by 0.05 Å and the NO bond is longer by 0.03 Å. Both NH_3 and H_2O being neutral ligands, the pentaammineruthenium affords a better comparison to the technetium case than does the *trans*-hydroxotetraammine.
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