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Relative Labilities of 1,3-Diaminopropane and Ammonia Ligands in Photoaquation of [Cr(tn)$_x$(NH$_3$)$_{6-2x}$]$^{3+}$ Complexes

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A series of mixed ammine/tn (1,3-diaminopropane) Cr(III) complexes has been prepared and characterized and their photochemistry studied in acidic aqueous solution. For the *cis*-and *trans*-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$ and the [Cr(tn)(NH$_3$)$_4$]$^{3+}$ complexes, respectively, the quantum yields of total base released are 0.24 ± 0.01, 0.34 ± 0.02, and 0.36 ± 0.02 and the ammonia yields as a percentage of the total base are 85 ± 3, 90 ± 4, and 97 ± 3%. The room-temperature doublet emission decay lifetimes and fractions of reaction via the doublet have been measured to be 2.7 (–), 2.4 (85%), and 2.2 μs (83%). For the reaction via the doublet state, the apparent rate constant calculated for loss of each ammonia ligand is the same for the first and third compounds in the sequence, and equal to that for the hexaammine complex. The corresponding rate constant is larger in *trans*-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$, suggesting that steric crowding leads to a form of anchimeric assistance of ammonia loss. In contrast, the analogous rate constant for loss of a single end of the tn ligand in either of the bis-tn compounds is less than half that for [Cr(tn)$_3$]$^{3+}$ and drops even further in going from the bis-tn pair to the [Cr(tn)(NH$_3$)$_4$]$^{3+}$ complex. Loss of the two ligands is therefore competitive, with the poorer tn leaving group losing out to the ammonia. Chromatographic analyses of the products formed on photoaquation of these complexes and of [Cr(tn)$_3$]$^{3+}$ confirm the above reaction mode ratios and, where investigated, show that the photoaquations occur with stereochemical change. The product expected for simultaneous loss of both ends of the tn ligand from [Cr(tn)$_3$]$^{3+}$ is not found. Rate constants for thermal loss at 60 °C of the first and second ends of the tn ligand from [Cr(tn)$_3$]$^{3+}$ are 3.1 × 10^{-6} and 5.8 × 10^{-5} s^{-1}, respectively. The activation energy of the second step is 25 kcal mol^{-1}.

Introduction

Studies of the photoaquation and photophysical properties of hexaammine complexes of Cr(III) have played an important part in helping clarify the interesting behavior of such compounds.[1-3] Also in many ways they have turned out to be archetypal for inorganic photochemical systems. The complexes show efficient, wavelength-independent photoaquation with 70–90% of the photoreaction quenchable, by virtue of its proceeding via the doublet state, a state having a room-temperature solution lifetime in the microsecond regime. The remainder of the photochemistry is fast and unquenchable but, where studied,[2,4,5] shows the same ratio of reaction as for the quenchable part, strong evidence for an intermediate common to both pathways.

The nature of this intermediate remains uncertain, but the results in this paper do not bear on this. Rather the concern is the degree to which and the manner in which steric effects can play an important role in determining the nature and stereochemistry of photoreaction in d^3 systems.

Important effects were noted previously for *trans*-dichloro-(cyclam)chromium(III), which was surprisingly photoinert[6,7] and photoaquated with low yield and retention of stereochemistry, unusual for a Cr(III) complex, and for the *cis-α*-(triethylene-tetramine)dichlorochromium(III) complex,[8] where the ligand forced chloride rather than amine aquation. More recently there have been reports of the effects of macrocyclic ligands on the relevant photophysical properties of Cr(III) excited states. The sepulchrate complex has been reported[9] to have a doublet lifetime slightly longer than that of Cr(en)$_3$$^{3+}$; in contrast, the similar macrocyclic compounds Cr(sar)$^{3+}$ and Cr(diamsar)$^{3+}$ have been reported[10] to have room-temperature solution lifetimes shorter than about 10 ns. Larger differences in lifetime and photochemical quantum yields have been reported[11] for the trans and cis isomers of [Cr(cyclam)(NH$_3$)$_2$]$^{3+}$. These results have demonstrated that

steric constraints that prevent stereochemical change (or ligand loss) have a marked effect on photochemical pathways and yields.

An apparently different, and in our view unusual, steric effect was found[12] for the *trans*-difluorobis(1,3-diaminopropane)chromium(III) ion. In contrast to the analogous diaminoethane complex, which shows amine loss[13-15] in accord with theoretical predictions,[16] the reaction mode changes to predominantly fluoride loss as a result of the increase in the chelate ring size from five to six atoms. Here there appears to be nothing to prevent the stereochemical change that we would expect to be associated with photoaquation of the tn ligand. With this system, it was not possible to decide whether the observed increase in proportion of fluoride with increasing ring size was due to a type of anchimeric assistance of the loss of fluoride associated with steric interactions in the larger ring or to reluctance of the tn ligand to play the role of leaving group.

It seemed unlikely that the effect resided in any difference in ligand field strength of en and tn since the spectral band maxima for the first ligand field band in the tris complexes are so similar. The present investigation was undertaken to try to distinguish between these two possibilities, encouraged by the success of an earlier study[17] in which it was possible to obtain information about the relative leaving group efficiencies of ammonia and en by study of the photochemistry of the various mixed-ligand complexes formed by these two ligands.

We report here the synthesis of the mixed tn/ammine complexes, their characterization and photochemistry, and our conclusion that tn is a reluctant leaving ligand, particularly when it has to compete with ammonia. The results also show that competitive loss of ligands occurs from the Cr(III) excited state. In addition a chromatographic technique has been developed that allows rapid separation of the 3+ and 4+ cationic photoproducts. Our results show that stereochemical change is associated with the photoreaction and that simultaneous loss of both ends of the tn ligands as earlier reported[18] is not seen.

Experimental Section

Syntheses. Both *cis*- and *trans*-[Cr(tn)$_2$Cl$_2$]$^+$ were prepared as the chloride salts by a literature method[19] based on heating chromium(III)

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chloride hexahydrate with the free diamine in a nonaqueous solvent.

trans-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$. Five grams of recrystallized *trans*-[Cr-(tn)$_2$Cl$_2$]Cl was transferred to a 50-mL Carius tube, and about 20 mL of anhydrous ammonia was condensed on to it by using liquid-nitrogen cooling under vacuum. After being sealed, the tube was allowed to warm to room temperature and left for about 0.5 h, during which time the green starting material had completely changed through red to yellow. The reaction mixture was cooled in dry ice and the tube opened. The ammonia was allowed to evaporate, with the last amounts requiring evacuation. The yellow-brown solid that remained was dissolved in the minimum amount of 10^{-3} M HClO$_4$ at 30 °C, the solution filtered and 70% perchloric acid added dropwise (*caution!* 70% perchloric acid may form explosive mixtures) until the first signs of crystallization appeared. When this mixture was cooled in ice, yellow crystalline needles of *trans*-[Cr-(tn)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$ formed. These were filtered off and washed with 50 mL of 95% ethanol and 10 mL of ether prior to drying in a vacuum desiccator; the yield was 6 g (60%) of first crop material. The crystallization step was repeated three times to ensure the complete conversion of the counterion from chloride to perchlorate.

cis-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$. In several preparations, the above procedure was repeated by starting with 5 g of *cis*-[Cr(tn)$_2$Cl$_2$]Cl as well as with the analogous bromo compound, and similar yields were obtained. For reasons discussed in the Results section, in some preparations lithium amide (10 mg; prepared by reaction of lithium with the ammonia in situ) was also included in the reaction mixture.

In the subsequent recrystallizations, the cis isomer is much more difficult to work with than the trans isomer, but with experience it was possible to obtain material that gave good analytical and spectroscopic data even though it appeared to be quite amorphous and was unsuitable for X-ray crystallographic study.

[Cr(tn)(NH$_3$)$_4$](ClO$_4$)$_3$. The four-step synthesis of the *cis*-[Cr-(NH$_3$)$_4$Cl$_2$]Cl starting material proceeded from chrome alum via aquopentaamminechromium(III) nitrate and (oxalato)tetraamminechromium(III) nitrate by using literature methods.[8,20,21]

Ten grams of the dichlorotetraammine compound was suspended in 100 mL of spectral grade dimethyl sulfoxide (Aldrich), 50 mL of 1,3-diaminopropane (Aldrich) was added, and the mixture was vigorously stirred for 8 h at a temperature between 70 and 80 °C. To the cooled solution, 200 mL of 100% ethanol was added and the mixture cooled on ice. The pink-yellow precipitate that formed was filtered off, washed with 20 mL of 100% ethanol, and air-dried. The yield of crude product was 3 g. This was dissolved in 10 mL of 10^{-3} M HClO$_4$ and filtered and 70% HClO$_4$ slowly added until precipitation just began (*caution!*). The pale yellow precipitate was filtered off, washed with 95% ethanol and ether, and air-dried. The substance was recrystallized three times in the same manner to give 1 g of purified material.

Isomers of [Cr(tn)$_2$(H$_2$O)$_2$]$^{3+}$. The trans and cis isomers of [Cr-(tn)$_2$(H$_2$O)$_2$]$^{3+}$ were prepared and characterized as described in the literature.[22]

Analyses. Elemental analyses were performed by Canadian Microanalytical Services (Vancouver, BC), except for chromium, which was carried out as follows. A 5–10-mg sample of the complex was digested in a sand bath with 10 drops of concentrated nitric acid for 10 min at about 90 °C. This mixture was cooled, 2 mL of organopure water, 3 pellets of sodium hydroxide, and 10 drops of 30% hydrogen peroxide (fresh) were added, and the solution was again digested at 90 °C until clear and bright yellow. The cooled solution was made up to 100 mL with organopure water (important) and the absorbance of the chromate ion measured at 373 nm (ϵ = 4.82 × 10^3 L mol^{-1} cm^{-1}).

UV–Vis and IR Spectra. UV–vis spectral measurements were made with a Unicam SP8-400 spectrophotometer and IR measurements with a Perkin-Elmer 283 spectrophotometer using KBr disks.

X-ray Powder Photography. X-ray powder photographs were taken with a Phillips PW 1024 camera and Cu Kα radiation. They were evaluated both by visual means and on the basis of a microdensitometer tracing.

Quantum Yield Measurements. Monochromatic light was obtained by using a water-cooled AH-6 1000-W capillary mercury lamp with infrared and 436-nm interference filters. Solutions were thermostated at 20 °C. All measurements were made in aqueous solutions that were about 10^{-2} M in complex with 1.452 × 10^{-3} M HClO$_4$ plus 0.1 M KClO$_4$ to serve as an ionic strength buffer.

Total base release was measured by proton uptake using the ΔpH method with an Ingold LOT electrode and a PDP-11 computer moni-

toring system. Standard additions of acid or base could be made by using a stepping-motor-driven burette.

Ammonia was determined by separation from the complex and its photolysis products by elution with 15 mL of 0.8 M sodium chloride solution through a short (2 cm × 0.8 cm diameter) column of sodium form CGC 241 (Baker) ion-exchange resin. The eluent was titrated coulometrically, with pretitrated buffer used to minimize blank corrections.[23,24] Standard additions to photolyzed solutions confirmed that the method was precise and that neither the complexes nor free 1,3-diaminopropane eluted from the column with the ammonium ion.

Reineckate actinometry[25] was used for light intensity measurements, and as a check, the light intensity was continuously monitored with an Alphametrics Model P1110S silicon diode detector and Model 1020 meter. In quantum yield determinations, the wavelength was chosen and conversions were kept lower than 12% to minimize complications from secondary photolysis. Calculations of the magnitude of secondary photolysis were carried out by using published equations.[26,27]

Emission Lifetimes and Fast/Slow Photoreaction Ratio. Doublet-state lifetimes were measured both by following the emission decay and from the slow conductivity change that followed 347-nm laser excitation in pH 3.0–3.4 acidic solution at room temperature (24–28 °C); other details of the method are to be found in the literature.[28,29] The two results were in good agreement, with the emission values (667 nm) being generally more consistent; these are therefore given. For *trans*-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$ and [Cr(tn)(NH$_3$)$_4$]$^{3+}$ the ratio of fast reaction to slow reaction was measured from the appropriate conductivity changes; the system was calibrated by using the hexaammine system and results in good agreement with those in the literature[29] were obtained.

Reversed-Phase Liquid Chromatography. The principles of ion separation using ion interaction reagents and competing ions have been published.[30,31] A Varian Model 5000 instrument with UV–vis detector and a 30-cm octadecylsilane 10-μm column (Scientific Products and Equipment, Ltd.) was used. The eluents were 25 mM butanesulfonate as an ion-pairing reagent and 25 mM triethylammonium (chloride) as a competing ion made up in 90% methanol/water and in water. Good separations were obtained with a 15% methanol isocratic elution. In many experiments the pH of the eluent was varied over the range pH 3–7, to examine the effect on the separation of cis and trans isomer aquo products. In an effort to quantify such isomer ratios, detector wavelengths were changed over the range 230–270 nm. Also peaks were collected after the detector cell and analyzed for chromium as described earlier.

Results

Characterization of Compounds. Table I gives the analytical and spectral data for the complexes. The chemical analyses are in satisfactory agreement with the theoretical values.

Table I also gives infrared wavenumbers for the Cr–N region for the cis and trans isomers of the diammine compounds. The observation of five bands in the cis and four bands in the trans is consistent with the assigned geometry based on a criterion found[32] for other cis/trans isomer pairs for which the counterion was perchlorate.[33] Although not included in the table, it was also observed that there were slight differences in the X-ray powder patterns of these two compounds.

All the complexes exhibit a first ligand field absorption band in the region 460–466 nm, consistent with quasi-octahedral coordination of six amine ligands. As the number of tn ligands increases, the molar absorbance of the band steadily increases, except for the *trans*-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$ isomer of higher symmetry.

As is seen in the third column, there are small variations in the calculated average Dq values, but these are likely to reflect somewhat different band shapes (as the symmetry changes), as well as the difficulty of exactly locating the band maxima of such broad peaks, rather than to indicate genuine significant differences

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Table I. Spectral and Analytical Data for $Cr[(NH_3)_{6-2x}(tn)_x]^{3+}$

complex	UV–vis bands λ_{max} nm (ϵ)		$10Dq$, μm^{-1}	IR[a] Cr–N, cm^{-1}	anal. found (calcd)				
	L_2	L_1			% C	% H	% N	% Cl	% Cr
$Cr(NH_3)_6^{3+}$ [b]	354 (34)	466 (41)	2.15						
$[Cr(tn)(NH_3)_4]^{3+}$ [c]	352 (39)	464 (45)	2.16		7.18 (7.31)	4.47 (4.50)	16.66 (17.06)	20.31 (21.59)	10.55 (10.56)
cis-$[Cr(tn)_2(NH_3)_2]^{3+}$ [c]	351 (48)	462 (54)	2.16	514 (s) 465 (w) 438 (m) 405 (sh) 350 (s)	14.19 (13.53)	4.96 (4.92)	15.55 (15.78)	19.63 (19.97)	9.60 (9.76)
trans-$[Cr(tn)_2(NH_3)_2]^{3+}$ [c]	352 (48)	460 (51)	2.17	517 (s) 465 (m) 420 (s) 350 (s)	13.53 (13.53)	4.85 (4.92)	15.53 (15.78)	19.83 (19.96)	9.70 (9.76)
$[Cr(tn)_3]^{3+}$ [d]	355 (51)	464 (59)	2.16						

[a] Legend: w = weak, s = strong, sh = shoulder, m = medium. [b] Reference 37 gives λ_{max} 354 (33.7), 466 nm (40.7). [c] This work. [d] Reference 19 gives λ_{max} (ϵ)354.7 (47.6), 464.4 nm (55.3).

in the strength of ammonia and tn as ligands.

For the pair of geometric isomers, both absorption bands were similar in shape and occurred at almost the same wavelengths. They also have similar $\epsilon(L_1)/\epsilon(L_2)$ ratios. It will be noted that the molar absorbances for the L_1 bands of the cis- and trans-diammine isomers are almost identical at 54 and 51 L mol^{-1} cm^{-1}, respectively. This observation is inconsistent with a UV–vis criterion of geometric configuration that we proposed earlier[33] based on studies of similar diaminoethane compounds. There it was found that the cis compound had a significantly higher molar absorbance than the trans and this was ascribed to its asymmetry.

Coupled with the not greatly dissimilar IR spectra and X-ray powder photographs of the supposed isomers, this caused concern as to whether both preparations might be giving the same trans product, impure when prepared from the cis starting materials, because of isomerization from cis to trans during the liquid ammonia reaction of both the *cis*-dichloro- and *cis*-dibromo-bis-tn starting materials. For this reason, in some experiments, lithium amide was added in small amounts to the reaction mixture to make it basic and facilitate base-catalyzed ammonia substitution at a lower temperature (−30 °C). The reaction did indeed proceed much more readily and at a lower temperature, yielding a product that had properties similar to those of the "cis" compound but which was distinctly different and again impossible to crystallize. Chromatography of these compounds resolved the uncertainty. Although it was found that the cis- and *trans*-bis-tn compounds had the same retention time and could therefore not be distinguished, the compound prepared by the lithium amide route was found to contain 10–20% of the mono- tn tetraammine complex, thereby accounting for its somewhat different properties.

Together with the different photochemical and chromatographic behavior for the two isomers discussed next, the overall evidence finally convinced us that the putative trans and cis isomers were indeed different pure compounds and assigned correctly as given in Table I. It follows that the liquid ammonia reactions are fairly stereoretentive, unlike the situation found earlier[34] for the diaminoethane analogues. We believe that the similar molar absorptivities of the two isomers misled us; this situation arises for the tn compounds because of the nearly perfect octahedral coordination around Cr discussed later.

Thermal Aquation. Qualitative studies of the thermal reactions showed that all the starting materials aquated only very slowly so that over the short periods (30 min) required for each photolysis run, thermal aquation was negligible. For $[Cr(tn)_3]^{3+}$, since there was particular interest in the monodentate protonated intermediate formed in the thermal and photochemical reaction, and since unambiguous chromatographic analysis was possible since we had authentic samples of both isomers of the bis-aquo-bis-tn product and all the possible products were separable, more detailed study was made.

The first-order rate constant at 60 °C for loss of the first end of a tn ligand was measured from the change with reaction time of the chromatographic peak area for the starting compound and found to be 3.1×10^{-6} s^{-1}. This value is consistent with a measurement[35] at 50 °C of 7.1×10^{-7} s^{-1} assuming an activation energy of about 25 kcal mol^{-1}. The loss of the second end of a tn ligand was based on the chromatographic analysis and identification of the two isomeric $[Cr(tn)_2(tnH)(H_2O)]^{4+}$ species, described later.

Solutions of $[Cr(tn)_3]^{3+}$ were photolyzed to about 12% conversion, and aliquots were respectively kept as blanks and allowed to react for 60 h at 25 °C and 60 min at 60 °C; these were then analyzed chromatographically. The peak assigned as the cis-4+ isomer actually increased 2% for the room-temperature experiment and was unchanged at 60 °C, while the peak assigned as the trans-4+ isomer decreased 9% at both temperatures. The results for the cis-4+ ion are obviously complicated by interference from thermal degradation of the starting compound, which will thermalize stereoretentively to the cis-4+ isomer as the major pathway. The results for the trans isomer are directly interpretable, however, and lead to first-order rate constants of 7.0×10^{-7} and 5.8×10^{-5} s^{-1} at 25 and 60 °C respectively; these values yield a crude estimate of the activation energy for the aquation of 25 kcal mol^{-1}, consistent with values for similar complexes.[36] The 60 °C rate constant calculated from Cimolino's[35] 50 °C result is 1×10^{-4} s^{-1}, reasonably consistent with our value.

Photolysis Studies. Photolysis of all the compounds in acidic aqueous solution led to proton uptake, accompanied by ammonia loss to different extents. For photolysis carried out at 20 °C it was also found that post photolysis thermal reactions were insignificant. Proton uptake measurements and ammonia analyses, coupled with reineckate actinometry, yielded the quantum yield data given in Table II. Also given in Table II are the doublet lifetimes measured by emission decay and the proportion of slow reaction via the doublet state. This additional data allows the calculation of apparent rate constants for the loss of ammonia and one end of tn from the doublet state, as shown.

Properties of the Photoproducts. The photoproducts, which include several monodentate protonated 1,3-diaminopropane complexes, are interesting molecules in their own right, but also they provide useful kinetic and mechanistic information. They were therefore studied by difference spectroscopy for the tris-tn compound and by reversed-phase chromatography generally.

$[Cr(tn)_3]^{3+}$. Photolysis of the tris-tn compound in 0.1 M acidic solution to 12% conversion, with recording of the difference spectrum of the photolyzed solution relative to an unphotolyzed solution, allowed a determination of the average spectrum of the mixture of photoproduct isomers. The spectrum showed two broad

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Table II. Total and Individual Ligand Quantum Yields, Lifetimes, and Apparent[d] Rate Constants for Doublet Photoaquation of $[Cr(NH_3)_{6-2x}(tn)_x]^{3+}$

complex	ϕ_{tot}[a]	$\phi_{tot\,tn}$[b]	$\phi_{per\,tn\,N}$	$\phi_{tot\,NH_3}$[c]	$\phi_{per\,NH_3}$	τ, μs	% slow	10^{-4} "k"$_{NH_3}$[d]	10^{-3} "k"$_{tn/2}$[d]	ref
$[Cr(NH_3)_6]^{3+}$	0.44 ± 0.02			0.440	0.073	1.6	74	3		e, 29
$[Cr(tn)(NH_3)_4]^{3+}$	0.36 ± 0.02	0.01 ± 0.01	0.005	0.350 ± 0.005	0.0875	2.2	83	3	2	e
cis-$[Cr(tn)_2(NH_3)_2]^{3+}$	0.24 ± 0.01	0.0336 ± 0.009	0.0084	0.210 ± 0.008	0.105	2.7	85[f]	3	3	e
trans-$[Cr(tn)_2(NH_3)_2]^{3+}$	0.34 ± 0.02	0.031 ± 0.01	0.0078	0.307 ± 0.03	0.154	2.4	85	6	3	e
$[Cr(tn)_3]^{3+}$	0.14 ± 0.00	0.14 ± 0.00	0.023			2.6	78		7	e, 29

[a] By the ΔpH method. [b] By difference of the ΔpH method and coulometric titration. [c] By coulometric titration. [d] The term apparent is used to emphasize that these single rate constants are the values calculated on the assumption of a simple doublet reaction; we do not imply that this is the true mechanism, but this forms a useful basis for discussion. Sample calcualtion for $[Cr(NH_3)_6]^{3+}$: "k"$_{NH_3}$ = $\phi_{per\,NH_3}$ × % slow/doublet lifetime = $0.073 \times 0.74/(1.6 \times 10^{-6})$ = 3.4×10^4 s^{-1}. The small temperature differences between the steady state and transient data have not been corrected for, so the derived values have been rounded to one significant figure. [e] This work. [f] Assumed value, see text.
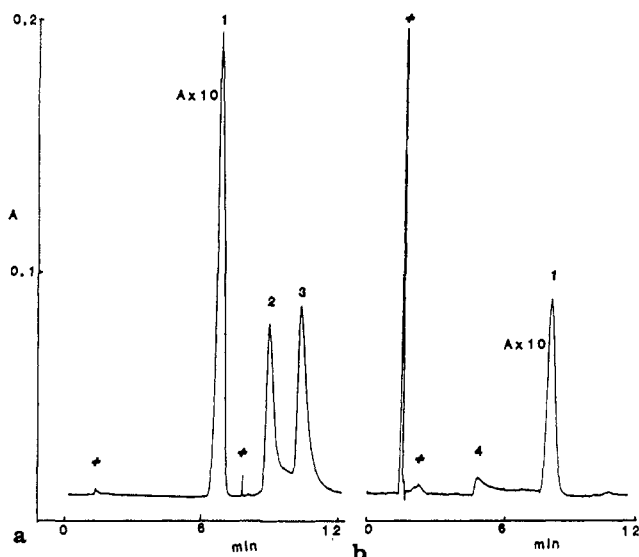

Figure 1. Chromatography of photoproducts of $[Cr(tn)_3]^{3+}$. General conditions: eluents were 25 mM butanesulfonic acid/25 mM triethylammonium chloride in water and in 90% methanol at pH 5 (these were used to create the gradients or isocratic mixtures given below); 25 °C; flow rate 2.0 mL min^{-1}; detection wavelength 240 nm; absorbance scales are given on the chromatograms. Peaks marked with a # are artifacts, anions, minor species, and/or absorbance range changes. (a) Solution photolyzed to 12% conversion, eluted with the following gradient [time, min (% methanol eluent)]: 0 (10%), 6 (10%), 9 (15%), 12 (15%), 15 (10%). Peaks: 1, $[Cr(tn)_3]^{3+}$; 2, cis-$[Cr(tn)_2(tnH)(H_2O)]^{4+}$; 3, trans-$[Cr(tn)_2(tnH)(H_2O)]^{4+}$. (b) Photolyzed solution a with cis-$[Cr(tn)_2(H_2O)_2]^{3+}$ added in an amount calculated for a quantum yield of 0.04, eluted isocratically with 10% methanolic eluent. Peak 4 corresponds to the added cis-$[Cr(tn)_2(H_2O)_2]^{3+}$.

bands in the visible as expected, with maxima (molar absorbance) at 484 (53) and 362 (55) nm; these wavelengths are concordant with those[37] for $[Cr(NH_3)_5H_2O]^{3+}$ of 488 (35) and 360 (29) nm. The larger molar absorbances for the chelate compounds are to be expected. This supports the conclusion that monosubstitution by water is the dominant photoaquation process, as has been reported earlier.[18] For this and the mixed complexes, more specific information on the nature of the products can be obtained by chromatographic techniques, so subsequent emphasis was placed on those experiments.

Samples photolyzed in 0.1 M acidic solutions to conversions of less than 12% gave chromatograms of which a typical example is shown for each complex in Figures 1 and 2, which, it should be noted, employed a variety of elution conditions with consequent changes in elution times for any given peak.

In the development of these techniques it was noted that the separations of the isomers of $[Cr(tn)_2(tnH)(H_2O)]^{4+}$ species and of $[Cr(tn)_2(H_2O)_2]^{3+}$ were sensitive to the eluent pH. Indeed for the latter pair, where we had authentic samples, we found that the sequence of elution of the two isomers could be completely
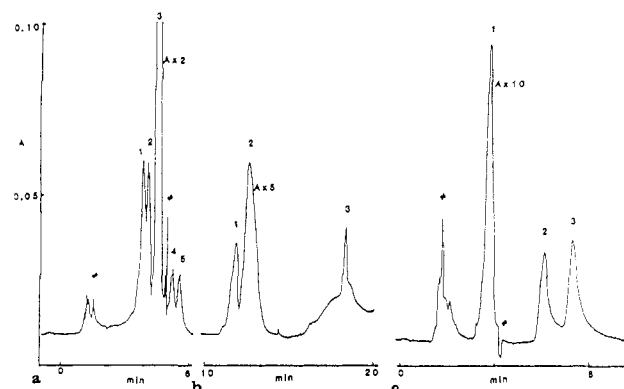
(37) Edelson, M. R.; Plane, R. A. *J. Phys. Chem.* **1959**, *63*, 327.

Figure 2. Photoproducts of cis- and trans-$[Cr(tn)_2(NH_3)_2]^{3+}$ and $[Cr(tn)(NH_3)_4]^{3+}$. General conditions: as in Figure 1. (a) cis-$[Cr(tn)_2(NH_3)_2]^{3+}$, eluted with the following gradient [time, min (% methanol eluent)]: 0 (10%), 6 (10%), 9 (15%), 12 (15%), 15 (10%). Peaks: 1, trans-$[Cr(tn)_2(NH_3)(H_2O)]^{3+}$; 2, cis-$[Cr(tn)_2(NH_3)(H_2O)]^{3+}$; 3, cis-$[Cr(tn)_2(NH_3)_2]^{3+}$; 4, cis-$[Cr(tn)(tnH)(NH_3)_2(H_2O)]^{4+}$ (see text); 5, trans-$[Cr(tn)(tnH)(NH_3)_2(H_2O)]^{4+}$ (see text). (b) trans-$[Cr(tn)_2(NH_3)_2]^{3+}$, eluted isocratically with 10% methanolic eluent. Peaks: 1, cis-$[Cr(tn)_2(NH_3)(H_2O)]^{3+}$; 2, trans-$[Cr(tn)_2(NH_3)_2]^{3+}$; 3, cis-$[Cr(tn)(tnH)(NH_3)_2(H_2O)]^{4+}$ (see text). Note: The broad absorption underlying peak 3 arises from the methanol/water gradient used in this run. (c) $[Cr(tn)(NH_3)_4]^{3+}$, eluted isocratically with 10% methanolic eluent. Peaks 2 and 3 are isomers of $[Cr(tn)(NH_3)_3(H_2O)]^{3+}$, but the sequence of *fac* and *mer* isomers has not been established.

reversed by changing the pH; there was, of course, an intermediate pH at which they were not resolved.

The direction of the change for the 3+ diaquo ions was that the trans isomer eluted prior to the cis at pH 5, the sequence changing to cis before trans at pH 3. The sequence in acid solution is explicable if the 3+ ions have an elution time inversely related to their dipole moment. This would be the reverse of the universal order found for ion-exchange separations, but is reasonable for this reversed-phase technique where the less polar solvent is the stronger of the two. Since the trans isomer is reported[18] to be the stronger acid of the two isomers, the reversal of sequence can then occur, because as the pH is raised, the trans isomer ionizes to the more rapidly eluting 2+ form to a greater extent than the cis isomer.

Since authentic samples of the 4+ ions were not available, and since pH altered the 4+ peak separations but did not cause an analogous sequence reversal, this created uncertainty as to the sequence of the 4+ isomers. Their identity was therefore established by indirect means, as follows.

Photolysis of $[Cr(en)_3]^{3+}$ has been shown to yield the 4+ ion photoproducts in a 35:65 cis:trans ratio; in that work, ion exchange was used to separate the products. Cimolino[35] attempted similar experiments with the tn system but was unable either to separate the 4+ ions from one another or to separate the two 3+ products from the starting material. As Figure 1 shows, all these products have been separated here. The two 4+ ions give a peak area ratio of very close to 4:6 in sequence of elution time. To properly calibrate the peak areas, these chromatographic peaks were collected and their Cr content measured. However, the experi-

mental errors arising from the very small amounts available made this too unreliable.

Further chromatographic runs were therefore carried out in which the detector wavelength was varied in the range 230 to 270 nm, and it was found that this variation did not alter the observed peak area ratio by more than about 5%. This, plus the fact that these are charge-transfer bands in complexes that have the same set of coordinating atoms and differ only in geometry, gives us some confidence that no great error will arise from the assumption that they have equal chromatographic sensitivities. Also we have measured the ratio of the molar absorbances at 240 nm of authentic samples of the two $[Cr(tn)_2(H_2O)_2]^{3+}$ isomers and find that they differ only by 5% at 240 nm.

These considerations suggest it is reasonable to assume roughly equal molar absorbances for the two 4+ ions at the analysis wavelength. Then, by analogy with the en case, the elution order is likely to be cis before trans if the same isomer ratio pertains for the en and tn analogues. Also this order is consistent with the low-pH behavior of the corresponding 3+ products. It is also supported by the results on the thermal reaction of $[Cr(tn)_3]^{3+}$, which gives a major 4+ peak (the stereoretentive cis product) followed by a small peak corresponding to the presence of a small amount of trans formed by isomerization. This assigned sequence is also supported by the parallel to the photochemistry of the bis-tn compounds described later.

Another feature of the data is of interest. It has been reported,[18] on the basis of rather indirect methods, that $[Cr(tn)_3]^{3+}$ undergoes a simultaneous aquation of both ends of the tn ligand with a quantum yield of 0.04. The chromatographic technique available here allowed a direct examination of this process.

$[Cr(tn)_3]^{3+}$ was photolyzed to less than 12% conversion at irradiation wavelengths of 540, 436, and 365 nm and analyzed under elution conditions that allowed determination of all the photoproducts; a typical chromatogram is shown in Figure 1a. No peak corresponding to the *cis*-diaquo product is present. To confirm this, this chromatogram was compared with that of the same photolyzed solution to which authentic *cis*-diaquo-3+ ion had been added in the amount calculated from our known conditions and the published quantum yield for the "two-ended" tn loss; this is shown in Figure 1b. Comparison of the two chromatograms leads to a estimated upper limit of 0.01 for any simultaneous two-ended-loss process.

When, however, the photolyzed solution was rephotolyzed to higher conversion at a wavelength of 540 nm, where the 4+ ions absorb to a greater extent than the starting complex, the *cis*-diaquo product rapidly appeared in the chromatogram, showing that it is readily produced by secondary photolysis.

Isomers of $[Cr(tn)_2(NH_3)_2]^{3+}$. The chromatographic study of the photoproducts for the isomer pair of $[Cr(tn)_2(NH_3)_2]^{3+}$ allowed confirmation of the quantum yield ratio for ammonia and tn photoaquation and identified the number and type of photoproducts. We could not investigate the question of complete tn loss here as the relevant product peaks would have been obscured by the other photoproducts.

Typical chromatograms for the photolysis products of the cis and trans compounds are shown in parts a and b of Figure 2, respectively. The cis compound leads to two pairs of photoproduct peaks. One pair, undoubtedly the $[Cr(tn)(tnH)(NH_3)_2(H_2O)]^{4+}$ compounds arising from tn aquation, elute after the starting peak, and the $[Cr(tn)_2(NH_3)(H_2O)]^{3+}$ pair from ammonia aquation elutes before. This basic assignment is supported by the good agreement between the ratio of the total 3+ peak area to the total 4+ peak area of 6.5 ± 1.3 and the directly measured quantum yield ratio for ammonia and tn loss of 6.3. Making this comparison of course implies that the charge-transfer molar absorbances of these very similar compounds are the same or nearly so. The arguments in favor of this were presented in detail for the tris-tn case above, and it is gratifying that here the agreement is so good.

The analogous trans isomer, Figure 2b, shows one major and one minor 4+ peak with the second being small and unresolved from the tail of the major peak. It also shows a small 3+ peak preceding the major 3+ peak, again incompletely resolved. Here

the NH₃/tn quantum yield ratio based on peak areas is 6.8 ± 0.8 compared with the directly measured ratio of 10 ± 5, in agreement within the large experimental error.

Note that these very different product distributions provide incontrovertible evidence that we are dealing with two different isomeric starting compounds, removing any residual doubts about this.

Again, as authentic samples of the products are not available and also because now some isomers may not be resolved, there is a problem with the assignment of the isomeric nature of the product peaks. Nevertheless the different distribution from the two starting compounds, coupled with parallels to the photochemistry of known compounds, enables most assignments to be made.

For example, photoaquation of an ammonia from the trans isomer could lead to two isomeric products. Theoretically, however, it should occur mainly with stereochemical change[2,16] yielding *cis*-$[Cr(tn)_2(NH_3)(H_2O)]^{3+}$, as shown in Figure 3 and discussed later; it is therefore reasonable to identify the major 3+ peak as this cis isomer. Presumably the small prior peak is a small amount of the trans species. The two isomeric 3+ products arising from ammonia loss therefore elute in the same trans before cis sequence as the isomers of $[Cr(tn)_2(H_2O)_2]^{3+}$ at pH 5.

Theoretical analysis of the results of tn photoaquation from this complex, given in Figure 3 and the later discussion, suggests a mixture of product isomers. The dominant predicted species have the tnH⁺ and the water ligand cis to one another. There are two isomers with this cis relationship that differ in the cis/trans arrangement of the two ammonia ligands, but our inability to resolve *trans*- and *cis*-$[Cr(tn)_2(NH_3)_2]^{3+}$ suggests that they would not be separable. We conclude that the two 4+ peaks correspond to a pair of isomers of the first kind and elute in the sequence cis (major product) before trans; this would again parallel the situation for the products of the tris-tn compound.

With reference to the cis starting compound, Figure 2a shows that the 3+ product isomers from ammonia aquation are produced in similar amounts. So also are the 4+ product peaks from tn aquation, but again it must be recognized that the cis peak, which elutes first, is probably a mixture of isomers differing in the relationship of the amine ligands.

Figure 2a now permits a determination of the approximate cis:trans ratios of the product isomers assuming equal molar absorbances. We have not attempted this for the trans starting complex as the minor peaks are too small to be reliably estimated. For the cis starting complex, the ratios are 1.3:1 for the $[Cr(tn)_2(NH_3)(H_2O)]^{3+}$ isomers and 0.95:1 for the $[Cr(tn)(tnH)(NH_3)_2(H_2O)]^{4+}$ isomers, information that provides an experimental background for a latter consideration of the photostereochemistry of this complicated system.

$[Cr(tn)(NH_3)_4]^{3+}$. Finally, Figure 2c shows the chromatogram for $[Cr(tn)(NH_3)_4]^{3+}$ photoaquation. Here, surprisingly, the two large product peaks are observed to elute after the starting compound. These have to be the products from ammonia loss because their total peak area is of the right order of magnitude for the major photolysis mode based on the conditions and the known quantum yield of the photolysis. Indeed, in this complex, the tn mode is so unimportant (Table II) that we have not been able to observe the corresponding chromatographic peaks. The two $[Cr(tn)(NH_3)_3(H_2O)]^{3+}$ isomers observed are produced in a ratio of 0.75:1 in sequence of elution. This is consistent with stereochemical change, but as discussed later, it does not provide it.

To the question as to why the 3+ aquo products elute after the starting compound in this instance, we have at present no answer. It appears to be another quirk of this chromatographic method. This system obviously will require further study with authentic synthesized complexes.

Discussion

From the data reported here, together with our previous study of the en analogues, it becomes apparent that there are a number of differences in behavior between analogous compounds of tn and en. In the first place, it appears that the six-membered tn
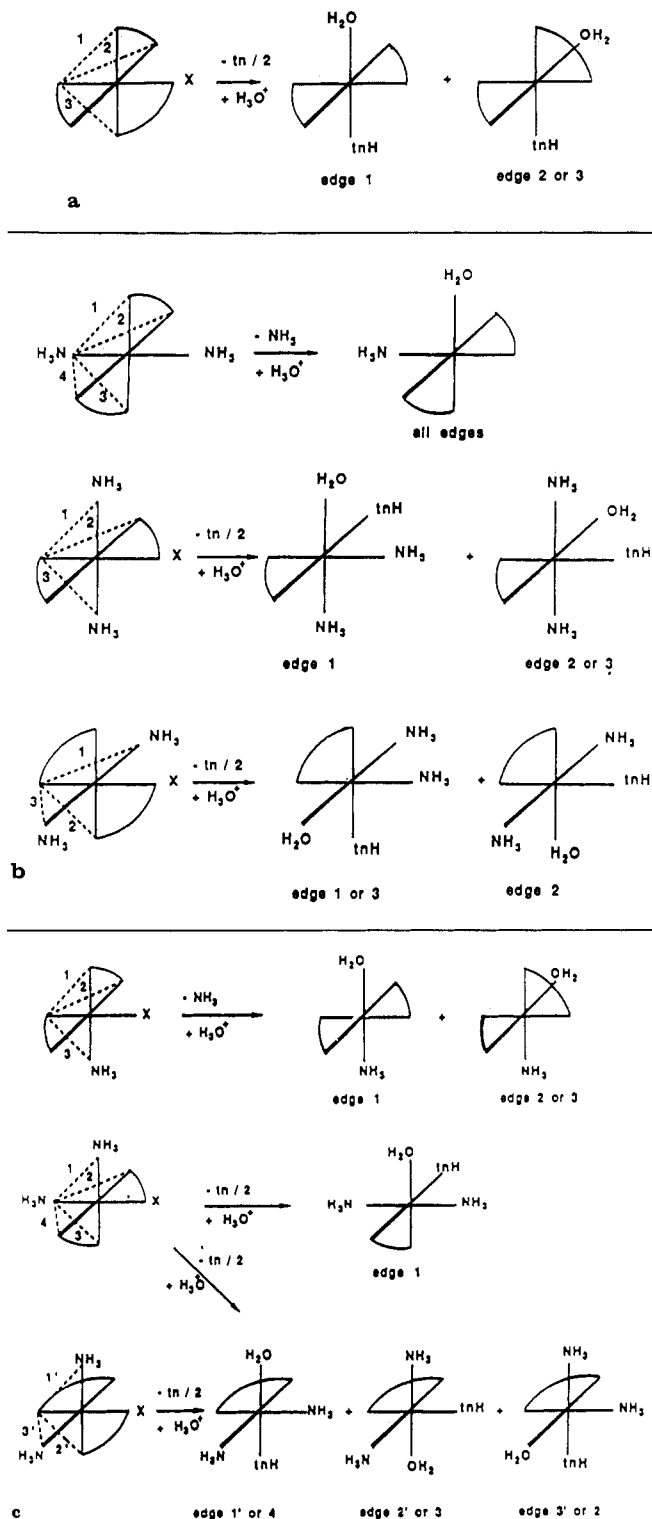
Figure 3. Symmetry rule predictions of the photoproducts: (a) [Cr-(tn)$_3$]$^{3+}$; (b) *trans*-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$; (c) *cis*-[Cr(tn)$_2$(NH$_3$)$_2$]$^{3+}$. See text for explanation. Since all the experiments were conducted with racemic compounds, any optical isomerism in the examples illustrated should be ignored.

ring is ideally suited to chromium(III) as evidenced by the N–Cr–N bond angle of 90.0° observed[38] for [Cr(tn)$_3$]$^{3+}$, whereas there is considerable strain in the Cr–en ring. Also for bis-en complexes, the direction of spontaneous isomerization is from trans to cis and the isomerization is fairly facile, for example occurring readily during the reaction of *trans*-diacido-bis-en-Cr(III) complexes with liquid ammonia.[33,34] In contrast, this and other work[39]

(38) Jurnak, F. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 2387.

shows that the geometric configuration of the bis-tn analogues is considerably more robust under similar conditions and that when isomerization does occur, the direction appears to be from cis to trans.[19,39]

It should also be noted that the thermal aquation rate constant for the tris(diaminopropane) compound is smaller than that for the analogous diaminoethane compound,[36] showing greater kinetic stability for the six-membered chelate ring. In apparent contrast with this conclusion, the stability constant[40] for formation of the first Ni(en)$^{2+}$ ring is 1 order of magnitude larger than for the Ni(tn)$^{2+}$ ring; on the basis of this type of information, it is often thought that the five-membered chelate ring is "more stable" than the six-membered analogue. Note however that the thermodynamic parameters given[40] show that the lower stability constant for the tn case arises largely from the unfavorable entropy effect associated with the longer hydrocarbon chain; the enthalpy term is actually more negative for the six-membered ring, showing that from a bond strength point of view, the six-membered ring is more favored.

This smaller rate constant considerably facilitates study of the photochemistry as competing thermal reactions of the starting complexes are slow and postirradiation thermal decompositions negligible, as has also been reported earlier for the tris-tn system.

Table II summarizes the photochemical quantum yields, doublet lifetimes, and percentage of slow photochemistry found for the mixed complexes as well as for the hexaammine and the tris-tn complexes. The overall quantum yields of the mixed compounds are intermediate to those of the hexaammine and tris-tn complexes; of more interest, however, is the breakdown of these yields into tn and NH$_3$ loss, shown in columns 4 and 6. This reveals that, in all the mixed complexes, the yield of tn is very much lower and the yield of ammonia much higher than would be expected on a purely statistical basis.

The justification for expecting such a statistical ratio comes from the similarity of the ligand field strengths of ammonia and tn, evidenced by the very similar wavelength maxima for the hexaammine, the tris-tn, and the mixed complexes, which all lie in the range 460–466 nm corresponding to 10Dq values of 2.17–2.15 μm^{-1}. By use of the angular overlap model for calculation of excited-state bond strengths,[41] this translates to almost identical values for the Cr–N bond in the two cases. It is clear from our results therefore, that some important factor other than excited-state bond strength operates to determine the quantum yield ratios.

In their study of [Cr(tn)$_3$]$^{3+}$, Gowin and Wasgestian[18] concluded that the low quantum yield relative to analogous nonchelate complexes could be ascribed to steric blocking of the ligand entering to form an associative transition state. While this seems quite reasonable, our results suggest that other factors than this must also be influencing the yields in our mixed complexes. It is also to be noted that because [Cr(tn)$_3$]$^{3+}$ has a longer doublet-state lifetime than the hexaammine complex, it should have a proportionately larger quantum yield of reaction, assuming equal labilities of the leaving ligands. We therefore believed that it was necessary to carry out a more detailed analysis including looking also at the fraction of the reaction that occurred via the doublet and the doublet lifetime.

With the kind assistance of J. Lilie measurements were made of the fraction of the reaction that occurred via the doublet state and the doublet emission lifetime; these data are included in Table II. Unfortunately, at the time the doublet reaction fraction measurements were done, an authentic sample of the *cis*-bis-tn compound was not available so it could not be included. The two mixed complexes that were measured gave values very similar to that for [Cr(NH$_3$)$_6$]$^{3+}$; in what follows, a value of 85% has been assumed for the *cis*-bis-tn complex, equal to that for its isomer.

(39) Vaughn, J. W. *Inorg. Chem.* **1981**, *20*, 2397.
(40) Sillen, L. G. *Stability Constants of Metal Ion Complexes*; Special Publication 17; Chemical Society: London, 1964; Entries 120 and 159.
(41) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208.

The lifetimes of the doublet state are all very similar and similar to that for the *trans*-tn complex; the lifetime for the mono-tn tetraammine complex is the shortest of the mixed compounds, consistent with the idea that the rate of the radiationless decay of the excited state correlates with the number of N–H vibrations coupled to the Cr(III) species.[42,43]

Using these values and assuming an intersystem crossing yield of 1, it becomes possible to calculate "apparent" rate constants for the rate of aquation of individual ammonia and individual ends of the tn ligand for the reaction via the doublet state. Since there is much evidence now that the "slow" and "fast" photochemistries go through a common intermediate, to the extent that the intersystem crossing efficiency does not vary throughout the series of compounds, the derived values will reflect the relative labilities of the ammonia and tn ligands in the overall photochemistry of each molecule. We do not wish to imply whether or not the reaction occurs directly from the doublet state; the relative leaving-group abilities obtained should be independent of this mechanistic question. The values so obtained are given in columns 9 and 10 of Table II. It is clear from a cursory glance at these data that the rate constant for ammonia loss differs less across the series than that for tn and that the leaving-group ability of ammonia is 10 times that of tn. Therefore tn is a reluctant leaving ligand.

We attribute this basic phenomenon not to steric blocking of trans entry of the entering ligand in these complexes (as this is not a problem for loss of tn in the mono-tn species, for example) but to the stability and possible rigidity of the six-membered tn ring in its preferred chair conformation. It may well be that while the Cr–N bond is weakened to the same extent for the two ligands in the Cr(III) excited state, the stable ring of the tn ligand tends to slow the movement of the N atom away from the Cr.

Furthermore the tn loss rate constant drops by a factor of 2 in passing from the tris-tn complex to the two bis-tn isomers and by a smaller further factor in the mono-tn species. This, to us, is clear evidence that the loss of the two ligands is competitive. Labilization in the excited state of d^3 systems has been shown both theoretically[16] and experimentally[2] to occur in a plane and not on an axis as was proposed in an earlier model.[44] In these mixed complexes, the possible planes of excitation contain varying numbers of ammonia and tn ligands. The observed trends in quantum yields are consistent with the idea that if a plane of excitation has at least one ammonia ligand, then the loss of tn from that plane will be lowered significantly, merely because the tn can not compete with the more rapidly leaving ammonia. The greater the number of ammonias present on the plane, the lower the apparent rate constant for tn loss. This accounts for the large drop in value in passing from tris-tn to the bis-tn compounds and the further drop in going to the mono-tn compound. In contrast to this behavior the apparent rate constant for ammonia varies only slightly. This can arise because nonradiative decay is the main process competing with and determining the quantum yield for ammonia loss; the observed variations in the smaller tn yield therefore do not lead to significant changes in the ammonia rate constants as might otherwise be expected.

Note also that there is a greater ammine loss rate constant for the *trans*-bis-tn isomer compared with the cis isomer. Again this can not logically be explained in terms of the degree of steric blocking by the methylenes of the tn since the situation is similar in the two isomers. On the basis of molecular models, we think that this arises because, assuming a pentagonal-bipyramidal transition state for the loss of ammonia from the trans isomer followed by trans entry of a water ligand, the methylene groups of the tn ligands interact with the departing ammonia molecule, hastening its departure. Models suggest this interaction is much less severe in the cis isomer and the mono-tn compound. Therefore this data supports a type of anchimeric assistance of ammonia loss in the trans isomer. In summary then, it seems that both in

these complexes and in the *trans*-[Cr(tn)$_2$F$_2$]$^+$ complex that stimulated this investigation, the main effects observed on the photochemical quantum yields result from the inherent stability of the six-membered ring. Additionally there is an influence from competition by the other ligands in the plane of excitation and, when the geometry favors it, some anchimeric assistance of the loss of the non-tn ligand.

Studies of the Photoproducts. The nature of the photoproducts was studied primarily to confirm the above reaction mode ratios obtained by direct chemical analysis. It is inherent to the starting molecules that in all cases they are not adequately "signposted" to allow definite conclusions to be drawn regarding the stereomobility or otherwise of the photoreactions. Nevertheless the results are not without value in this context, and in what follows, both the reaction mode ratios and the stereochemistry will be considered to the extent possible. One of our problems was that in most instances, authentic samples of the products were not available, and also the amount of material present in the chromatographic peaks was too small to characterize directly, a limitation of the present chromatographic technique. Therefore much of the peak identification had to be based on comparison of thermal products and photoproducts, coupled with the observed behavior of the isomers of [Cr(tn)$_2$(H$_2$O)$_2$]$^{3+}$, the known stereoretentivity of the thermal aquations and the stereochemical change invariably associated with the excited-state reaction.

For the compound [Cr(tn)$_3$]$^{3+}$, the results discussed earlier show that the photoreaction stereochemistry parallels that found earlier for the analogous ethylenediamine compound, even to the 60:40 trans:cis proportion of the [Cr(tn)$_2$(tnH)(H$_2$O)]$^{4+}$ product. The photoreaction is therefore stereomobile as has consistently been found for the photoreactions of Cr(III) complexes. It may well be completely stereomobile but this is not proven because of the ambiguity mentioned earlier; the cis isomer can arise either by a retentive mechanism or one involving stereochemical change.

The theoretical predictions, shown in Figure 3, can be obtained by a simple pictorial model. Edge displacement of the leaving ligand by the entering solvent molecule occurs via a seven-coordinate transition state in which the ligand rearrangements resulting in ligand interchange take place exclusively in the plane of the excitation. This is equivalent to the elegant photostereochemical theory of Vanquickenborne and Ceulemans.[45] This was presented as involving a trigonal-bipyramidal intermediate, but in view of the evidence[46] for associative photoreaction of cationic Cr(III) complexes, our picture is likely to be closer to reality.

In the derivation of Figure 3, it has also been assumed that excitation occurs to an equal extent on all three of the orthogonal planes of the molecule. On each plane, the excitation corresponds to a 45° rotation of charge density, which results in the labilization of all four ligands on that plane because of the σ-antibonding character of the orbital occupied in the excited state. The departing ligand has been marked with an X, and the entering water molecule can displace it by attack on any one of the free trans edges (since there are two orthogonal excitation planes containing the leaving ligand); the ligand on the attacked edge that was originally cis to the leaving ligand then migrates into the position vacated by it.

The prediction is that both *trans*- and *cis*-[Cr(tn)$_2$(tnH)(H$_2$O)]$^{4+}$ should be produced in the photochemical reaction as is found. The predominance of the trans isomer is not predicted and is an interesting feature of the behavior for both this and the tris(diaminoethane) system.

Note also that the diaquo products expected to arise from complete loss of tn from the complex were not observed at any of the three wavelengths of irradiation studied, one of which was essentially the same as that used by Gowin and Wasgestian.[18] In view of the observed thermal stability of the 4+ primary photoproducts, the disagreement seems strange, but one possibility is

(42) Kuhn, K.; Wasgestian, F.; Kupka, H. *J. Phys. Chem.* **1981**, *85*, 665.
(43) Mvele, M.; Wasgestian, F. *Inorg. Chim. Acta* **1986**, *119*, 25.
(44) Adamson, A. W. *J. Phys. Chem.* **1967**, *71*, 768.

(45) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978**, *100*, 475.
(46) Angermann, K.; van Eldik, R.; Kelm, H.; Wasgestian, F. *Inorg. Chem.* **1981**, *20*, 955.

that they were formed by secondary photolysis during the analysis phase of their experiments, which would have been more time consuming than ours.

For the isomers of $[Cr(tn)_2(NH_3)_2]^{3+}$, the chromatographic results gave 4+:3+ product ratios that were in good agreement with the directly measured ratios of tn to NH_3 photoaquation. This assumed that the molar absorptivities of these compounds are all very similar, an assumption that is justified mainly by this concordance, as these compounds now differ pairwise in the number, if not the type, of the ligating atoms. Nevertheless, the agreement gives us some confidence that the measured reaction mode ratios and also those given for the product isomers are not seriously in error.

The stereochemistry predicted for the photoaquations leads to a mixture of products as is shown in Figure 3b for the trans compound and Figure 3c for the cis compound, based on the same procedure as before. For the products arising from tn aquation, in this discussion cis is intended to indicate the relationship of the aquo and monodentate protonated tn ligands to one another; as explained earlier, isomers differing in the cis/trans relationship of the ammonia ligands would not be resolved.

For the trans isomer the prediction is for only cis products to be formed both from loss of ammonia (upper third of Figure 3b) and from the tn mode (lower two-thirds of Figure 3b). This is completely in agreement with experiment and demonstrates that both modes of photoaquation of this compound occur with almost complete stereochemical change in this complex.

For the cis isomer, Figure 3c, the situation is inherently more ambiguous. However the results are consistent with the predictions. For both loss of ammonia (upper third of figure) and of tn (lower two-thirds) the cis and trans products are predicted to be produced in roughly equal amounts; however, as mentioned above, where several different isomers are produced via different edge displacements, the ratio is not predictable with any reliability. Therefore the observed consistency with experiment is as much as can be expected. Again the results for both modes require the partial, if not complete, occurrence of stereochemical change.

The mono-tn compound provides no further insights than already discussed.

Conclusions. In summary it has been found that tn is a much poorer leaving ligand than ammonia, and this in large measure accounts for the lower quantum yield of photoaquation in $[Cr(tn)_3]^{3+}$ without the need to invoke concepts such as the steric blocking of water attack on edges trans to the leaving ligand. Although this blocking can be expected to occur, it seems likely that any free edge will lead to substitution, since potential water ligands are ubiquitous. This therefore does not seem to be as viable an explanation as simply to recognize the stability of the Cr(tn) ring and its consequent slow rate of reaction. This conclusion is strongly supported by our observation of very low tn yields from the mono-tn complex, where steric blocking of the trans edges is nonexistent.

Our results have also demonstrated that ligand loss from the plane of excitation is a competitive process between the ligands on that plane and therefore that a yield can be lower than expected if it is in competition with a more facile process. Also there is evidence that steric enhancement of loss of a ligand can take place, as evidenced by the enhanced ammonia yield found for the trans-bis-tn complex.

Finally the results have shown that stereochemical change occurs in some and possibly all of these complexes. It has also been confirmed that the monodentate protonated intermediates in these systems are among the most stable so far reported for Cr complexes, and they invite attempts to isolate them and directly determine their structure and properties.

Hydrogen Atom Abstraction from Amine Complexes of Iron(II), Cobalt(II), and Ruthenium(II) by Superoxide. Influence of Driving Force on Rate

Paul Bernhard and Fred C. Anson*

The unusual chemistry associated with superoxide's acting as an oxidant is examined with several amine complexes of iron(II) and ruthenium(II) as reductants. In each case the reaction is believed to proceed by means of hydrogen atom transfer from the nitrogen atom in the coordinated secondary amine to O_2^-. The metal center participates in the mechanism by stabilizing the ligand radical intermediate involved. The rate of the reaction exhibits a weak but definite dependence on driving force that is consistent with a proposed mechanism.

The superoxide anion radical, O_2^-, and the perhydroxyl radical, HO_2, are intermediates in autoxidation processes.[1,2] Their high kinetic reactivity can control both the stoichiometry and the mechanism of autoxidation processes, as was illustrated in a recent study of the autoxidation of the Ru(sar)$^{2+}$ complex (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane).[3] At pH values above 5, O_2^- generated in the first step of the reaction was found

to act as a catalyst for the overall autoxidation process. A key step in the catalytic mechanism was the fast reaction between O_2^- and Ru(sar)$^{2+}$, in which O_2^- acted as an oxidant. Because O_2^- is generally a poor outer-sphere oxidant, our results were interpreted in terms of a hydrogen atom transfer from the ruthenium(II) amine complex to O_2^- with concomitant oxidation of the metal.

The data obtained in the earlier study were not sufficient to permit a rate constant for the unusual hydrogen atom transfer reaction from Ru(sar)$^{2+}$ to O_2^- to be evaluated. The present work was undertaken in an attempt to measure the rate of this reaction directly in stopped-flow experiments at high pH, to explore the generality of the reaction by examining some additional amine

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