more stable precursor complex (by reducing electrostatic repulsions) than might be found with a symmetric $M(H_2O)_6^{2+}$ ion. This factor may also contribute to the dependence of the derived $VO(OH)^{+/2+}$ self-exchange rate constant on the nature of the oxidant. Less of a variance in the derived k_{11} value for the symmetrical $Fe(H_2O)_6^{2+/3+}$ couple (10^{-4}–10^{-2} M^{-1} s^{-1}) is observed with the same set of oxidants.[13]

A measurement of direct electron exchange between $VO^{2+}(aq)$ and $VO_2^+(aq)$ has been made by using ^{51}V NMR techniques.[14] The rate constant in 6.5 M hydrochloric acid is reported to be 1.5×10^6 M^{-2} s^{-1} with the rate expression having a first-order dependence on $[VO_2^+]$ and second-order dependences on $[VO_2^+]$ and $[H^+]^{-1}$. While no mechanism was established, an inner-sphere process is suggested by two recently reported observations: (a) a mixed-valence dimer $V_2O_3^{3+}(aq)$ exists in equimolar solutions of $VO^{2+}(aq)$ and $VO_2^+(aq)$, with $K = 0.8$ M^{-1} in 5 M $HClO_4$,[15] and (b) the ^{18}O exchange between $VO^{2+}(aq)$ and water is catalyzed by $VO_2^+(aq)$, with $k(VO_2^+) = 3.9$ M^{-1} s^{-1}.[24] The proposed mechanism for catalysis involves electron transfer in an inner-sphere $V_2O_3^{3+}(aq)$ complex followed by rapid ^{18}O exchange in $VO_2^+(aq)$ ($t_{1/2} = 0.15$ s).[25] The rate and equilibrium data suggest that electron transfer between $VO^{2+}(aq)$ and $VO_2^+(aq)$ is principally a rapid inner-sphere process.

The outer-sphere-exchange rate constants for metal aquo ion couples have been estimated by using a semiclassical model in which the rate constant k_{11} is expressed as a product of a preequilibrium constant K_A, an effective nuclear frequency ν_n, and electronic and nuclear factors κ_{el} and κ_n.[5,23] The nuclear factor contains contributions from inner-sphere and solvent reorganization energies along with a tunneling factor Γ_n.

$$\kappa_n = \Gamma_n \exp[-(\Delta G_{out}^* + \Delta G_{in}^*)/RT] \qquad (16)$$

For metal aquo couples the solvent term ΔG_{out}^* is about 7 kcal mol^{-1} for an activated complex radius of 6.5 Å. The relative magnitudes of k_{11} for metal aquo couples have been shown to depend largely on the size of the inner-sphere reorganization energy ΔG_{in}^*, which is a function of the difference in the equilibrium M–O bond distances in the two oxidation states. The instability of the $VO(OH)^+$ and $VO(OH)^{2+}$ ions would likely prevent a determination of the V–O bond distances in this couple. The V–O bond distances have been measured for $VO(H_2O)_5^{2+}$ by using X-ray crystallography[26] and for $VO(H_2O)_5^{2+}$ and $VO_2(H_2O)_4^+$ in solution by EXAFS techniques.[27] In the $VO^{2+}(aq)$ ion a short V═O bond distance of 1.59 (1) Å is found while the V—O bond distance in the trans position is 2.3 (1) Å. The four equatorial bonds have an average length of 2.06 (1) Å. For the $VO_2^+(aq)$ ion two short V═O bonds of length 1.65 (5) Å were observed. The distance of the two V—O bonds trans to the short V═O bonds is 2.3 (1) Å, while the two remaining V—O bonds have an average length of 2.15 (5) Å. In the $VO(OH)^{+/2+}$ couple, the deprotonation of V^{IV}—OH_2 and the protonation of V^V═O would likely reduce the respective bond distance differences for the V^{IV}—OH/V^V═OH bond and the V—O bond in the trans position. While a definitive value of ΔG_{in}^* appropriate for the $VO(OH)^{+/2+}$ couple cannot be determined, it is not expected to be significantly different from other metal aquo ion couples with similar electronic configurations. The $VO(OH)^{+/2+}$ couple is isoelectronic (d^1/d^0) with the $Ti^{3+/4+}(aq)$ and $Ti(OH)^{2+/3+}(aq)$ couples, for which self-exchange rate constants of $>3 \times 10^{-4}$ M^{-1} s^{-1} and $\sim 1 \times 10^{-2}$ M^{-1} s^{-1},[17] respectively, have been estimated from Marcus correlations in cross-reaction kinetic studies. These couples, along with $Fe(H_2O)_6^{2+/3+}$ ($k_{11} = 1.1$ M^{-1} s^{-1})[5] and $V(H_2O)_6^{2+/3+}$ ($k_{11} = 1 \times 10^{-2}$ M^{-1} s^{-1}),[2] involve the exchange of an electron from a nonbonding πd orbital. This range of rate constants is consistent with the moderate bond length changes (0.10–0.15 Å) observed for these couples. The average V–O bond length change accompanying electron exchange in $VO(OH)^{+/2+}$ is likely to fall within this range.

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Registry No. $Ru(dmbpy)_3^{3+}$, 65605-26-7; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ni(dmbpy)_3^{3+}$, 65336-48-3; $Ni(bpy)_3^{3+}$, 64592-13-8; 4,4′-$(CH_3)_2$bpy, 1134-35-6; 4,4-$(C_6H_5)_2$bpy, 6153-92-0; 5,6-$(CH_3)_2$phen, 3002-81-1; 4,7-$(C_6H_5)_2$phen, 1662-01-7; 5-CH_3phen, 3002-78-6; phen, 66-71-7; bpy, 366-18-7; 5-Clphen, 4199-89-7; $VO(H_2O)_5^{2+}$, 15391-95-4; $VO_2(H_2O)_4^+$, 81738-79-6; $VO(OH)^+$, 73949-60-7; $VO(OH)^{2+}$, 41015-85-4.

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Photoaquation of *trans*-$[Cr(tn)_2F_2]^+$ in Acidic Aqueous Solution

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The photochemistry of the title molecule has been studied in acidic aqueous solution at room temperature. The main reaction mode is loss of fluoride ($\phi = 0.34$) with a smaller yield for amine aquation ($\phi = 0.18$). Firm evidence was obtained for the production of "one-ended" tn products in the latter reaction. The photostereochemistry of the reactions is consistent with the usual stereochemical change seen for Cr(III) complexes. The unusual reaction mode ratio can be ascribed to steric interactions with the six-membered tn ring.

Introduction

A central and continuing theme in Cr(III) photochemistry has been the importance and interplay of electronic and steric factors in determining the identity of the ligand(s) photosolvated and also the stereochemistry of the subsequent photosubstitution process. Approaches to the first aspect have ranged from the initial proposal of a set of rules[1] through molecular orbital theoretical calculations of metal/ligand bond labilization[2–5] to a fairly successful ligand field model for bond strengths in the excited state.[6–8] The stereochemical aspect has also progressed from the stage of a simple

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rule[9] to an apparently successful theory of symmetry-restricted ligand substitution.[7,8,10]

The fluoro–ammine complexes have played an important part in the testing of theory;[8,11] fluoride seems more photoinert than would be expected simply on the basis of its low ligand field strength. This was attributed to its π-donor strength, which causes a π-bond-strength increase in the putative reactive quartet excited state compensating for the σ-bond-strength decrease arising from population of σ antibonding orbital[11] (ref 5 presents a dissenting view). This behavior of fluoro complexes is correctly accommodated by the VC model for ligand loss whereas the simpler Adamson rule, for example, incorrectly predicts major loss of fluoride in *trans*-$[Cr(NH_3)_4F_2]^+$.

Also of considerable current interest are steric effects in photochemistry of Cr(III) complexes,[12–14] both for developing basic understanding and for probing mechanistic details by using particular steric constraints. It may be possible eventually to control, direct, inhibit, or promote particular modes of photochemistry by steric means.

That steric effects could be crucially important was shown dramatically[15,16] by the photochemistry of *trans*-$[Cr(cyclam)Cl_2]^+$. The molecule had a chloride quantum yield only $^1/_{1000}$th that of the ethanediamine analogue and photoaquation was stereoretentive, contrasting the usual stereochemical change.

Sheridan and co-workers[17,18] observed a different outcome of steric constraint in triethylenetetramine and triaminotriethylamine complexes; here the *cis*-diacido derivatives photosubstituted halide ion in contrast to the expectation of amine photoaquation. These and more recent studies with constraining ligands show that steric effects can change the course of a photosubstitution reaction or prevent it completely.

In this paper we wish to report a remarkable contrast between the photochemistry of *trans*-$[Cr(tn)_2F_2]^+$ and its ethanediamine and ammine analogues, apparently related to steric interactions of a subtle nature.

Experimental Section

Preparative Methods. *trans*-$[Cr(tn)_2F_2]Cl{\cdot}H_2O$ was prepared as described,[19] but by substituting 1,3-propanediamine for ethanediamine, and purified by several recrystallizations from aqueous 10^{-3} M HCl solution. The final material was washed well with ice-cold 95% ethanol and dried in a vacuum desiccator. The presence of one lattice water was shown by using a Cahn electrobalance with the sample being heated in dry nitrogen. Analytical data confirmed the identity and purity of the substance. Found (calcd for monohydrate): Cr, 17.45 (17.80); C, 24.67 (24.70); H, 7.76 (7.60); N, 19.16 (19.21); F, 13.79 (13.03); Cl, 12.03 (12.15). Ion exchange showed that any resolvable 1+ or 2+ impurities were present at much less than 1% of the total. The UV–vis spectrum agreed with literature values. Found (λ, nm (ϵ)): 540 (16.8), 466 (21.4), 398 (16.9), 360 (16.4). Literature[19] (λ, nm (ϵ)): 542 (16.5), 462 (20.9), 397 (16.8), 360 (16.4).

Chromium Analysis. Aqueous solutions of the complexes were oxidized with alkaline hydrogen peroxide and chromate ion determined at 372 nm (4.82×10^3 L mol^{-1} cm^{-1}). *trans*-$[Cr(tn)_2F_2]^+$ gave obviously low results, owing to its stability. An acid hydrolysis step was therefore included. About 5 mg of the complex was digested with 12 drops of concentrated nitric acid until the reaction appeared complete. After dilution with nanopure water, two NaOH pellets and 30% H_2O_2 were added and the mixture heated at 100 °C for 2 h. Conversion to chromate was quantitative.

Fluoride Analysis. Photolyzed samples (2.5 mL) containing about 5 mg of the complex were mixed with 7.5 mL of TISAB with CDTA buffer and determined by using an Orion 96-09 combination fluoride electrode with a Metrohm E388 potentiometer. Standard additions and calibration with standards showed that the metal complexes did not interfere. No measurable postirradiation thermal loss of fluoride from the starting complex or photoproducts occurred.

UV–Vis Difference Spectra. Both Unicam SP8-400 and Cary 17 spectrophotometers were used. Difference spectra for the thermal reaction were obtained by maintaining the reference solution of complex at room temperature and the sample at 50 °C. For the photoreaction, both solutions were at room temperature and the reference was kept dark while the sample was irradiated periodically.

Ion-Exchange Chromatographic Analysis. A Technicon autoanalyzer with a 6.5×0.6 cm column of Hamilton HC-X8 (20–25 μm) cation-exchange resin at 14–20 °C was used with 130 mL h^{-1} ammonium sulfate eluent either isocratically or as a nonlinear 0.1–0.5 M gradient. Where it was necessary to collect peaks and analyze for chromium, pH 3 sodium sulfate was used. Peak detection was by oxidation with alkaline hydrogen peroxide and measurement of chromate. Calibrations showed that *trans*-$Cr(tn)_2F_2]^+$ gave a peak of variable height about 20% of theoretical. This brings into question the exact sensitivity for some thermal product and photoproduct peaks, although we found that conversion of several aquo–chromium(III) complexes including *trans*-$[Cr(tn)_2(H_2O)F]^{2+}$ was near quantitative.

Peaks were identified by comparison of retention times with authentic samples together with spectra and Cr:F ratios of collected peaks. Typically, 15–20 mL of solution was collected, containing about 0.2 μmol complex. Spectra were taken in a 10-cm cell (0–0.1 absorbance), absorbances at the maxima being about 0.01–0.05. To test for the presence of aquo ligands in the complex, the solutions were made basic with 1 drop of 4 M ammonia and the spectra were rerecorded. They were then reacidified and rerun to confirm that no significant base hydrolysis had occurred. Solutions were then analyzed in triplicate for Cr, to obtain the quoted molar absorptivities (±25%), and then for fluoride, to obtain the Cr:F ratio for the peak.

Photolysis and Quantum Yield Measurements. Reineckate actinometry[21] was used for light intensity measurements. In quantum yield determinations, conversions were kept lower than about 8% to minimize complications from secondary photolysis.

For the quantitative studies, 2.7-mL samples of 10^{-2} M solutions of the compound in 1.319×10^{-3} M $HClO_4$ with 0.04 M $KClO_4$ were irradiated in stirred 1-cm rectangular spectrophotometer cells. Quantum yields were measured at 405 and 546 nm.

Thermal and Photochemical Amine and Fluoride Loss. Amine aquation was followed by proton uptake with an Ingold combination LOT glass electrode and a PDP-11 computer monitoring system. Standard additions of acid, base, or fluoride could be made by using a stepping motor-driven microburet.

Determination of released amine is complicated by protonation of a pH-dependent fraction of any released fluoride. The mV reading was therefore monitored before, during, and after photolysis. The titer of standard acid needed to return to the starting mV reading was then recorded. Separate standard additions of fluoride and back-titrations showed that the fluoride is 46% protonated at pH 3.0. The titer therefore measured the released amine plus 46% of the released fluoride, since free amine groups are protonated, any aquo product complexes are in their acid forms, volumes of titrant added were small (10–20 μL), and thermal reactions were negligible in extent. The total released fluoride was then determined as described above, and the two measurements were combined to obtain the free amine.

Results

Thermal Reactions of *trans*-$[Cr(tn)_2F_2]^+$. Reaction of *trans*-$[Cr(tn)_2F_2]^+$ for 30-min intervals at 50 °C in 1.32×10^{-3} M $HClO_4$/0.04 M $KClO_4$ leads to spectral changes, but no isosbestic points are seen, and the difference spectrum shows that at all wavelengths studied the product mix has a higher molar absorptivity than the starting complex. The main absorbance increase occurs at about 500 nm with subsidiary peaks at 575, 420, and 370 nm, but the changing shape of the growing envelope also suggests some complexities in the path of the thermal reactions. The acid hydrolysis of *trans*-$[Cr(tn)_2F_2]^+$ shows no

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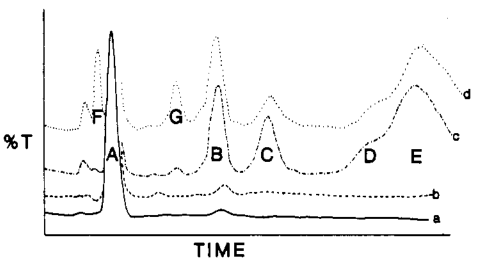

Figure 1. Ion-exchange chromatograms of products of *trans*-$[Cr(tn)_2F_2]^+$: (a) 30-min thermal reaction at 50 °C; (b) 1.5-h thermal reaction at 50 °C; (c) extensive photolysis at room temperature; (d) solution of (c) heated at 50 °C for 30 min (see text for identification of labeled peaks).

isosbestic points,[22] and the single product is *trans*-$[Cr(tn)_2(H_2O)F]^{2+}$. The spectral data for the complexes suggest, and we observe in runs at low pH, that the main absorbance increase occurs at around 375 nm, considerably different from the spectral changes for the higher pH.

Measurement of the rate of proton uptake at 37 °C gave an overall first-order rate constant of 5.0×10^{-7} s^{-1}. The extent of the three possible thermal reactions corresponding to loss of fluoride and loss of the first and second ends of the tn ligand was examined by ion exchange. A solution thermalized for 30 min in 1.3×10^{-3} M $HClO_4$ at 50 °C gave only a peak with a retention time (two eluents) appropriate to an isomer of *trans*-$[Cr(tn)(tnH)(H_2O)F_2]^{2+}$ (peak B, Figure 1a). The composition of this peak was investigated with photochemically produced material, described later, which gives better yields. As the thermal aqueous solution reactions of Cr(III) are stereoretentive, this is the isomer with trans fluorides (*mer*-FWF). No isomerization to *cis*-$[Cr(tn)_2F_2]^+$ was observed. No *trans*-$[Cr(tn)_2(H_2O)F]^{2+}$ was observed, but because of its longer retention time a small amount might be unobservable. For the very low conversion of this experiment, <1%, the major aquation mode seems to be aquation and protonation of one end of the tn ligand, with lesser contributions of complete tn loss or fluoride aquation. The rate constant of 5×10^{-7} s^{-1} at 37 °C is therefore of the order of that for loss of the first end of the tn ligand.

The rate of loss of the second end of the tn ligand is discussed further later; we note here only that thermalization for 3 times as long at 50 °C leads to obvious complications with little growth of the tnH^+ intermediate and the appearance of new peaks in the chromatogram presumably due to aquation of fluoride, tnH^+, and tn from the intermediate (Figure 1b).

From the point of view of the photochemical study, *trans*-$[Cr(tn)_2F_2]^+$ is sufficiently stable thermally that primary thermal reactions do not interfere.

Photolysis of *trans*-$[Cr(tn)_2F_2]^+$. In contrast to the thermal reaction, photolysis at 436 nm leads to good isosbestic points, located at 330, 410, and 455 nm, for at least the first 15% of decomposition. The difference spectrum shows growth of a major peak at 505 nm, with a subsidiary peak at 375 nm; the photoproducts are clearly quite different from the thermal products at any pH. Since *cis*-$[Cr(tn)_2(H_2O)F]^{2+}$ has a spectrum with peaks at 375 (30.8) and 511 (27.0) nm (L mol^{-1} cm^{-1}) these results suggest it is a major photoproduct. The products have lower molar absorptivities than *trans*-$[Cr(tn)_2F_2]^+$ only from 410 to 455 nm, so 436 nm was chosen as a convenient irradiation wavelength that would minimize errors owing to secondary photolysis.

On irradiation, rapid proton uptake ensued at a rate proportional to the absorbed light intensity. Subsequent to irradiation, thermal proton uptake was unchanged from the very small value prior to photolysis. Analysis showed that fluoride release was a significant mode of photoreaction, and determination of the total base released and the total free fluoride gave a fluoride to amine ratio of 1.70 ± 0.15 (5 determinations) after allowance for the 46% protonation of the fluoride.

Quantum yields for the two modes were measured by combining measurements of the above type at 405 and 546 nm with light intensity measurements by Reineckate actinometry.[21] Quantum yields for amine loss were observed to be 0.18 (405 nm, four runs) and 0.19 (546 nm, two runs). Fluoride yields were more variable, but no consistent wavelength dependence could be discerned; the average of the data for the two wavelengths was 0.34 (six runs). Thus, no significant wavelength changes in yield or yield ratio were observed. These quantum yields give a fluoride:amine ratio of about 1.8, in good agreement with the directly determined ratio at 436 nm.

Further product identification, confirmation, and detail on the photoreaction path was obtained from the ion-exchange relative retention times, spectra, and Cr:F ratios on collected chromatographic peaks and comparisons of chromatograms of thermal products and photoproducts.

A separation of four primary photolysis products was obtained (Figure 1c). In this chromatogram, peak A is for *trans*-$[Cr(tn)_2F_2]^+$. The pattern of product peaks is reminiscent of those observed[23] for *trans*-$[Cr(NH_3)_4F_2]^+$ but with an important lengthening of retention times for several products relative to *trans*-$[Cr(tn)_2F_2]^+$. This arises because the labilized tn ligand remains coordinated and protonates to give a unit charge increase for the product ion, here to the 2+ species. Such species are only "pseudo 2+ ions" chromatographically; that is, they elute with a retention time between those for analogous 1+ and 2+ ions, since the dangling plus charge does not contribute fully to the effective charge seen by the ion-exchange resin surface. The first three product peaks, B, C, and D, are possibly such species. The last peak shown, E, is *cis*-$[Cr(tn)_2(H_2O)F]^{2+}$ as the collected photoproduct peak has a Cr:F ratio of 1.01 ± 0.03 (five runs), spectral absorptions at about 500 (30) and 366 (20) nm (L mol^{-1} cm^{-1}, ± 25%), shift to the red in base, and the peak elutes just after the authentic trans isomer as expected. The spectral data differ from the literature[20] values 511 (27) and 376 (31) nm (L mol^{-1} cm^{-1}), but this may reflect the real uncertainties in our data for the small amounts collected.

Peak B has the same retention time as the thermal product of amine aquation; the collected peak had a Cr:F ratio of 2.1 ± 0.15 (five runs) and absorption bands at 512 (40), 400 (30), and 360 (33) nm (L mol^{-1} cm^{-1}), which red-shift in base. This supports peak B being *mer*-FWF. The splitting seen in the second ligand field band was previously observed[23] for the analogous triammine.

That peak C is an isomer of B is supported by the similar retention time, the observation that its Cr:F ratio is 2.05 ± 0.25 (six runs), and the similar locations and absorptivities of the spectral peaks, 512 (35) and 380 (33) nm (L mol^{-1} cm^{-1}), which again red-shift in base. The very similar retention time to peak B strongly suggests that this peak is *mer*-WFF rather than either of the two possible facial isomers.

The remaining peak, D, proved too small and, in the required sodium sulfate eluent, too close to peak E for completely reliable collection, spectral, and Cr:F analysis to be performed. From the retention time it could be either or both *trans*-$Cr(tn)_2(H_2O)F]^{2+}$ and isomers of *fac*-WFF. Fortunately, this is a minor product.

Thermal Decomposition of Photoproducts. Further useful information was obtained by heating the photoproducts at 50 °C for 30 min prior to chromatographic analysis (Figure 1d). The peak for *trans*-$[Cr(tn)_2F_2]^+$ decreased as would be expected, peaks B and D remained essentially unaltered, C was halved, *cis*-$[Cr(tn)_2(H_2O)F]^{2+}$ decreased about 10%, and new peaks F and G appeared. These observations support the assignments given above. B (*mer*-FWF) should thermalize tn stereoretentively to give *trans*(F_2)-$[Cr(tn)(H_2O)_2F_2]^+$, and F elutes at the expected location. Since *trans*-$[Cr(tn)_2F_2]^+$ decomposes thermally to B and B is approximately in a steady state, from the concentration ratio of the two species we can estimate k_2/k_1 to be between 2 and 20. This is a rough estimate if only because of incomplete oxidation to chromate of the more stable complexes, which may or may not include B. It is likely that the higher estimate is the better.

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Peak G probably arises in similar fashion from decomposition of C and is the cis isomer corresponding to F. The rates of production of F and G are similar, as would be expected for tn loss from close isomers of $[Cr(tn)(tnH)(H_2O)F_2]^{2+}$. In assigning G it is important to realize that loss of either F^- or one end of tn from *cis*-$[Cr(tn)_2(H_2O)F]^{2+}$, the remaining major product, would lead to products with ionic charges greater than two that would not elute in the accessible region being considered. However, anation of *cis*-$[Cr(tn)_2(H_2O)F]^{2+}$ could lead to *cis*-$[Cr(tn)_2F_2]^+$, which would elute about where we find peak G. We consider such anation processes extremely improbable, however, and favor G being *cis*(F_2)-$[Cr(tn)(H_2O)_2F_2]^+$.

Anation reactions resulting from the high concentrations of sulfate in the collected fractions confused our attempts to study directly the thermal decomposition products of peaks B and C.

Supporting the above assignments of the primary products is that the peak area ratio $E/(B + C) = 2.2$, which is in acceptable agreement with the observed fluoride to amine aquation ratio of 1.7. If D is also a tnH^+ product and is included in the denominator, the agreement is even better. This in turn implies that problems with the quantitative oxidation to chromate are not severe for these product peaks.

In summary, therefore, the major thermal and photochemical process observed are as follows:

$$\begin{aligned}
&\textit{trans}\text{-}[Cr(tn)_2F_2]^+ \rightarrow \textit{cis}\text{-}[Cr(tn)_2(H_2O)F]^{2+} + F^- \text{ (HF)} \quad \phi = 0.30\\
&\qquad \rightarrow \textit{trans}\text{-}[Cr(tn)_2(H_2O)F]^{2+} + F^- \text{ (HF)} \quad \phi = 0.04?\\
&\qquad \rightarrow \textit{mer}\text{-FWF} \quad \phi = 0.09\\
&\qquad \rightarrow \textit{mer}\text{-WFF} \quad \phi = 0.09\\
&\qquad \rightarrow \textit{mer}\text{-FWF} \quad k_1(37\ ^\circ C) = 5 \times 10^{-7}\ s^{-1}
\end{aligned}$$

$$\textit{mer}\text{-FWF} \rightarrow \textit{trans}(F_2)\text{-}[Cr(tn)(H_2O)_2F_2]^+ \quad k_2 \approx 20k_1$$

$$\textit{mer}\text{-WFF} \rightarrow \textit{cis}(F_2)\text{-}[Cr(tn)(H_2O)_2F_2]^+ \quad k_3 \approx k_2$$

Discussion

Thermal Reactions. DeJovine and co-workers[22] studied the acid-catalyzed loss of fluoride from *trans*-$[Cr(tn)_2F_2]^+$ to yield *trans*-$[Cr(tn)_2(H_2O)F]^{2+}$ and found no evidence for an acid-independent path for fluoride loss or for any amine aquation. There was no steric enhancement of loss of the acido ligand in *trans*-$(tn)_2$ complexes over analogous $(en)_2$ complexes of Cr(III), which contrasts the large effect observed[24] in Co(III) and ascribed to steric interaction of the tn ligand with the axial ligands in the favored skew-boat conformation present in the Co compounds.

Our results are consistent since at pH 3 no thermal fluoride loss occurs and amine is aquated with a small rate constant that would have been unobservable at the low pH of the earlier work. This rate constant is almost 2 orders of magnitude smaller than that measured for *trans*-$[Cr(en)_2F_2]^+$ at the same temperature, consistent with earlier conclusions that there is significantly less ring strain in the six-membered chelate ring. For tn complexes there is little information available for the relative magnitudes of k_1 and k_2. It has been reported that, unlike $[Cr(en)_3]^{3+}$, a monodentate protonated amine intermediate cannot be obtained from the thermal reaction.[25] Nevertheless, $[Cr(tn)_3]^{3+}$ photolyzes to both $Cr-tnH^{2+}$ species and free tnH_2^{2+} in single-step processes,[26] and the monodentate ligand complex appeared thermally stable. Our ion-exchange data for the thermal decomposition of the two tnH^+ complexes, produced photochemically, suggest $k_2 \approx 20k_1$. This contrasts with the ethanediamine analogue where $k_2 = 5k_1$, reflecting an enhanced aquation rate of the first end of the en ligand arising from ring strain. Overall, however, there seems to be nothing particularly unusual about the ground-state thermal reactions of *trans*-$[Cr(tn)_2F_2]^+$.

Photochemistry of *trans*-$[Cr(tn)_2F_2]^+$. The observation that the major reaction mode of *trans*-$[Cr(tn)_2F_2]^+$ is fluoride loss contrasts sharply with the behavior of the analogous ethanediamine and ammine complexes. The reported fluoride quantum yields increase slightly from the ammine[23] to the bis(ethanediamine)[27] compound but not enough to foreshadow the reversal of major reaction mode seen in the tn complex. Other than this, our data show that the photochemistry, particularly the photostereochemistry, is as expected from analogy to other complexes and the present understanding of d^3 photochemistry.

Table I. Spectral Data for Cr(III) *trans*-Diacido Bis(diamine) Complexes

Cr complex	${}^4B_{1g}$	${}^4E_g$
$(tn)_2F_2$[a]	462–468 (21)	538–542 (17)
$(pn)_2F_2$[a]	466 (23)	522–530 (17)
$(en)_2F_2$[b]	466 (21)	525–530 (16)
$(tn)_2Cl_2$[c]	457 (25)	595 (26)
$(pn)_2Cl_2$[b]	450 (27)	577 (27.9)
$(en)_2Cl_2$[b]	453 (23)	578 (24.5)
$(tn)_2Br_2$[c]	458 (27)	623 (36)
$(pn)_2Br_2$[c]	460 (28)	606 (37)
$(en)_2Br_2$[b]	460 (24)	607 (35)

[a] Reference 20. [b] Reference 29. [c] Reference 35.

Thus, the amine loss mode leads to an approximately equal proportion of *mer*-FWF and *mer*-WFF, paralleling our earlier findings for the difluoro tetraammine complex. In the present work we cannot be certain whether or not some *fac* isomer may be formed, but in any event it is the minor contributor. These results are consistent with theoretical predictions.[23,28]

Photochemical fluoride loss gives the *cis*-aquofluoro compound with possibly a small amount of the trans isomer. If this process originates from the lowest excited quartet state as usually assumed, allowed N–Cr–N bending will lead to the ground state of the tbp having the remaining fluoride in the trigonal plane. The substituting water ligand theoretically then enters cis to fluoride, yielding the *cis*-aquofluoro product (see Figure 2B of ref 23), as observed. Theory does not predict formation of the trans isomer, so the minor peak D remains unexplained.

The unusual feature of this system is the marked enhancement of the fluoride mode, a genuine anomaly because the fluoride yields of the ammine and ethanediamine analogues are both quite small. We do not think the usual σ and π parameters for fluoride and amine fail to apply to the tn complex; spectroscopically, the ligand field strength of fluoride is only slightly reduced relative to that of the analogues, which does not change the VC calculations significantly.

However, the larger splitting of the first ligand field band for all the diacido–$(tn)_2$ complexes of Table I does suggest a common, unusual feature. Although no crystal structure has been reported for the present complex, analogous compounds are known to have the six-membered rings in chair conformation in a trans arrangement.[31,32] The crystal structure of *trans*-$[Cr(tn)_2(NH_3)F]^{2+}$ confirms both the trans arrangement of the rings and the chair conformation of the ring on the same face as the fluoride ligand. Models and NMR studies[32] show that in this trans-chair arrangement the axial methylene protons of the α-carbon atoms are close to and create a very unsymmetric interaction with the z-axis ligand. The spectral data of Table I suggest this causes a small reduction in the ligand field strength of the axial ligand, although it does not affect the ground-state thermal reaction rates.

According to VC theory the ligand rearrangements leading to photoreaction occur in the plane containing the σ-antibonding

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electron. To simplify calculations, reaction via a tbp intermediate is assumed, but an equivalent pathway through a pentagonal bipyradmidal (pbp) intermediate is easy to imagine and may be more realistic considering the activation volume[33] evidence supporting associative photosubstitution in cationic Cr(III) complexes.

In such a seven-coordinate transition state of the $(tn)_2$ complex the steric crowding is severe, particularly in the equatorial plane. A model shows that as a water molecule approaches the FNFN plane of labilization, one of the two N–F equatorial edges trans to the amine ligand is blocked by a methylene group, favoring entry on the other. As the N–Cr–F angle then closes toward 70°, the axial proton on the tn α-carbon interacts strongly with the fluoride ligand trans to the entering water molecule. As this interaction occurs on only one side of the fluoride, it could promote its loss from the coordination sphere, further facilitated by the proximity of a hydrogen-bonding proton of the adjacent amine group. This provides the best explanation for the observed unusual fluoride aquation. The concept of a seven-coordinate transition state seems to be needed to explain the large excited-state effect in the absence of any ground-state enhancement of fluoride aquation.

Models show that the ring configuration of the ethanediamine analogue is such that no analogous interactions occur. Therefore, in this molecule, as in the tetraammine, the entering water molecule has easy access to the equatorial plane and the fluoride ligand does not experience any notable interactions with other ligands during the course of an expansion to a pbp intermediate.

Endicott has also proposed[34] that the photoreactions of Cr(III) occur via a seven-coordinate "associative" transition state, emphasizing its ground-state nature. While we agree that the main photochemistry in this system occurs via such a ground-state intermediate, we note that some of our earlier studies and some features of this system also require a small proportion of reaction via excited-state intermediates for consistency with the VC theory of d^3 photostereochemistry.

In summary, the change in photochemical reaction mode seen on increasing the chelate ring size by one methylene group is explicable in terms of a steric effect on the lability of fluoride in the excited state, without any concomitant effect in the ground state. Although the VC theory is capable of giving good predictions of the excited-state labilizations for many molecules, steric effects can play an important part in either completely stopping photochemistry or dramatically changing its course. We have found a major photochemical effect can be induced by a structural change that, to a casual glance, may seem unimportant.

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Registry No. *trans*-$[Cr(tn)_2F_2]^+$, 42476-30-2; *cis*-$[Cr(tn)_2(H_2O)F]^{2+}$, 42476-40-4; F^-, 16984-48-8.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 7. Formation and Redox Reactions of Sulfur-Bonded Aqua(sulfito)- and Bis(sulfito)[bis(phenanthroline) or -bis(bipyridine)]cobalt(III) Complex Ions[1,2]

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Unlike the case for all the other aquo amine cobalt(III) complexes so far studied, SO_2 uptake in the range $2 < pH < 7$ by *cis*-$[Co(phen)_2(OH_2)_2]^{3+}$ and the $(bpy)_2$ congener does not form an observable O-bonded species but goes directly to the S-bonded aqua sulfito complex at rates much too rapid to observe by stopped-flow procedure. However, the rate of the substitution by a second sulfite group of the remaining aqua ligand to form the *cis*-bis(sulfito) complexes is within stopped-flow times. This involves solely the ionic reactants HSO_3^- and SO_3^{2-} and appears to proceed by the S_N1(lim) or D mechanism. At higher pHs, the only observable products are S-bonded *cis*-$[Co(phen)_2(SO_3)(OH)]$ and its $(bpy)_2$ analogue, and their formations involve reactions of SO_2, HSO_3^-, and SO_3^{2-} with the $(OH)(OH_2)$ and $(OH)_2$ forms of the diaqua species, describable by three rate constants. Internal redox reactions to yield Co(II) and SO_4^{2-} in a 2:1 ratio occur only at elevated temperatures and acidities, and only the fully protonated forms of either the bis(sulfito) or aqua mono(sulfito) complexes undergo this reaction.

Introduction

A number of earlier papers in this series[2] have demonstrated that various aqua amine cobalt(III) complex ions react with aqueous sulfur dioxide by direct addition to yield oxygen-bonded sulfito complexes. These products are unstable in acid (pH <2), reverting to the original reactants. Similar behavior has been observed for the aqua pentaammine complexes of rhodium(III), chromium(III), and platinum(IV), as well as for the hexaaquachromium(III) species.[3]

None of the O-bonded mono(sulfito) cobalt(III) compounds has been isolated due to instability factors other than acid-catalyzed decomposition. These factors are their tendencies (a) to undergo internal redox, (b) to isomerize to a stable S-bonded form, or (c) to add a second sulfito ligand. These secondary reactivities vary considerably, depending upon the nature of the amine ligand moiety. Thus, $[Co(NH_3)_5OSO_2]^+$ very rapidly undergoes intramolecular electron transfer,[4] while its long-chain tetraethylenepentamine analogue, $[Co(tetren)OSO_2]^+$, isomerizes to the stable S-bonded form with no evidence for redox even at elevated temperatures.[5] Similarly, the bis(ethylenediamine) species, *cis*-$[Co(en)_2OSO_2]^+$, exhibits redox[2] over the pH range 3–7 as the

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(1) Based on the Ph.D. dissertation of V. K. Joshi, State University of New York at Buffalo, 1984. Copies are available from University Microfilms, Ann Arbor, MI. Detailed data for many of the experiments discussed in this paper are given in the dissertation.

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