$[Co(dppe)_2]$ would be expected to have a D_{2d} structure lying between square planar and tetrahedral. In contrast, PP_3 would be expected to impose a pyramidal structure on $[Co(PP_3)]$ as is observed for $[Ni(PP_3)](ClO_4)$.[21] Since the pyramidal geometry is energetically less favored than a D_{2d} geometry, the corresponding reduction would be expected to be more difficult.

For nickel(II), the PP_3 ligand stabilizes a five-coordinate trigonal-bipyramidal structure, while dppe and PP_2 form four-coordinate square-planar complexes. For all three nickel complexes three oxidation states are available in the potential range of −0.7 to −1.3 V vs. ferrocene, and all exhibit a reversible or quasi-reversible one-electron wave for the Ni(II/I) couple. The Ni(I/0) couple is reversible for $[Ni(dppe)_2](BF_4)_2$ and irreversible for $[Ni(PP_3)(CH_3CN)](BF_4)_2$ and $[Ni(PP_2)(CH_3CN)](BF_4)_2$. For $[Ni(PP_3)(CH_3CN)](BF_4)_2$ the irreversibility of the Ni(I/0) couple is due to a ring opening process in which a metal–phosphorus bond is broken and a Ni(0) dimer, $[Ni(PP_3)]_2$, is formed. The rupture of the nickel–phosphorus bond is attributed to ring strain in the transient pyramidal $[Ni(PP_3)]$ complex. In contrast, $[Ni(dppe)_2](BF_4)_2$ is free to distort to a tetrahedral structure on reduction, and the Ni(I/0) couple is reversible. For $[Ni(PP_2)(CH_3CN)](BF_4)_2$ the irreversibility of the Ni(I/0) couple probably arises from loss of acetonitrile on reduction to Ni(0).

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Synthesis, Characterization, and Photobehavior of Macrocyclic Difluoro Complexes of Chromium(III)

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The Cr(III) complexes *cis*-$[Cr(cyclam)F_2]ClO_4$ and *trans*-$[Cr(tet\ a)F_2]ClO_4$, where cyclam and tet a are the macrocyclic tetraamines 1,4,8,11-tetraazacyclotetradecane and *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively, have been synthesized by refluxing the macrocycle in methoxyethanol with *trans*-$[Cr(py)_4F_2]ClO_4$. The cis complex is quite photoactive in room-temperature aqueous solution (ϕ_{F^-} = 0.24 (350-nm excitation), 0.28 (514.5-nm excitation); ϕ_{cyclam} = 0). These results contrast sharply with the photobehavior observed for the analogous nonmacrocyclic complex *cis*-$Cr(NH_3)_4F_2^+$ (ϕ_{NH_3} = 0.45; $\phi_{F^-} < 0.06$) but are in accord with the preferential F^- loss previously noted for $Cr(tren)F_2^+$ (tren = β,β′,β″-triaminotriethylamine). Normal $^2E_g \rightarrow {}^4A_{2g}$ (O_h) phosphorescence is observed from *cis*-$Cr(cyclam)F_2^+$, but only weakly in room-temperature solution. In contrast, the corresponding tet a species *trans*-$[Cr(tet\ a)F_2]ClO_4$ is photoinert on ligand field excitation and exhibits relatively intense, long-lived $^2T_{1g} \rightarrow {}^4A_{2g}$ (O_h) phosphorescence in room-temperature solution. Furthermore, under the same experimental conditions this trans complex displays an 8-fold increase in both its steady-state emission intensity and lifetime on N–H deuteriation ($\tau_{undeutd}$ = 30 μs; τ_{deutd} = 234 μs; 20 °C, acidified aqueous solution). The presence of a *solvent*-deuterium isotope effect ($\tau_{deutd(H_2O)}$ = 234 μs; $\tau_{deutd(D_2O)}$ = 430 μs; 20 °C) indicates contributions to $^2T_{1g} \rightsquigarrow {}^4A_{2g}$ (O_h) relaxation in room-temperature solution from vibrational coupling with the solvent. The contrast in photobehavior between *trans*-$Cr(tet\ a)F_2^+$ (photoinert, long-lived emission) and its nonmacrocyclic counterpart *trans*-$Cr(en)_2F_2^+$ (photolabile, short-lived emission) is discussed with reference to possible pathways for doublet excited-state deactivation.

Introduction

We have recently noted[1] the striking difference in photobehavior between the cis and trans isomers of the Cr(III) complex $Cr(cyclam)(NH_3)_2^{3+}$, where cyclam is the macrocyclic tetradentate amine ligand 1,4,8,11-tetraazacyclotetradecane. The trans isomer is characterized by a near absence of discernible photochemistry and an exceptionally intense, long-lived $^2A_{1g}$, $^2B_{1g} \rightarrow {}^1B_{1g}$ (D_{4h}) phosphorescence that exhibits a strong N–H deuterium isotope effect in room-temperature solution. In contrast, the cis species under comparable conditions is photochemically active (ϕ_{NH_3} = 0.2) and displays a much shorter lived phosphorescence signal and a weak deuterium isotope effect. These observations and related data[2] for *trans*-$Cr(cyclam)(CN)_2^+$ have provided support for a viewpoint that argues for a *direct* photochemical role for the ^2E_g (O_h) excited state of corresponding nonmacrocyclic complexes such as $Cr(NH_3)_6^{3+}$ and *trans*-$Cr(en)_2(CN)_2^+$.

In each of these cases it was suggested that $^2E_g \rightsquigarrow {}^4T_{2g}$ (O_h) back-intersystem crossing (back-ISC) was relatively unimportant as a ^2E_g deactivation pathway at room temperature, due to the substantial activation barrier anticipated.[1-3] However, many Cr(III) systems are expected to have significantly smaller barriers to ^2E_g back-ISC, and the photochemical role of the ^2E_g state could prove even more difficult to assess. Difluoro complexes of the general type *cis*/*trans*-$Cr(N_4)F_2^+$ belong to this latter category of species[4,5] and have been the subject of considerable prior study.[6-14] As part of our continuing study of the photobehavior of complexes with macrocyclic ligands, we have therefore investigated several analogous difluoro Cr(III) complexes containing macrocyclic tetradentate amine ligands. This report describes

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the synthesis, characterization, and contrasting photobehavior of two such macrocyclic species: *cis*-Cr(cyclam)F_2^+ and *trans*-Cr(tet a)F_2^+, where tet a is *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. Although the two macrocyclic ligands differ for the two isomers,[15] our recent studies on diammine and dicyano Cr(III) complexes of tet a reveal photochemical and photophysical properties essentially identical with those of their cyclam analogues.[16]

Experimental Section

Reagents. The free ligands cyclam and (tet a)·$2H_2O$ were used as received from Strem Chemicals. The Cr(III) salts $CrCl_3·6H_2O$ and $Cr(NO_3)_3·9H_2O$ were obtained from Fisher Scientific. The complex *trans*-$[Cr(py)_4F_2]NO_3$ (py = pyridine) was synthesized by the published method.[20] The corresponding perchlorate salt *trans*-$[Cr(py)_4F_2]ClO_4$ was isolated by the addition of $NaClO_4$ to an aqueous solution of the nitrate salt. Ammonium hexafluorophosphate (NH_4PF_6) was purchased from Alfa Products, while D_2O (99.8 atom % D) was obtained from Aldrich Chemicals. Anhydrous lithium perchlorate was procured from G. Frederick Smith Co.

Measurements. Electronic absorption spectra were recorded on a Cary 118C spectrophotometer, and infrared data were collected on a Perkin-Elmer 283 (using KBr pellets). A Markson Electromark Analyzer (Model 4403) was used for conductance measurements. Routine emission spectra were recorded on a modified Aminco-Bowman spectrophotofluorimeter (Model 48203-D), described previously.[2] Higher resolution steady-state emission spectra were obtained on a Jarrell-Ash 500 laser Raman spectrometer equipped with a red-sensitive Hamamatsu 666 PMT as detector. The optical design of the Raman instrument incorporated an F/6.5 double monochromator with a 0.5-m focal length. The equipment and procedures for obtaining emission lifetimes have been described elsewhere.[2] An Aminco solid-sample accessory (Model C73-62140) was used as the sample compartment for both steady-state emission and lifetime studies on crystalline solids at room temperature. An Aminco Dewar (Model B28-62140) was employed for all emission measurements at 77 K. Ligand field (LF) photolyses were carried out by using either the 514.5-nm line of a Coherent Radiation argon ion laser (Model 52) or the 350-nm output of a Rayonet RPR-100 photochemical reactor. Quantum yields at 350 and 514.5 nm for photorelease of fluoride ion from *cis*-Cr(cyclam)F_2^+ in aqueous solution were determined by using a F^- ion indicator electrode (Orion Research) and a saturated calomel reference electrode coupled to a Markson Model 90 pH/Temperature Meter.[9] Standard NaF solutions were used to calibrate the F^- ion electrode. Voltage readings for irradiated and thermal blank solutions of *cis*-Cr(cyclam)F_2^+ were recorded at natural pH. Photolyses were not carried past 10% photoreaction for quantum yield measurements. Absolute light intensities at 350 and 514.5 nm were determined by irradiating absorbance-matched solutions of *cis*-Cr(cyclam)F_2^+ and optically active $Cr(en)_3^{3+}$ and measuring F^- release and loss of optical activity for the former and latter species, respectively. A value of 0.39 was used for the quantum yield for loss of $Cr(en)_3^{3+}$ optical activity on 350- and 514.5-nm excitation, on the basis of results of earlier studies by Linck and co-workers.[21,22] All chemical analyses were performed by Midwest Microlabs.

Syntheses. ***cis*-[Cr(cyclam)F_2]ClO_4.** A 0.315-g sample (6.8×10^{-4} mol) of *trans*-$[Cr(py)_4F_2]ClO_4$ was dissolved in 4 mL of ethylene glycol monomethyl ether, and to this solution was added 0.126 g (6.29×10^{-4} mol) of cyclam ligand. This mixture was heated to reflux while being stirred for 40 min and was then allowed to cool to room temperature. The resulting pink-red precipitate was collected by suction filtration and washed with acetone and then ether. Yield: 0.204 g or 5.23×10^{-4} mol (85%). Anal. Calcd for $CrC_{10}H_{24}N_4ClF_2O_4$: C, 30.81; H, 6.22; N, 14.38; F, 9.72; Cl, 8.69. Found: C, 30.91; H, 6.40; N, 14.14; F, 9.54; Cl, 8.79.

***trans*-[Cr(tet a)F_2]ClO_4.** A solution composed of 0.766 g (1.5×10^{-3} mol) of *trans*-$[Cr(py)_4F_2]ClO_4$ and 0.713 g (2.51×10^{-3} mol) of tet a ligand in 100 mL of ethylene glycol monomethyl ether was magnetically stirred and heated to boiling on a hot plate. More solvent was periodically added in order to maintain the volume. After a period of 3 h, the volume was reduced to 25 mL and the solution was allowed to cool to room temperature. The red crystalline precipitate that resulted was collected by suction filtration and washed with ethylene glycol monomethyl ether (1 mL), a 4:1 ether/acetone solution (75 mL) and ether (40 mL). Yield: 0.250 g. The volume of the mother liquid was then increased to 100 mL with the addition of ethylene glycol monomethyl ether, and the solution was reheated to boiling as described above. Another crop of red precipitate (0.210 g) was collected in this manner and washed as above. Total yield: 0.460 g or 9.35×10^{-4} mol (62%). Anal. Calcd for $CrC_{16}H_{36}N_4ClF_2O_4$: C, 40.54; H, 7.66; N, 11.82; F, 8.02; Cl, 7.48. Found: C, 40.60; H, 7.72; N, 11.56; F, 8.07; Cl, 7.56.

N-H-Deuteriated *trans*-[Cr(tet a)F_2]ClO_4. A 0.150-g sample (3.5×10^{-4} mol) of *trans*-$[Cr(tet\ a)F_2]ClO_4$ was dissolved in a warm solution (50 °C) composed of 8 mL of D_2O (99.8% deuteriated) and 1 drop of concentrated aqueous sodium hydroxide (~20 M). The solution was then left standing in a stoppered glass vial at room temperature. After 22 min the solution was acidified with 3 drops of concentrated nitric acid and filtered to remove impurities. Upon the addition of excess solid anhydrous $LiClO_4$ to the filtrate, a red precipitate formed, which was collected by suction filtration and washed with a 2:1 ether/acetone solution (10 mL) and then ether (8 mL). Yield: 0.142 g or 2.85×10^{-4} mol (93%). The IR spectrum of this sample revealed a high level of deuteriation (>95%). *Caution*! Perchlorate salts of transition-metal complexes are potentially explosive.

***trans*-[Cr(en)$_2$$F_2$]$PF_6$.** The compound was prepared, with minor modification, according to the procedure given in the literature[23] for *trans*-$[Cr(en)_2F_2]ClO_4$. A deuteriated sample (>95% N–D, IR) was obtained via a procedure analogous to that described above for *trans*-$[Cr(tet\ a)F_2]ClO_4$, except that NH_4PF_6 was used for precipitation.

Table I. UV–Vis Spectral Data for Cis and Trans Cr(III) Difluoro Complexes in Aqueous Solution

complex	λ_{max}[a]	ref
cis-Cr(cyclam)F_2^+	511 (114.9), 372 (57.5)	this work
Cr(tren)F_2^+	526 (116), 377 (56.8)	20
cis-$Cr(NH_3)_4F_2^+$	526 (42.1), 380 (18.1)	25
cis-$Cr(en)_2F_2^+$	516 (75.5), 378 (39.5)	23
trans-Cr(tet a)F_2^+	520 (17.6), 440 (26.8); 390 sh (24.6), 342 (27.2)	this work
trans-$Cr(NH_3)_4F_2^+$	535 sh (13.8), 492 (14.9), 405 (10.9), 358 (11.1)	25, 26
trans-$Cr(en)_2F_2^+$	530 sh (16.5), 465 (21.0), 397 (13.2), 351 (14.4)	20, 26

[a] Absorption wavelengths in nm. Values in parentheses are the molar absorptivities.

Results and Discussion

Syntheses. The general synthetic procedure employed for the two macrocyclic difluoro complexes was adapted from that recommended by Glerup and co-workers[20] and involved the use of *trans*-$[Cr(py)_4F_2]ClO_4$ as starting material.

$$trans\text{-}[Cr(py)_4F_2]ClO_4 + N_4 \xrightarrow[\text{reflux}]{\text{methoxyethanol}} [Cr(N)_4F_2]ClO_4 + 4py \quad (1)$$

This synthetic approach, in general, leads to trans products, but in the present case a trans product was only obtained for the tet a system. At this time it is not clear whether kinetic or thermodynamic factors are responsible for the preferential formation of *cis*-Cr(cyclam)F_2^+.

Characterization. ***cis*-[Cr(cyclam)F_2]ClO_4.** The microanalysis results noted earlier for this pink-red product are consistent with its formulation as $[Cr(cyclam)F_2]ClO_4$. The molar conductance of a 2.2 mM aqueous solution of this difluoro complex (90 Ω^{-1} cm^2 mol^{-1}) is reasonable for a 1:1 electrolyte. The UV–visible

(15) As yet unresolved synthetic difficulties have prevented our isolation of *trans*-Cr(cyclam)F_2^+ (see text). Due to the marked steric preference of complex tet a systems for a planar macrocyclic geometry,[16-19] a stable *cis*-Cr(tet a)F_2^+ species is not anticipated.
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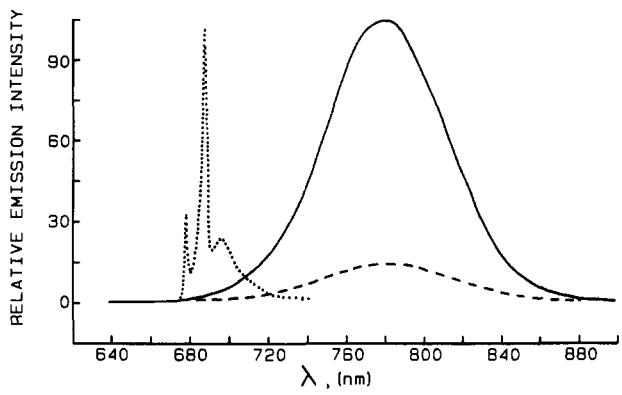

Figure 1. Steady-state emission spectra at 20 °C: *cis*-[Cr(cyclam)F_2]ClO_4 in 2:1 EGW, 514.5-nm excitation (···); *trans*-[Cr(tet a)F_2]ClO_4 in acidified aqueous solution, 436-nm excitation (—, deuteriated sample; ---, undeuteriated sample).

absorption spectrum in aqueous solution exhibits a first LF band ($^4A_{2g} \rightarrow {}^4T_{2g}$; O_h parentage) at 511 nm and a second LF band ($^4A_{2g} \rightarrow {}^4T_{1g}$; O_h parentage) at 372 nm. In Table I, UV–visible spectral parameters are collated for several related cis and trans tetraamine difluoro complexes. The complex *cis*-Cr(cyclam)F_2^+ displays spectral properties very similar to those reported for the well-established species *cis*-Cr$(NH_3)_4F_2^+$ and *cis*-Cr$(en)_2F_2^+$. The trend in amine ligand field (LF) strength observed here for these difluoro complexes (cyclam > en > NH_3) agrees with previous findings for analogous dicyano[2] and diammine systems.[1]

The title complex displays only very weak steady-state emission in room-temperature solution but emits strongly in the solid state at room temperature. This emission is characteristic of $^2E_g \rightarrow {}^4A_{2g}$ (O_h) phosphorescence and is very similar to that reported previously for the nonmacrocyclic analogues *cis*-Cr$(NH_3)_4F_2^+$ and *cis*-Cr$(en)_2F_2^+$.[13,14] Thermally, the compound is resistant to both acid and base hydrolysis, with no spectral evidence for reaction in 0.02 M $HClO_4$ or 0.10 M NaOH after several hours at room temperature. This robustness is reminiscent of the thermal behavior of cis-Cr$(en)_2F_2^+$[24] and contrasts with the lability of Cr(tren)F_2^+ toward loss of F^-.[9]

***trans*-[Cr(tet a)F_2]ClO_4.** The microanalysis results given earlier are consistent with the formulation [Cr(tet a)F_2]$ClO_4 \cdot H_2O$. A trans configuration is expected, on the basis of the known geometric preference of tet a systems[15-19] and the trans structure of the Cr$(py)_4F_2^+$ starting reagent. The molar conductance of a 1 mM aqueous solution of the title compound (93 Ω^{-1} cm^2 mol^{-1}) is in the range expected for a 1:1 electrolyte. The UV–visible absorption spectrum in aqueous solution exhibits a first LF band at 520 nm and other bands of LF origin at 440 and 342 nm. In Table I, the UV–visible spectral parameters of several related compounds are listed for comparison purposes. The complex *trans*-Cr(tet a)F_2^+ displays spectral properties similar to those of the other trans species reported, although the first LF band (520 nm) occurs at a somewhat shorter wavelength. The ordering of the tetraamine ligands in the spectrochemical series is concluded to be tet a > en > NH_3.

The emission spectrum of *trans*-Cr(tet a)F_2^+ in acidified aqueous solution (20 °C) on 436-nm excitation is very similar to that for the corresponding bis(ethylenediamine) complex,[4] only considerably more intense (Figure 1). The broad structureless emission centered at 778 nm is given the same spectral assignment as that by Forster and co-workers[13] and Flint and Mathews[11] for *trans*-Cr$(en)_2F_2^+$ (i.e. $^2T_{1g} \rightarrow {}^4A_{2g}$ (O_h) phosphorescence). A recent paper by Forster and co-workers[14] on the influence of solvent on the emitting states in quadrate Cr(III) complexes included a 77 K emission spectrum of *trans*-Cr(tet a)F_2^+. However, no preparative details or photochemical or emission lifetime information was given for this compound. Waltz and co-workers[27] have noted that *trans*-Cr$(en)_2F_2^+$ exhibits essentially no emission quenching in aqueous basic media, in contrast to the marked base sensitivity of "normal" ^2E_g emitters. They suggested that inefficient quenching by hydroxide ion could be characteristic of $^2T_{1g}$ (O_h) parent excited-state emitters. In accord with these findings, we find that for *trans*-Cr(tet a)F_2^+ only in aqueous media of pH ≥11.3 does significant emission lifetime quenching occur (30 μs, natural pH or acidic solution; 8 μs, pH 11.3). The steady-state emission shows analogous quenching, and upon reacidification both the lifetime and emission intensities of the title complex return to their original values. Thermally, the complex is reasonably robust in neutral or mildly acidic aqueous solution.

Photobehavior. *cis*-[Cr(cyclam)F_2]ClO_4. The complex is quite photolabile under LF excitation in room-temperature solution. For neutral or acidic aqueous solution, photoreaction proceeds in two distinct stages following irradiation into the first (514.5 nm) or second (350 nm) spin-allowed LF absorption band. Only minor absorbance changes accompany the first-stage reaction, with a small shift in the two absorption maxima to shorter wavelength and maintenance of an isosbestic point at 388 nm. This initial spectral shift is consistent with stereoretentive fluoride photoaquation (reaction 2). An alternative aquation mode involving

$$cis\text{-Cr(cyclam)}F_2^+ + H_2O \xrightarrow{h\nu} cis\text{-Cr(cyclam)(F)}(H_2O)^{2+} + F^- \quad (2)$$

cyclam ring opening would have resulted in a spectral shift to longer wavelength. Confirmation of fluoride activation comes from monitoring F^- ion release potentiometrically with a F^--selective electrode. Complete loss of one F^- ligand occurs during this first stage and proceeds with a quantum yield of 0.24 and 0.28 for 350- and 514.5-nm excitation, respectively. Subsequent photoreaction involves no further loss of coordinated F^- ion but is associated with a large decrease in absorbance and a further spectral shift to lower wavelength. These observations are consistent with a second-stage reaction involving cis → trans photoisomerization.

It is noteworthy that the initial photoreaction involving F^- ligand loss is *not* in agreement with expectations arising out of the additive-angular-overlap model of Vanquickenborne and Ceulemans (VC) for Cr(III) ligand field photochemistry.[10] Although *cis*-Cr(cyclam)F_2^+ has only C_2 symmetry, conventionally this is approximated as D_{4h} by averaging σ- and π-donor strengths on the x and y (equatorial) axes containing the F^- ligands. In VC theory, photosubstitution is assumed to originate from the lowest lying component of the $^4T_{2g}$ (O_h) excited state, or states thermally accessible from this level. For *cis*-Cr(cyclam)F_2^+ the $^4B_2$ (xz, yz, $x^2 - y^2$) component lies lowest, and theory predicts cleavage of an equatorial Cr–cyclam amine bond ($I^*_{Cr\text{-amine(eq)}} = 0.90$; $I^*_{Cr\text{-amine(ax)}} = 1.44$; $I^*_{Cr\text{-}F} = 1.46$). Even should reaction include contributions from the higher energy ^4E component, VC theory in this instance predicts Cr–amine (axial) bond cleavage.

These present results contrast sharply with the "normal" photobehavior observed for the analogous nonmacrocyclic complex *cis*-Cr$(NH_3)_4F_2^+$ ($^4B_2$ excitation: $\phi_{NH_3} = 0.45$; $\phi_{F^-} < 0.06$).[8] However, preferential F^- loss has also been previously noted for the species Cr(tren)F_2^+.[9] Although nonmacrocyclic, the tetradentate tren ligand, like cyclam, would sterically constrain an activated equatorial amine from leaving the Cr(III) coordination sphere. Thus, the absence of amine photosubstitution is not surprising for these tren and cyclam systems. On the basis of the VC model, one might then have anticipated photoinert complexes, rather than species that exhibit efficient F^- photoloss.

However, for these constrained amine systems, initial equatorial amine–Cr bond cleavage might be followed by nucleophilic displacement of a fluoride ligand by the free equatorial amine. Photolysis data obtained in 5 M HNO_3 argue, however, against such a F^- displacement mechanism. Production of a ring-opened amine species with a spectral shift to longer wavelength is anticipated under these conditions, since protonation of the equatorial amine lone pair will prevent subsequent nucleophilic attack at the

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Table II. Phosphorescence Lifetimes (in μs) for $Cr(N_4)F_2^+$ Complexes[a]

compd	temp, K	τ_{D_2O}	τ_{H_2O}	τ_{EGW}(2:1)	τ_{Me_2SO}	τ_{solid}
trans-Cr(tet a)F_2^+	293		30, 8[e]	27	24	42[b]
	77			49		49[b]
deutd *trans*-Cr(tet a)F_2^+	316		194			
	305		209			
	293	430	234	250	205	1100[b]
	283		244			
	77			1250		1240[b]
trans-Cr(en)$_2F_2^+$	293		1.3[c]			11[b]
	77			36		
deutd *trans*-Cr(en)$_2F_2^+$	293		ND[f]			130[d]
	77			310		250[d]
cis-Cr(cyclam)F_2^+	293			ND[f]		1.2[b]
	77			80		7.2[b]

[a] Unless otherwise stated, all solutions were acidified with 1 drop of 0.5 M HNO_3 to prevent possible base quenching. [b] ClO_4^- salt. [c] Value reported in ref 5. [d] PF_6^- salt. [e] pH 11.3. [f] ND = nondeterminable.

F^- coordination position. Instead, absorption spectral shifts to *shorter* wavelength were observed, as previously noted for photolysis under neutral or mildly acidic conditions.

As Saliby et al. point out,[9] earlier $^4T_{2g}$ (O_h) reaction models more successfully accommodate loss of F^- from *cis*-$Cr(N_4)F_2^+$ species. These latter models attach greatest significance to bond energy changes accompanying LF absorption and identify a specific labilized axis. For both *cis*-Cr(cyclam)F_2^+ and Cr(tren)F_2^+, these models indicate excitation energy will be concentrated along the *x* and *y* axes. Since the tetradentate ligands inhibit Cr–amine (equatorial) bond scission, significant F^- photoloss is instead anticipated. Alternatively, F^- loss may be associated with the onset of excited-state doublet ($^2T_{1g}/^2E_g$; O_h) reaction.[28] Whereas *cis*-[Cr(cyclam)F_2]ClO_4 displays only very weak, short-lived $^2E_g \rightarrow {}^4A_{2g}$ (O_h) phosphorescence in room-temperature solution (Figure 1, Table II), the complex exhibits strong, long-lived phosphorescence in the *solid state* where no photoreaction is observed (Table II). This behavior is reminiscent of that shown by other photoreactive Cr(III) complexes such as $Cr(NH_3)_6^{3+}$ and *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ and is in accord with phosphorescence and photoreaction being competitive processes out of the doublet level.[1] However, in view of the small energy barrier anticipated for *cis*-Cr(cyclam)F_2^+, efficient $^2E_g \rightarrow {}^4T_{2g}$ (O_h) back-ISC may be responsible for the very weak emission in room-temperature solution; i.e., the differences in solution and solid-state photobehavior may simply reflect a larger *effective*[29] rate constant for back-ISC under solution conditions.

***trans*-[Cr(tet a)F_2]ClO_4.** The complex *trans*-Cr(tet a)F_2^+ was found to be photoinert upon ligand field excitation. Photolysis in 0.01 M $HClO_4$ or 0.02 M NaOH solution at 514.5 nm (argon ion laser) for an extended period yielded no changes in the absorption spectrum. This photoinertness is to be contrasted with the marked photolability of the corresponding nonmacrocyclic system *trans*-Cr(en)$_2F_2^+$, which primarily involves the amine ligands ($\phi_{en} = 0.35$; $\phi_{F^-} \leq 0.08$).[6,7] The quenching of photoreaction in room-temperature aqueous solution for *trans*-Cr(tet a)F_2^+ is accompanied by a marked lengthening of the $^2T_{1g} \rightarrow {}^4A_{2g}$ phosphorescence lifetime (20 °C: tet a, 30 μs; en, 1.3 μs, Table II).

Furthermore, on N–H deuteriation, *trans*-Cr(tet a)F_2^+ displays an even greater deuterium isotope effect in room-temperature solution than the 5-fold enhancement reported for *trans*-Cr(cyclam)$(CN)_2^+$,[2] a complex containing the same number of N–H bonds subject to deuteriation. The emission lifetime of deuteriated *trans*-Cr(tet a)F_2^+ in acidified aqueous solution at 20 °C was 7.8 times greater than that of the undeuteriated species ($\tau_{deutd} = 234$ μs; $\tau_{undeutd} = 30$ μs). The strong deuterium isotope effect observed indicates a significant role for weak coupled $^2T_{1g} \rightsquigarrow {}^4A_{2g}$ (O_h) deactivation in $^2T_{1g}$ excited-state relaxation in room-temperature solution. An identical enhancement was also observed for the steady-state emission intensity (7.9), from a study comparing the emission intensity of absorbance-matched acidic aqueous solutions (20 °C) excited at 436 nm. These results suggest that the ϕ_{ISC} and radiative rate constant, k_r, terms for deuteriated and undeuteriated *trans*-Cr(tet a)F_2^+ are identical and that the difference in their phosphorescence intensities is associated with a smaller net radiationless rate constant, k_{nr}, for $^2T_{1g} \rightsquigarrow {}^4A_{2g}$ deactivation for the deuteriated complex.[1,2]

This conclusion is supported by the observation that the lifetime of the deuteriated complex is fairly insensitive to temperature changes in *aqueous* solution (from the H_2O data in Table II an apparent activation energy of 1.3 ± 0.1 kcal mol^{-1} is obtained). This small temperature term eliminates $^2T_{1g} \rightsquigarrow {}^4T_{2g}$ (O_h) back-ISC as an important process in room-temperature solution. The emission lifetime of *trans*-Cr(tet a)F_2^+ was also investigated in 2:1 ethyleneglycol/water (EGW) and Me_2SO solvent. In both cases, the lifetimes at room temperature were similar to those obtained in aqueous solution (Table II), and the deuterium isotope effect on the lifetimes was also comparable to that previously noted in water (20 °C: $\tau_{deutd}/\tau_{undeutd}$ = 8.5 (Me_2SO), 9.3(EGW)—Table II).

A revealing characteristic of the deuteriated complex is the dramatic increase in the room-temperature emission lifetime on switching from solution to the solid state, despite the absence of photoreaction in solution (example: $\tau_{H_2O} = 234$ μs; $\tau_{solid} = 1100$ μs). Also noteworthy is the larger deuterium isotope effect in the solid state at room temperature (example: $\tau_{deutd}/\tau_{undeutd}$ = 7.8 (H_2O), 26.2 (solid)—Table II). Furthermore, the room-temperature solid-state lifetime for the deuteriated sample is almost identical with that obtained at 77 K ($\tau_{rt} = 1100$ μs; $\tau_{77K} = 1240$ μs). It may therefore be concluded that some strong coupled process (other than direct $^2T_{1g}$ reaction) is also an important decay pathway for *trans*-Cr(tet a)F_2^+ in room-temperature solution. We propose that this strong coupled process involves contributions to $^2T_{1g} \rightsquigarrow {}^4A_{2g}$ relaxation from vibrational coupling with the solvent. Thus, in the solid state $k_{nr} = k_{intra}$, whereas in solution $k_{nr} = k_{intra} + k_{solv}$.[31] The k_{solv} term is assumed to have a small temperature dependence, while k_{intra} is almost temperature independent. Some experimental support for solvent vibrational coupling comes from the observation of a solvent deuterium isotope effect in room-temperature solution. For deuteriated *trans*-[Cr(tet a)F_2]ClO_4 in D_2O the $^2T_{1g}$ emission lifetime at 20 °C is 84% longer than that in acidified aqueous solution ($\tau_{H_2O} = 234$ μs; τ_{D_2O} =

(28) Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 53.

(29) According to the terminology employed by Porter[30] $k_{BISC} = (1 - \phi_{ISC})k_{-4}$, where k_{-4} is the *intrinsic* rate constant, k_{BISC} is the *effective* rate constant for back-ISC, and ϕ_{ISC} is the quantum yield for ISC. The lifetime of the doublet emitting level is directly influenced by k_{BISC} rather than k_{-4}. When the molecule is photoinert, ϕ_{ISC} may approximate unity; and thus k_{BISC} may be quite small despite a large value for k_{-4}.

(30) Porter, B. G. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 2.

(31) k_{intra} is the $^2T_{1g} \rightsquigarrow {}^4A_{2g}$ radiationless rate constant when the vibrational accepting modes are intrinsic to the molecule. The presence of a strong deuterium isotope effect identifies a prominent role for the high-frequency N–H vibration.[1,2]

430 μs). The value of k_{solv} should decrease on changing from H_2O to D_2O, due to lowering of the solvent stretching frequency used for vibrational coupling with the $^2T_{1g}$ excited state. Since the $^2T_{1g}$ lifetime for *trans*-Cr(tet a)F_2^+ in room-temperature solution is, to a good approximation, given by $1/k_{nr}$ (where $k_{nr} = k_{intra} + k_{solv}$), then a longer lifetime is anticipated in D_2O.

Finally, the marked contrast in photobehavior between *trans*-Cr(tet a)F_2^+ (photoinert, long-lived emission) and its nonmacrocyclic counterpart *trans*-Cr(en)$_2F_2^+$ (photolabile, short-lived emission) requires comment. We feel these differences are most consistent with the short $^2T_{1g}$ lifetime of *trans*-Cr(en)$_2F_2^+$ in solution being associated with *direct* reaction out of the $^2T_{1g}$ level. This interpretation also rationalizes the much longer lifetime and substantial deuterium isotope effect observed for *trans*-Cr(en)$_2F_2^+$ when photoreaction is suppressed, such as in frozen glasses (77 K) and in the solid state (Table II). Alternatively, it may be argued that $^2T_{1g} \rightsquigarrow {}^4T_{2g}$ back-ISC is primarily responsible for the short $^2T_{1g}$ lifetime of *trans*-Cr(en)$_2F_2^+$ in room-temperature solution, while the $^2T_{1g}$ level is assumed inert toward direct chemical reaction. Since *trans*-Cr(tet a)F_2^+ is photoinert, the quantum yield for $^4T_{2g} \rightsquigarrow {}^2T_{1g}$ ISC (ϕ_{ISC}) may be close to unity and the effective rate constant for back-ISC relatively small in room-temperature solution.[29] However, one might then also anticipate the observation of delayed $^4T_{2g} \rightarrow {}^4A_{2g}$ (O_h) fluorescence for *trans*-Cr(tet a)F_2^+ (since the $^4T_{2g}$ level is now photoinert). We have looked carefully (without success) for evidence of a broad fluorescence signal in room-temperature solution and the solid state, using the high-resolution capabilities of the Jarrell-Ash laser Raman instrument (514.5-nm excitation). A *direct* photochemical role for the $^2T_{1g}$ level for *trans*-Cr(en)$_2F_2^+$ is also supported by the observation by Waltz and co-workers from pulsed-laser conductivity studies[27] that 100% of the photoreaction is associated with the doublet level.

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Registry No. *cis*-[Cr(cyclam)F_2]ClO_4, 105140-76-9; *trans*-[Cr(tet a)F_2]ClO_4, 88415-77-4; *trans*-[Cr(py)$_4F_2$]ClO_4, 27731-45-9; D_2, 7782-39-0.

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Mechanism of Chiral Recognition of Octahedral Metal Complexes Effected by Bis(μ-*d*-tartrato)diantimonate(III) Anion in Solution. 2. Cage Complexes of the Type $[Co(N)_6]^{3+}$

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Some hexaamine cage complexes such as $[Co(sep)]^{3+}$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) and [Co(diNOsar)]$^{3+}$ (diNOsar = 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) were subjected to ion-exchange chromatography with the bis(μ-*d*-tartrato)diantimonate(III) anion, $[Sb_2(d\text{-tart})_2]^{2-}$, employed as a chiral eluent. It was found that the Λ enantiomers are eluted always first and that the more bulky the alkyl cap that each cage complex has, the better the degree of optical resolution of the complex attained. These experimental results were interpreted reasonably on the basis of the C_2 association model in which two NH protons directed along the (pseudo) C_2 axis of the complex are hydrogen-bonded to two oxygen atoms of the $[Sb_2(d\text{-tart})_2]^{2-}$ ion. It was concluded that chiral recognition of the cage complex is effected through the steric repulsion expected stereoselectively between the alkyl cap of the Δ enantiomer and the distal carboxylate group of the chiral anion.

Introduction

In the preceding paper,[1] we proposed two association models called as the C_3 and C_2 models, which account for how bis(μ-*d*-tartrato)diantiomonate(III) anion, $[Sb_2(d\text{-tart})_2]^{2-}$ ion, recognizes the chirality of some octahedral complexes of the type $[Co(N)_6]^{3+}$ in solution. In the C_3 association model where two or three NH protons directed along the (pseudo) C_3 axis of the compex are hydrogen-bonded to the oxygen atoms of $[Sb_2(d\text{-tart})_2]^{2-}$ ion, the Λ enantiomer forms a more favorable ion pair with the chiral anion than does the Δ enantiomer. In the C_2 association model, on the other hand, two NH protons directed along the (pseudo) C_2 axis participate in the hydrogen bonding to the chiral anion, and the Δ enantiomer associates more smoothly with the chiral anion than does the Λ enantiomer.

Recently, Sargeson and coworkers[2,3] have prepared some hexaamine cage complexes with alkyl caps along the C_3 axis, e.g., $[Co(sep)]^{3+}$, $[Co(diNOsar)]^{3+}$, $[Co(azaMEsar)]^{3+}$, and $[Co(MENOsar)]^{3+}$, starting with $[Co(en)_3]^{3+}$ or $[Co(sen)]^{3+}$,[4] and some of them have been resolved by ion-exchange chromatography using $[Sb_2(d\text{-tart})_2]^{2-}$ ion as an eluent, with the Λ enantiomers eluted first.[2,5] Since these cage complexes have alkyl caps that block the access of $[Sb_2(d\text{-tart})_2]^{2-}$ ion along the C_3 axis, the chiral anion probably approaches each complex along the (pseudo) C_2 axis. Then, the formal application of our C_2 association model leads us to expect that the Δ enantiomers of these cage complexes interact more smoothly with $[Sb_2(d\text{-tart})_2]^{2-}$ ion than do the antipodes. Nevertheless, the Λ enantiomers are actually eluted first by $[Sb_2(d\text{-tart})_2]^{2-}$ ion in ion-exchange chromatography, which stimulated us to elucidate the mechanism by which

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(4) Abbreviations; en = ethylenediamine, sen = 1,1,1-tris(((2-aminoethyl)amino)methyl)ethane, sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, diNOsar = 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane, azaMEsar = 8-methyl-1,3,6,10,13,16,19-heptaazabicyclo[6.6.6]eicosane, MENOsar = 1-methyl-8-nitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane, AMsartacn = 9-amino-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane, NOsartacn = 9-nitro-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane, and azasartacn = 1,4,7,9,11,14,19-heptaazatricyclo[7.7.4.2^{4,14}]docosane.
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