remain close to the F_R parameter of the octahedral species; it does not change very much in the series of compounds, the influence of the hetero ligand perpendicular to the N–Cr–N plane being small. The parameter values of F_1 describing the force along the Cr–N bond trans to the halogen ligand are all increased compared to F_R of O_h, indicating a pronounced trans effect caused by a withdrawal of d electrons in antibonding metal orbitals. This leads to a strengthening of Cr–N bonds, in particular of those in positions trans to the hetero ligand. In the iodo complex, this effect is partially reduced due to the large internuclear distance.

From the angular force constants, it is the F_6 parameter that is closest to F_α of O_h; it belongs to bond angles in the N–Cr–N plane and is hardly affected by the hetero ligand as was equally observed for F_2. The parameter values of F_2 and F_6 and obviously also of some others are similar for different compounds and therefore can be transferred from one compound to another. Force constants that belong to angles containing the trans Cr–N bond (F_4) or the Cr–X bond (F_5) are also similar, as long as the size of the halogen ligand does not exceed the space necessary for the NH_3 ligands and thus restrict the angular vibrations because of steric hindrance. In fact, the F_5 parameters of the bromo and iodo complex are calculated to be much higher, adopting the value of the octahedral complex, which indicates the importance of the ligand size for angular vibrations.

A similar discussion of parameter sequences could not be carried out for the normal-coordinate analysis of the $[Co(NH_3)_5X]^{2+}$ homologues[4] since in these calculations all force constants belonging to the Co–N atom groups are transferred from the hexaammine complex and assumed to be invariant in the series of the halogeno compounds. Since this leads to artificial effects also on the Co–X force constants, they are not comparable with our results.

Nondiagonal F matrix elements of the mixed-ligand compounds, in general, are calculated to be larger than the corresponding parameters of the octahedral parent system, indicating enhanced interactions in molecules of lower symmetry and larger environ-mental effects in the crystal. While F_7 does not differ very much for all compounds, the parameters F_8 and F_9 resulting from $F_{RR'}$ vary from the fluoro to the iodo compound in an unspecific way. Values of F_8 belonging to the force along the hetero axis (eq 1b) grow from Cl, Br, to I in this series possibly due to the increasing halogen polarizability. For $[Cr(NH_3)_5F]^{2+}$, this parameter is the largest which can be attributed to the high electronegativity of F and to the small Cr–F distance. In a similar way, other variations of force constants may be explained from physical properties of halogen ligands.

Conclusions

An assignment of vibrational spectra of low-symmetry complex compounds by normal-coordinate analyses applying a slightly modified Labonville force field on chromophore skeletons can be carried out with some confidence. The frequencies calculated for stretching modes are generally in better agreement with the experiment than those of angular vibrations since, for the latter, off-diagonal elements of the force field matrix are more important relative to diagonal elements. In addition, long wavelength modes are not as well reproduced by the calculation owing to the larger intermixing with lattice modes. Variations of smaller off-diagonal force constants do not add very much to the overall quality of the results. Also, the neglect of ligand vibrations (e.g. rocking vibrations of NH_3 ligands) does not interfere significantly with the results. Force constants belonging to corresponding atom groups can be transferred from one compound to another.

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Perturbations of the Low-Energy Doublet Excited State of Chromium(III). Competing Heavy-Atom and Macrocyclic Ligand Effects in Thermally Activated Relaxation Pathways[1]

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The thermally activated relaxation of the lowest energy doublet state has been examined in several families of chromium(III) complexes. The effective rate constant for excited-state relaxation can be approximately represented as $k(obsd) = k^\circ + k(T)$, where k° is a low-temperature limit that is nearly temperature and medium independent, and $k(T)$ can be approximately represented in an Arrhenius form. The repression of the thermally activated pathway (i.e., $k(T) < k^\circ$, for $T \leq 300$ K), which has been reported for *trans*-$Cr^{III}(N_4)X_2$ complexes in which N_4 is a macrocyclic tetraamine ligand and X = NH_3 or CN^-, is not observed when X = Cl^- or Br^-. Rather $k(T)$ dominates the behavior of these and other chloro and bromo complexes, even in glassy matrices at temperatures between 160 and 200 K. The medium dependence of $k(T)$ is dramatically illustrated by the orders of magnitude decrease of its contribution to the decay of $(^2E)Cr(NH_3)_5Cl^{2+}$ doped into a $[Rh(NH_3)_5Cl]Cl_2$ solid matrix. Stereochemical and "heavy-atom" perturbations of the ^2E excited state have been further examined by using macrocyclic ligands containing pyridyl and thioether donor groups. These and related observations require that several different mechanisms (decay channels) can contribute to $k(T)$. The evidence is evaluated for differing contributions of surface crossing channels such as formation of an intermediate in its ground electronic state or the thermal population of a higher energy quartet excited state (BISC). It is inferred that these are plausible competitive decay channels with intermediate formation being important for strong-field ligands (NH_3, CN^-) and BISC being important for weak-field ligands (Cl^-, Br^-).

Introduction

While chromium(III) photochemistry and photophysics have long and distinguished histories,[2] recent studies have turned up some surprising features of the excited-state behavior and provided some important insights into the mechanisms of excited-state

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relaxation in fluid solutions at ambient temperatures. One of the most striking "surprises" is the contrast between the very long, nearly temperature independent doublet excited-state lifetimes but small photoaquation yields[2] found for certain *trans*-$Cr^{III}(N_4)X_2$ complexes (N_4 = a tetraaza macrocyclic ligand) and the shorter, temperature-dependent lifetimes but large photoaquation yields found for either the $Cr^{III}(NH_3)_5X$ or *cis*-$Cr^{III}(N_4)X_2$ analogues. For example, when X = CN^-, the lowest energy excited-state (^2E) lifetimes at 25 °C are reported to be 300–400,[3–5] 14,[4,5] and 2[4,5] μs, respectively. Similar photophysical behavior has been reported for the complexes with X = NH_3.[2g,h,6] The striking influence of macrocyclic ligand stereochemistry in effectively eliminating a thermally activated, solvent-mediated pathway for excited-state relaxation has been attributed[2g,h,5b] to the nuclear reorganizational constraints that result from the motion of ligand atoms necessary to promote the formation of a chemical intermediate as the (^2E)Cr(III) excited state relaxes along the thermally activated pathway. It seems most plausible that such an intermediate must be in its lowest energy electronic state so that the electronic relaxation energy contributes to the driving force for intermediate formation.[2g,h,7] Waltz and co-workers have very recently presented the first direct evidence for such an intermediate.[8] These workers reported that the electronic relaxation of *cis*-(^2E)Cr([14]-aneN$_4$)(NH$_3$)$_2^{3+}$ [9] in water is accompanied by the formation of a relatively long-lived, seven-coordinate intermediate.

The quantum yield for photoaquation of *trans*-Cr([14]-aneN$_4$)Cl$_2^+$ has also been reported to be very small,[10] and one might be tempted to infer that similar mechanistic constraints are imposed on the relaxation pathway in all the trans macrocyclic complexes. Yet the ambient lifetime of *trans*-(^2E)Cr([14]-aneN$_4$)Cl$_2^+$ has been reported to be only 10 ns,[11] about 0.01% of the 77K lifetime[2g,4] and in dramatic contrast to the photophysical behavior of the cyano and ammine analogues. Since *trans*-(^2E)Cr([14]aneN$_4$)Cl$_2^+$ is thermally activated even at low temperatures,[4] a different relaxation mechanism is almost certainly implicated for this complex than for its cyano and ammine analogues.[2g,h,12] Among the relaxation mechanisms that might be possible when X = Cl$^-$, but not when X = CN$^-$ or NH$_3$, are (1)
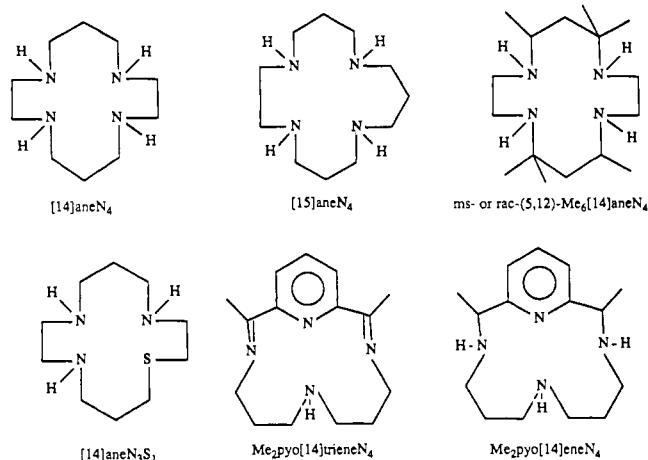

Figure 1. Skeletal structures of macrocyclic ligands. See ref 9 for explanation of abbreviations.

a heavy-atom effect mediating more efficient electronic coupling of the ^2E and the reaction intermediate potential energy surfaces and (2) thermally activated back intersystem crossing to a higher energy quartet excited state that can relax more efficiently than the ^2E excited state.

This paper describes our studies of the photophysical behavior of a number of (^2E)Cr^{III}(MCL)X$_2$ complexes (MCL is a tetradentate macrocyclic ligand) and their simpler ammine analogues. These studies were undertaken with a view of attempting to clarify some of the mechanistic issues and contrasts summarized above.

Experimental Section

A. Preparation of Complexes. The pentaammine complexes were prepared by using standard literature procedures.[13,14] The syntheses of [*trans*-Cr([14]aneN$_4$)Cl$_2$]ClO$_4$,[15] [*cis*-Cr([14]aneN$_4$)Cl$_2$]ClO$_4$,[16] [*trans*-Cr([14]aneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$,[6] [*trans*-Cr(*ms*-(5,12)-Me$_6$[14]-aneN$_4$)(NCS)$_2$]NCS,[17] [*cis*-Cr(*rac*-(5,12)-Me$_6$[14]aneN$_4$)(NCS)$_2$]-NCS,[17] [*trans*-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(CN)$_2$]CN,[18] [*trans*-Cr-(*ms*-(5,12)-Me$_6$[14]aneN$_4$)Br$_2$]Br,[17] and [Ni(Me$_2$pyo[14]trieneN$_4$)]-(ClO$_4$)[19] are also described in the literature. The macrocyclic ligands[9] are illustrated in Figure 1.

Warning! The perchlorate salts of chromium am(m)ines are extremely hazardous.

[***trans*-Cr([14]aneN$_4$)Br$_2$]Br.** A 0.5-g sample of [*trans*-Cr([14]-aneN$_4$)(CN)$_2$]CN[3] was placed in 20 mL of water, and 10 mL of 48% HBr was added. This mixture was heated to reduce the volume to 10 mL and a green solid began to form. The mixture was cooled and suction filtered. The yield was 0.58 g or 78%.

[***trans*-Cr([14]aneN$_4$)(NH$_3$)$_2$]Br$_3$.** A 1.0-g sample of solid [*trans*-Cr-([14]aneN$_4$)Br$_2$]Br was added to 25 mL of liquid NH$_3$, and then the NH$_3$ was allowed to evaporate. This procedure was repeated a second time. The yield was 1.1 g or 100%. The product may be recrystallized from water and salted out with anhydrous NaBr.

[***trans*-Cr([14]aneN$_4$)(NH$_3$)(H$_2$O)]Cl$_3$.** The procedure of Kane-Maguire and co-workers[6] was modified as follows: 0.25 g of [*trans*-Cr-([14]ane N$_4$)(NH$_3$)$_2$]Br$_3$ was dissolved in 0.1 M NaOH and allowed to react for 3 min. The solution was then acidified with 1 M HCl and rotary evaporated to dryness. Then 20 mL of 3 M HCl was added, the resulting solution was rotary evaporated to dryness again, and the solid was removed mechanically. The yield was 0.19 g or 100%.

[***trans*-Cr([14]aneN$_4$)(NH$_3$)Cl](ClO$_4$)$_2$.** The solid from the preparation of [*trans*-Cr([14]aneN$_4$)(NH$_3$)(H$_2$O)]Cl$_3$ was placed in a beaker and then into a vacuum oven at 90 °C for 72 h. The solid changed color from orange to red as the water was removed. The red solid was dissolved in a few milliliters of 1 M HCl and suction filtered to remove any decomposition products. Solid, anhydrous NaClO$_4$ was then added and the solution was cooled in an ice bath. A reddish orange solid formed, which was then removed by suction filtration, washed with acetone and ether,

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(9) Abbreviations: [14]aneN$_4$ = cyclam = 1,4,8,11-tetraazacyclotetradecane; [9]aneN$_3$ = 1,4,7-triazacyclononane; *ms*-(5,12)-Me$_6$[14]aneN$_4$ = teta = 5,12-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; *rac*-(5,12)-Me$_6$[14]aneN$_4$ = tet*b* = 5,12-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; [14]-aneN$_3$S = 1,4,8-triaza-11-thiacyclotetradecane; Me$_2$pyo[14]trieneN$_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]septadeca-1-(17),2,11,13,15-pentaene; Me$_2$pyo[14]eneN$_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]septadeca-1(7),13,15-triene.

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Table I. Elemental Analysis

complex	% C	% H	% N
[*trans*-[Cr([14]aneN$_3$S)Br$_2$]Br	24.36 (24.41)^a	5.11 (4.92)	11.22 (11.39)
[*trans*-[Cr([15]aneN$_4$)Cl$_2$]ClO$_4$	30.13 (30.25)	6.06 (6.00)	12.71 (12.83)
[Cr([14]aneN$_3$S)Cl$_2$]Cl	31.97 (31.97)	6.67 (6.17)	10.93 (11.18)
[*trans*-Cr([14]aneN$_4$)(NH$_3$)Cl](ClO$_4$)$_2$	24.49 (23.89)	5.69 (5.40)	13.85 (13.90)
[Cr([14]aneN$_3$S)(NH$_3$)$_2$]Br$_{1.5}$(ClO$_4$)$_{1.5}$	21.03 (20.98)	4.92 (5.10)	12.34 (12.29)
[Cr(Me$_2$pyo[14]eneN$_4$)(CF$_3$SO$_3$)$_2$]CF$_3$SO$_3$·H$_2$O	27.66 (27.73)	3.66 (3.61)	7.20 (7.19)

^{a} Theoretical values are in parentheses.

and air-dried. The yield was 0.15 g or 60%.

[*trans*-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$. A 1.0-g sample of [*trans*-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)Br$_2$]Br was placed in a flask and enough anhydrous liquid NH$_3$ was added to completely cover the complex. The mixture was stirred and the NH$_3$ was allowed to evaporate in the dark. This procedure was repeated a second time. The remaining yellowish orange solid was mechanically removed and washed on a frit with ethanol and then ether. The solid was recrystallized from 1 M HClO$_4$ and salted out with anhydrous NaClO$_4$. The yield was 0.83 g or 75%.

[*trans*-Cr([15]aneN$_4$)Cl$_2$]ClO$_4$. A 1.0-g sample of [15]aneN$_4$ and 2.0 g of Cr(THF)$_3$Cl$_3$[20] (THF = tetrahydrofuran) were placed in 20 mL of dry DMF (*N*,*N*-dimethylformamide) and refluxed for 10 min. A green solid formed in the bottom of the flask as it cooled. The mixture was suction filtered, the remaining solution was boiled down to 10 mL and a second crop of green solid was obtained. The green solid was washed with cold acetone and then ether. The green solid was then dissolved in a minimum amount of water and then salted out by adding a few drops of concentrated HClO$_4$. The mixture was cooled in an ice bath and then suction filtered and washed with cold acetone and ether. The yield of the initial green product was 1.34 g or 77%.

[Cr([14aneN$_3$S)Cl$_2$]Cl. A 0.28-g sample of [14]aneN$_3$S·2HCl[21] was placed in a 50-mL round-bottom flask with 20 mL of dry DMF and 0.8 g of Cr(THF)$_3$Cl$_3$. The mixture was refluxed for 1 h. The solution was reddish purple during the reaction, not much different from Cr(THF)$_3$Cl$_3$ in color. When the solution was cooled, it turned deep red, and cooling in an ice bath resulted in the formation of a purple solid. The mixture was suction filtered, and the purple product was washed with cold ethanol and ether. The filtrate was evaporated to about 5 mL, ethanol was added to the cooled mixture, and a second crop of product was obtained. The yield was 0.183 g or 51%.

[Cr([14aneN$_3$S)Br$_2$]Br. A 0.42-g sample of [Cr([14]aneN$_3$S)Cl$_2$]Cl was dissolved in 28 mL of 0.1 M NaOH. Upon dissolving, the purple complex turned blue. The solution of Cr([14]aneN$_3$S)(OH)$_2$$^+$ was acidified with concentrated (48%) HBr until the solution was approximately 5 M in HBr, at which time the solution changed from blue to purplish red in color. The solution was placed in the dark for several days until a deep purple solid formed. The mixture was suction filtered; the solid was air-dried on a frit and then washed with ether. The yield was 0.43 g or 76%.

[Cr([14]aneN$_3$S)(NH$_3$)$_2$]Br$_3$. A flask containing solid [Cr([14]-aneN$_3$S)Br$_2$]Br was cooled in a dry ice–acetone bath, and then liquid NH$_3$ was added with stirring. After a few minutes the solution turned orangish. The NH$_3$ was allowed to evaporate, and the procedure was repeated one more time. The solid was mechanically removed from the flask. The yield was 100%.

[Ni(Me$_2$pyo[14]eneN$_4$)](ClO$_4$)$_2$.[9] A 5.0-g sample of [Ni(Me$_2$pyo-[14]trieneN$_4$)](ClO$_4$)$_2$ was placed in a 500-mL flask along with 90 mL of water. The undissolved solid was removed by suction filtration, and the filtrate was cooled in an ice bath. Next, 1.1 g of NaBH$_4$ was added in small portions over a 10-min period. A black solid formed following the addition of the NaBH$_4$. The solution was then heated to 65 °C for 1.5 h (until the bubbling stopped). The mixture was quickly filtered, while it was warm, and then 6 mL of concentrated HClO$_4$ was added. The solution was then placed in an ice bath, and a yellow solid formed after 5 min. Some orange-red crystals also appeared. The filtered solid was orange. The yield was 3.2 g or 63%.

Me$_2$pyo[14]eneN$_4$. This ligand was prepared by a literature procedure,[22] except for the following modification. The cake that solidified, after removal of the Ni^{2+} with NaCN, was placed in 1 L of ether, and the mixture was heated to boiling. The ether was then decanted and the

residual slurry was extracted several more times with ether. All of the ether solutions were combined, and the ether was evaporated. The remaining solid was then recrystallized from ether. The melting point of the final product was 80–81 °C. The NMR spectrum indicated that two isomers were present (see ref 19). The yield, based on 5 g of [Ni-(Me$_2$pyo[14]eneN$_4$)](ClO$_4$)$_2$, was 2.0 g or 79%.

[Cr(Me$_2$pyo[14]eneN$_4$)Cl$_2$]Cl. A 1.0-g sample of Me$_2$pyo[14]eneN$_4$ ligand was placed in a 100-mL round-bottom flask and 50 mL of DMF was added, together with 2 g of Cr(THF)$_3$Cl$_3$. This mixture was refluxed for 30 min. The solution was then cooled in an ice bath. A purple solid formed after cooling. The mixture was suction filtered. The yield was 0.65 g or 46%.

[Cr(Me$_2$pyo[14]eneN$_4$)(CF$_3$SO$_3$)$_2$]CF$_3$SO$_3$. A 0.76-g sample of [Cr-(Me$_2$pyo[14]eneN$_4$)Cl$_2$]Cl was placed in 6 mL of concentrated HCF$_3$SO$_3$ (3 M technical grade under a stream of N$_2$). The HCl immediately bubbled off. The solution was warmed to remove all of the HCl. The solution was cooled, and 20 mL of ether was added slowly to induce precipitation. The mixture was suction filtered, and the solid was washed with ether. The complex was air-dried. The yield was 1.3 g or 95%.

[*cis*-Cr(Me$_2$pyo[14]eneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$. A 2.0-g sample of [Cr-(Me$_2$pyo[14]eneN$_4$)(CF$_3$SO$_3$)$_2$]CF$_3$SO$_3$ was placed in a flask, and 25 mL of liquid ammonia was added. The ammonia was allowed to boil off, and this procedure was repeated once more. The remaining brownish orange solid was dissolved in a few drops of 1 M HCF$_3$SO$_3$ and the orange solid was salted out by the addition of anhydrous NaClO$_4$. The solids isolated from this procedure were generally found to be mixtures of orange and yellow crystals. These products could be separated by successive recrystallization and were found to have very different properties. We suspect the orange compound was an aquoammine, but it has not yet been well characterized. The yellow compound was the desired diammine. The solids isolated were washed with ethanol and then ether. The total yield was 1.2 g or 99%.

Commercial [Rh(NH$_3$)$_5$Cl]Cl$_2$ (Johnson Matthey) was purified by recrystallization. Doped solids of [Cr(NH$_3$)$_5$Cl]Cl$_2$/[Rh(NH$_3$)$_5$Cl]Cl$_2$ and [Cr(NH$_3$)$_5$Cl]Cl$_2$/[Ru(NH$_3$)$_5$Cl]Cl$_2$ were prepared by dissolving the respective chloropentaammine complexes, in the desired stoichiometric ratios, in 0.1 M HCl. The desired doped solid was then precipitated by the addition of concentrated HCl. Trifluoromethanesulfonic acid was purified by vacuum distillation of the technical grade material. Sodium trifluoromethanesulfonate was prepared by the reaction of trifluoromethanesulfonic acid with anhydrous sodium carbonate. The sodium trifluoromethanesulfonate was purified by recrystallization from ethanol and water and dried by heating in a vacuum oven.

Elemental analyses were obtained from Midwest Microlabs, Indianapolis, IN, and are summarized in Table I. The analysis of chromium was performed by the standard chromium(III) oxidation to chromium-(VI) with hydrogen peroxide in sodium hydroxide. The concentration of chromium(VI) was determined by monitoring the absorption maximum at 374 nm and a molar absorptivity of 4815 cm^{-1} M^{-1}.[23] The experimental percentage of chromium(III) agreed with the theoretical percentage for all the compounds used. The molecular weights were determined from the oxidation performed above. These experimental molecular weights were in accord with expectation.

B. Instrumental Studies. Visible spectra were determined by using a Cary 14 spectrophotometer, and infrared spectra of complexes (in KBr pellets) were determined by using either a Perkin-Elmer 283 B infrared spectrophotometer or a Nicolet 20 DX Fourier transform infrared spectrophotometer. pH was determined by using an Orion Research 801A digital ion analyzer and Radiometer GK 2321C combination electrode. The spectroscopic observations are summarized in Table II. A General Electric QE300 nuclear magnetic resonance spectrometer was used to obtain NMR spectra.

The electronic absorption spectra of the spin-allowed transitions are summarized in Table II. The maximum ligand field absorptions for this series of macrocyclic amine complexes have energies and intensities similar to other, previously reported chromium(III) complexes.

(20) This complex was synthesized by means of a procedure provided by Professor G. R. Brubaker. Anhydrous CrCl$_3$ has also been successfully used to prepare the Cr^{III}(MCL) complexes.

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Table II. Electronic Absorption Spectral Data for the Complexes

complex[a]	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
[*trans*-Cr([14]aneN$_4$)Br$_2$]Br[b]	609 (43), 420 (79),[c] 362 (87)
[*trans*-Cr([15]aneN$_4$)Cl$_2$]ClO$_4$	591 (54), 464 (84), 417 (89.5)
[Cr([14]aneN$_3$S)Cl$_2$]Cl	548 (202), 414 (166)
[*trans*-Cr([14]aneN$_4$)(NH$_3$)Cl](ClO$_4$)$_2$	507, 410, 357
[*trans*-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(NH$_3$)$_2$]Br$_3$	436 (46), 345 (57)
[Cr([14]aneN$_3$S)(NH$_3$)$_2$](PF$_6$)$_3$	486 (224), 359 (141)
[*cis*-Cr(Me$_2$pyo[14]eneN$_4$)(NH$_3$)$_2$](PF$_6$)$_3$	468 (48), 352 (39)
[Ni(Me$_2$pyo[14]eneN$_4$)](ClO$_4$)$_2$	462 (74)[d]

[a] All complexes are in aqueous solution unless noted. All values are from this work unless noted. [b] In 9 M HBr. [c] Very broad shoulder centered at $\cong$420 nm. [d] In acetone.

C. Photophysical Techniques. Photophysical data of complexes above 150 K were determined in 1-cm path length rectangular curvettes made from nonfluorescent quartz. Samples were thermostated at temperatures above 250 K in a Photochemical Research Associates cell housing by means of a Polyscience KR 60A refrigerator and a Model 80 heater–circulator. For temperatures between 150 and 250 K a Dewar system was used in which the refrigerant was gaseous nitrogen that had been bubbled through liquid nitrogen. Temperature could be varied in this way by changing the nitrogen flow rate. Measurements at 77 K were performed by immersing a 2-mm fluorescence cell in liquid nitrogen contained in a quartz EPR Dewar.

Temperatures were monitored by using an Omega 5900 digital thermometer or an Omega type E thermocouple thermometer, Model 650, with sensors in the cell housing.

Details of the luminescence system can be found elsewhere.[18,24] Samples were excited with monochromatic radiation from a Molectron UV-1000 nitrogen laser-pumped DL-14 tunable dye laser. Lifetimes were determined by using a RCA 980 photomultiplier interfaced to a Gould Biomation 4500 digital oscilloscope. Time constants were determined by two different methods: (1) by least-square fits of the digital data using a Zenith ZW-158-43 computer with software developed by On-Line-Instrument Systems (OLIS), Jefferson, GA; (2) by taking the time required for the decay of $1/e$ of the initial intensity of either 64 or 256 averaged decays. Spectral regions for lifetime determinations were isolated with a Jobin-Yvon J-100 spectrometer. A Princeton Applied Research OMA-1 with SIT vidicon detector was used to obtain emission spectra. Luminescence spectra were wavelength calibrated by the superposition of resonance radiation from a Philips Ne arc lamp. This lamp was also used to calibrate the relative intensity response across the vidicon detector. Lifetimes and emission spectra were mainly measured in the mixed-solvent system DMSO/H$_2$O (1:1, v/v); sometimes 0.1 M acid was used in the place of water (details in notes to Table IV).

Results

A. Stereochemistry of the Macrocyclic Ligand Complexes. Several new complexes have been synthesized in the course of this study. The stereochemical proclivities of the [14]aneN$_4$, [15]-aneN$_4$, *ms*-(5,12)-Me$_6$[14]aneN$_4$, and *rac*-(5,12)-Me$_6$[14]aneN$_4$ ligands are sufficiently well established that it is reasonably clear whether the isolated complexes have the cis or the trans geometries. This is not the case with complexes containing the [14]aneN$_3$S and Me$_2$pyo[14]eneN$_4$ ligands. We have found no simple criteria on which to base the geometrical assignments of these complexes.

The spectroscopic observations on the Cr^{III}([14]aneN$_3$S)X$_2$ complexes were a little surprising since even for the Cr(III) complexes, the bound thioether appears to result in relatively large d-orbital splittings. Thus the absorption and emission spectra (Tables II and III and Figures 2 and 3) of Cr([14]aneN$_3$S)-(NH$_3$)$_2$$^{3+}$ and the Cr(Me$_2$pyo[14]eneN$_4$(NH$_3$)$_2$$^{3+}$ complexes are remarkably similar. The yellow Cr(Me$_2$pyo[14]eneN$_4$)(NH$_3$)$_2$$^{3+}$ complex has been shown by X-ray crystallography to be a *cis*-diammine.[25] This is the analog of the cis isomers found for the analogous cobalt(III) complexes by Ochiai and Busch.[26]
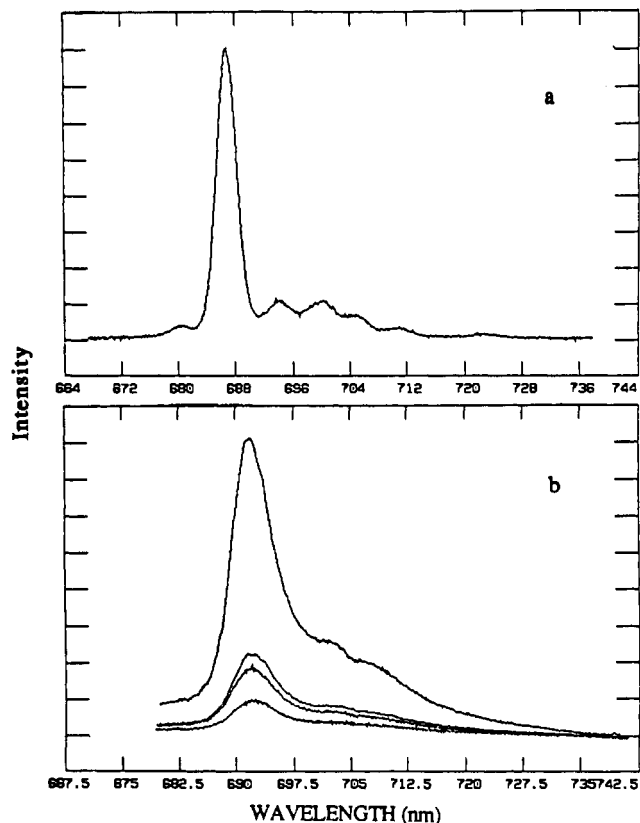

Figure 2. Emisson spectra of *trans*-Cr([14]aneN$_4$)(NH$_3$)Cl^{2+} (a) at 77 K in DMSO/H$_2$O glass and Cr([14]aneN$_3$S)(NH$_3$)$_2$$^{3+}$ (b) at 236, 228, 221, and 198 K (from low to high intensity) in DMSO/H$_2$O solution.

Figure 3. Contrasting emission spectra of *trans*-Cr(*ms*-(5,12)-Me$_6$-[14]andN$_4$)(NH$_3$)$_2$$^{3+}$ (a) and Cr(Me$_2$pyo[14]eneN$_4$)(NH$_3$)$_2$$^{3+}$ (b) at 77 K in DMSO/1 M HCF$_3$SO$_3$ (1:1, v/v) and DMSO/0.1 M HCl (1:1, v/v), respectively.

B. Emission Spectra. Emission spectra of several of the complexes are presented in Figures 2–6. The *trans*-Cr^{III}(N$_4$)X$_2$

(24) Ryu, C. K.; Endicott, J. F. *Inorg. Chem.* **1988**, *27*, 2203.
(25) Heeg, M. J.; Perkovic, M. W.; Endicott, J. F. Work in progress.
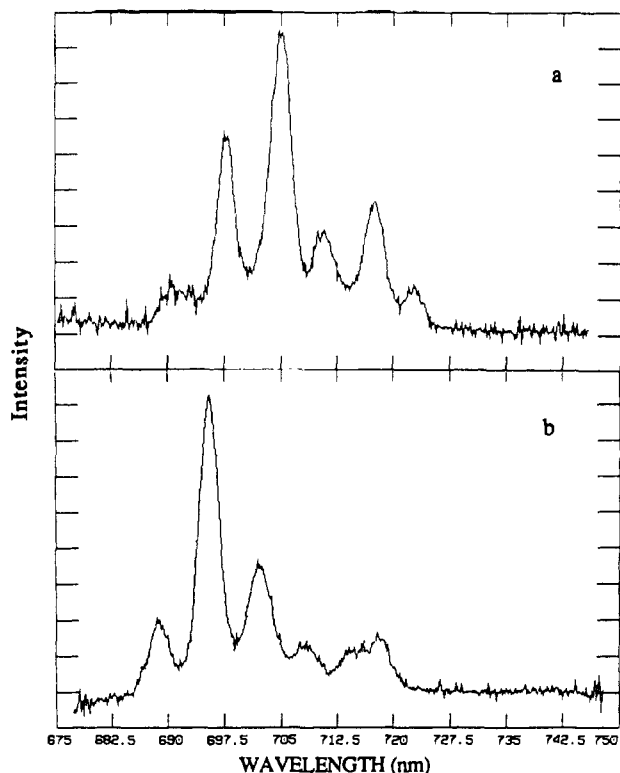(26) Ochiai, E.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 1474.

Figure 4. Emission spectra at 77 K, in DMSO/0.1 M HCl (1:1, v/v), of *trans*-Cr([14]aneN$_4$)Cl$_2^+$ (a) and *trans*-Cr([15]aneN$_4$)Cl$_2^+$(b).

complexes typically exhibit relatively intense vibronic side bands, while the emission spectra of noncentrosymmetric complexes tend to be dominated by a very intense 0–0 line. The *cis*-Cr^{III}(N$_4$)X$_2$ complexes have relatively large band widths. The emission spectrum of Cr(Me$_2$pyo[14]aneN$_4$)(NH$_3$)$_2^{3+}$ is characteristic of the low-symmetry complexes and differs markedly from the typical trans complex spectrum (Figure 3). Part of this contrast probably arises from the contrasting σ-donor and π-acceptor properties of the am(m)ine and imine nitrogens. The emission band widths of the Cr^{III}([14]aneN$_3$S)X$_2$ complexes are relatively broad (Figures 2 and 4), somewhat more like those of the *cis*- than of the *trans*-Cr^{III}(N$_4$)X$_2$ complexes. However, the relatively high energy of the Cr^{III}([14]aneN$_3$S)X$_2$(^{4}A$_2$ $\rightarrow$ ^{4}T$_2$) absorption indicates that the thioether functions as a relatively strong field ligand. Yet the electronic origins of the emissions are at relatively low energies. These contrasting spectroscopic shifts deomonstrate an appreciable t$_{2g}$(Cr^{III}) $\rightarrow$ pπ(S) back-bonding interaction.

C. Excited-State Lifetime Behavior. The ^{2}E excited states of all the complexes reported here are strongly temperature dependent. At sufficiently low temperatures the lifetimes approach a limit that is matrix and temperature insensitive (τ_{77}). The high-temperature, thermally activated decays tend to be matrix dependent. For simplicity of discussion it is convenient to represent the ^{2}E decay rates by

$$k_{obsd} = k^\circ + k(T) \qquad (1)$$

where the limiting, low temperature decay rate constants are

$$k^\circ = (\tau_{77})^{-1} = k_r + k^\circ_{nr}$$

and k_r is the radiative rate constant and k°_{nr} the limiting nonradiative rate constant. For our purposes it is sufficient to represent the thermally activated decay in an Arrhenius form

$$k(T) = A \exp(-E_a/RT) \qquad (2)$$

This behavior is illustrated in Figure 7 for the Cr^{III}(NH$_3$)$_5$X complexes. In order to further simplify the presentation and discussion of our observations, we define a "transition temperature", T_{tr}, as the temperature at which linear fits of the strongly temperature dependent, $k(T)$, and nearly temperature independent, $k_r + k^\circ_{nr}$, decay rates intersect in an Arrhenius plot.
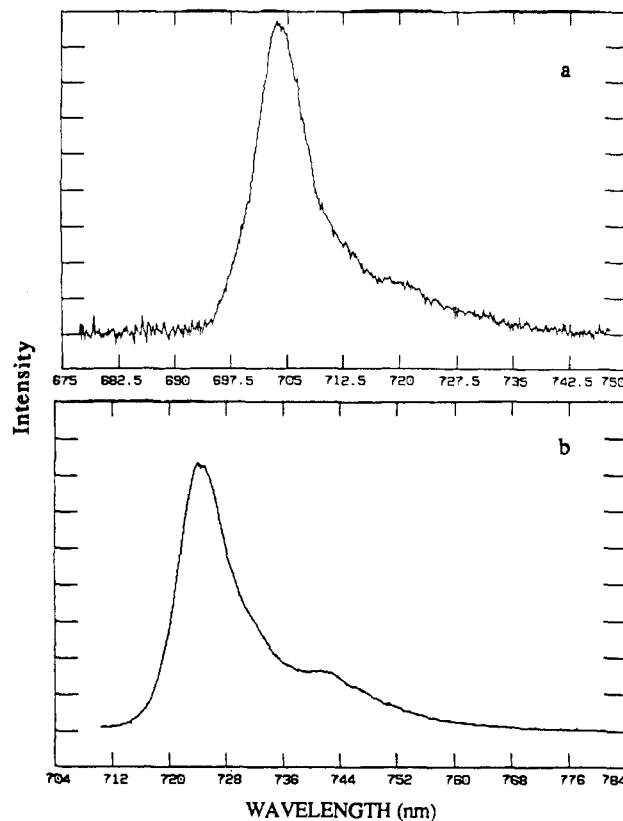

Figure 5. Comparison of the 77 K emission spectra of *cis*-Cr([14]-aneN$_4$)Cl$_2^+$ (a) and Cr([14]aneN$_3$S)Cl$_2^+$ (b) in DMSO/0.1 M HCl (1:1, v/v).

Values of T_{tr} vary with the complex (e.g., see Figure 7) and with the matrix (e.g., see Figure 8). The liquid–glass transition is near 190 K for the DMSO/H$_2$O mixtures. There is no correlation between T_{tr} and the liquid–glass transition region in DMSO/H$_2$O (e.g., see Table IV and Figure 7). However, Arrhenius plots for some of the systems with thermally activated decays in the glassy regime show slight inflections, and a few may even change slope as the medium becomes more fluid. Much of the variation in room-temperature lifetimes of the Cr(III) complexes originates from variations in the temperature-independent contributions to $k(T)$ (i.e., in T_{tr} or the Arrhenius "A" factor; see Table IV).

D. Cr(NH$_3$)$_5$Cl^{2+} Doped into [M(NH$_3$)$_5$Cl]Cl$_2$ Solids. Dilute solutions of Cr(NH$_3$)$_5$Cl^{2+} in [M(NH$_3$)$_5$Cl]Cl$_2$ crystalline solids (M = Ru or Rh) resulted in dramatic decreases in emission band widths (Figure 6) and, for the [Rh(NH$_3$)$_5$Cl]Cl$_2$/[Cr(NH$_3$)$_5$Cl]Cl$_2$ solid, a spectacular increase in the ambient lifetime (Figure 8). The [Ru(NH$_3$)$_5$Cl]Cl$_2$/[Cr(NH$_3$)$_2$Cl]Cl$_2$ solid exhibited intermediate lifetime behavior, possibly the result of impurity quenching or of mixing of the Cr(d–d) and Ru(charge-transfer) states. The Cr(III) emission bands broadened as the temperatures of the doped solids were raised, and the "hot" band increased in relative intensity as expected, but no new emission was detected that could be attributed to delayed fluorescence.

Discussion

In this study we have systematically investigated the photophysical behavior of several classes of Cr(III) complexes. A major purpose of this research has been to explore the stereochemical effects of macrocyclic ligands on the ^{2}E relaxation pathway(s). In order to develop the necessary perspectives, we have prepared a variety of complexes with macrocyclic ligands, varying the ligating atoms, the substituents on the rings, the coordination geometry, and the nonmacrocyclic ligands. As noted in the preliminary reports of this work,[2g,h,5b] the stereochemical influence of the macrocyclic ligand can be dramatically altered when the nonmacrocyclic ligands are changed. Partly to gain further insight into the influence of the monodentate ligands and partly to be able to develop comparison with stereochemically unconstrained
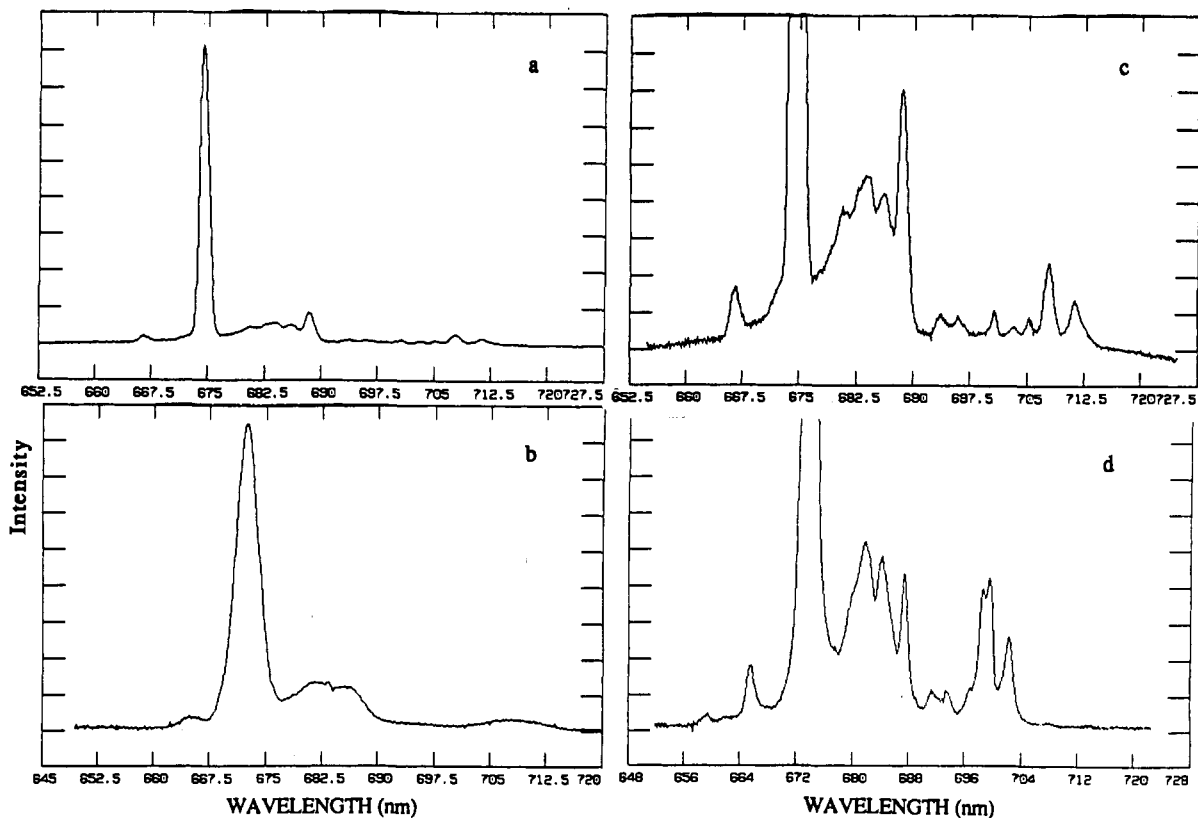
Figure 6. Emission spectra at 77 K of $Cr(NH_3)_5Cl^{2+}$ doped into $[M(NH_3)_5Cl]Cl_2$ crystalline matrices (a, c, and d) compared to the $Cr(NH_3)_5Cl^{2+}$ emission (b) obtained in DMSO/0.1 M HCl (1:1, v/v) glass. For spectrum a, M = Ru and Ru:Cr = 30.1; for spectrum c the metals are the same as for spectrum a but greater amplification was used; for spectrum d, M = Rh and $Cr(ND_3)_5Cl^{2+}$ was the dopant with Rh:Cr = 30:1.

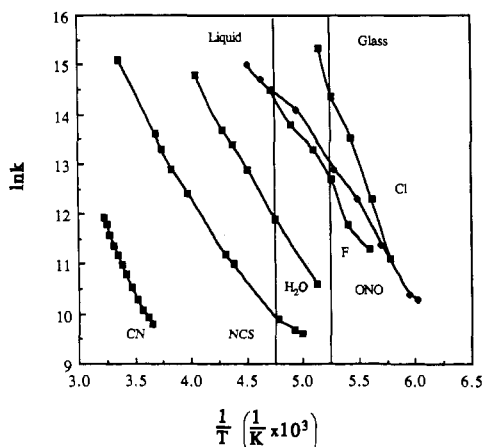**Figure 7.** Temperature dependence of the $(^2E)Cr(NH_3)_5X^{2+}$ relaxation rates in DMSO/H_2O (1:1, v/v). For all these complexes, the limiting low-temperature relaxation rate constants fall into the range ln $k° = 8.5 \pm 0.5$ (see Table IV). The pentaammine complexes, from left to right, have X = CN^-, NCS^-, H_2O, F^-, ONO^-, and Cl^-.

complexes, we have also examined the photophysical behavior of several acidopentaammine complexes.

A. Some Characteristics of the Thermally Activated Regime Based on the Behavior of $Cr^{III}(NH_3)_5X$ Complexes. Many experiments have demonstrated that the matrix dependence of $k(T)$.[2,5a] However the most dramatic demonstration of this matrix-dependent behavior is the contrasting thermally activated $(^2E)Cr(NH_3)_5Cl^{2+}$ in DMSO/0.1 M HCl glass and in the doped [Rh(NH_3)_5Cl]Cl_2 solid (figure 8). Clearly $k(T)$ is a property of the complex *and* its environment. In such a situation it may be more appropriate to discuss the relaxation mechanism in terms of free energy, rather than energy comparisons. In this vein, there is a rough correlation between ln $[k(T)]$, for the pentammines, and $10Dq = E(^4T_{2max})$ or $\Delta E_{DQ} = E(^4T_2°) - E(^2E°)$ as indicated in Figure 9. The tendency of $k(T)$ to decrease as ΔE_{DQ} (or $10Dq$)

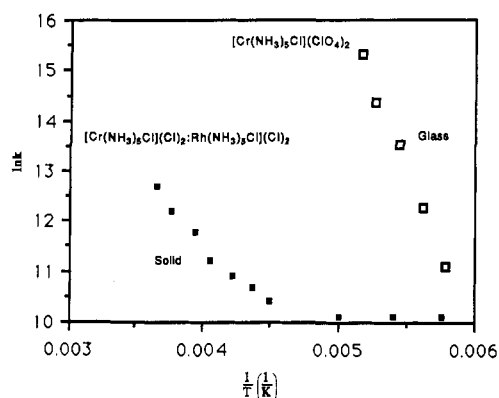**Figure 8.** Contrasting temperature-dependent relaxation rates for (^2E)-$Cr(NH_3)_5Cl^{2+}$ in DMSO/0.1 M HCl glass (□) and for $(^2E)Cr$-$(NH_3)_5Cl^{2+}$ doped into $[Rh(NH_3)_5Cl]Cl_2$ solid (■).

does is observed for limited classes of chromium complexes in a given medium.[28,27] However, the scatter of data points in such "correlations" is always appreciable. Despite the limitations, such correlations do raise interesting issues. There are at least three mechanisms that would lead to decreases of $k(T)$ with increasing ΔE_{DQ} or $10Dq$.

The first is thermal population of the lowest energy quartet excited state (back intersystem crossing or BISC). This mechanism would lead to rate expressions of the form $k(T) = k^c \exp(-\Delta E_{DQ}/RT)$, where k^c is an "intrinsic" (or barrierless) intersystem crossing rate. There are at least three problems with such a mechanism: (a) this is an energy correlation requiring that ΔE_{DQ} and E_a correlate, which they do not; (b) there is no obvious way to accommodate the solvent dependence of $k(T)$; (c) the value, inferred from such correlations, of $k^c \cong 2 \times 10^{15}$ s^{-1} seems too large for such a mechanism.

(27) Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* **1979**, *33*, 53.

Table III. Summary of Spectroscopic Data

complex	$E(^4T_2^{max})$, cm^{-1}	$E(^2E)$, cm^{-1}	$E(^4T_2^{max}-{}^2E)$, cm^{-1}	$E(^4T_2^0)^a$ 5% rule, cm^{-1}	$E(^4T_2^{0-2}E)$, cm^{-1}
trans-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)Br$_2^+$	16 700[b]	14 350	2350	15 300	950
Cr(NH$_3$)$_5$Cl^{2+}	19 250[c]	15 110[d]	4140	17 500	2390
cis-Cr([14]aneN$_4$)Cl$_2^+$	18 900[e]	14 170[f]	4730	16 600	2430
trans-Cr([14]aneN$_4$)Cl$_2^+$	17 500[e]	14 330[f]	3170	16 100	1770
trans-Cr([15]aneN$_4$)Cl$_2^+$	16 900	14 370	2170	15 400	1030
Cr[(14]aneN$_3$S)Cl$_2^+$	18 200	13 810	4390	15 400	1590
trans-Cr([14]aneN$_4$)(NH$_3$)Cl^{2+}	19 700	14 560	5140	17 300	2740
Cr[(14]aneN$_3$S)(NH$_3$)$_2$Cl^{3+}	20 600	14 450	6150	18 300	3850
Cr(NH$_3$)$_6^{3+}$	21 640[g]	15 230[h]	6410	19 600	4370
[*trans*-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(NH$_3$)$_2^{3+}$	22 900	14 950	7950	19 500	4550
cis-Cr([14]aneN$_4$)(NH$_3$)$_2^{3+}$	21 400[i]	15 000[i]	6400		
trans-Cr([14]aneN$_4$)(NH$_3$)$_2^{3+}$	22 500[i]	14 930[i]	7570	20 000	5070
cis-Cr(Me$_2$pyo[14]eneN$_4$)(NH$_3$)$_2^{3+}$[j]	21 150	14 376		19 680	5304
Cr([14]aneN$_4$)(en)$^{3+}$	21 500[g]	14 800[g]	6700	19 800	5000
Cr(sen)$^{3+}$	22 200[f]	14 810[f]	7390	20 200	5390
Cr(NH$_3$)$_5$CN^{2+}	22 170[k,l]	14 660[m]	7510	20 100	5440
trans-Cr([14]aneN$_4$)(CN)$_2^+$	24 160[n]	13 950	10210	21 600	7650
trans-Cr([15]aneN$_4$)(CN)$_2^+$	22 100	13 900	8200	20 300	6400
trans-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(CN)$_2^+$	23 470[f,m]	14 260[f,m]	9210	21 300	7000
cis-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(CN)$_2^+$	21 640[f,m]	13 790[f,m]	7850	18 300	4510
Cr(NH$_3$)$_5$NCS^{2+}	20 500[c,o]	14 530	5970	18 600	4070
cis-Cr([14]aneN$_4$)NCS$_2^+$	20 600[e]	13 690	6910		
trans-Cr([14]aneN$_4$)NCS$_2^+$	20 700[p]	14 600	6640		
trans-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)(NCS)$_2^+$	20 000[b]	14 280	5720		
trans-Cr(*rac*-(5,12)-Me$_6$[14]aneN$_4$)(NCS)$_2^+$	19 000[b]	13 760	5240		
Cr(NH$_3$)$_5$H$_2$O^{3+}	20 800[c,q]	15 130[d]	5670	18 000	2870
Cr(NH$_3$)$_5$ONO^{2+}	20 730[c,q]	14 910	5820	18 200	3290
cis-Cr([14]aneN$_4$)(H$_2$O)$_2^{3+}$	18 300[c]	15 000	3300		
trans-Cr([14]aneN$_4$)(H$_2$O)$_2^{3+}$	19 600[e]	14 830	4770	18 000	3170
cis-Cr([14]aneN$_4$)F$_2^+$	19 500[g]	14 600[g]	4900		
trans-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)F$_2^+$	19 200[g]	12 800	6400		
Cr(NH$_3$)$_5$F$_2^+$	20 000[c]	15 100	4900	17 600	2500

[a] Calculated from the procedure described in ref 2b. [b] Reference 18. [c] Reference 14. [d] Flint, C. D.; Mathews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1111. Schlafer, H. L.; Martin, M.; Gausman, H.; Schmidtke, H. H. *Z. Phys. Chem. (Munich)* **1971**, *76*, 61. [e] Reference 15. [f] Reference 2g. [g] Kane-Maguire, N. A. P.; Wallace, K. C.; Speece, D. G. *Inorg. Chem.* **1986**, *25*, 4650. [h] Flint, C. D.; Greenough, P. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 665. [i] Reference 6. [j] Reference 25. [k] Zinato, R.; Riccieri, P. *Inorg. Chem.* **1973**, *12*, 1651. [l] Riccierri, P.; Zinato, E. *Inorg. Chem.* **19808** *19*, 3279. [m] Reference 4. [n] Reference 17. [o] Tsuchida, R.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1948**, *13*, 471. [p] Reference 16. [q] Reference 13.
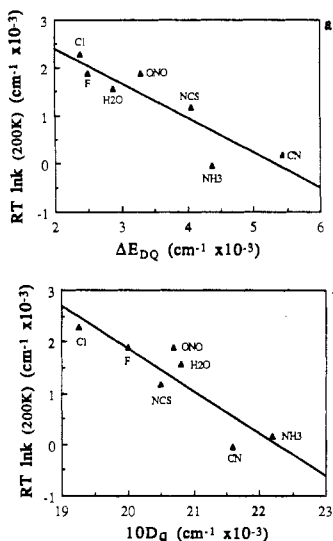

Figure 9. Approximate correlation of the (^{2}E)Cr^{III}(NH$_3$)$_5$X relaxation rates with estimates of $E(^4T_2^0) - E(^2E)$ (a) or d-orbital splitting (10Dq) (b).

The second is mixing of upper quartet ($^4T_2$) character into the electronic matrix elements for the $^2E \rightarrow {}^4A_2$ coupling in the transition state of the doublet state relaxation channel. The mixing would appear through a spin–orbit coupling mechanism, but only the coupling (and the perturbing energy gap) for the transition state of the reaction channel would be relevant. Since the ^2E and $^4A_2$ states are electronically orthogonal, very weakly coupled, and clearly nested near their potential energy minima, this mechanism would promote relaxation through distortion of the ^2E state along

a nuclear coordinate that enhances spin–orbit coupling to the $^4T_2$ state (e.g., an e_g vibrational mode). Since the spin–orbit coupling perturbation would not be strongly temperature dependent while the nuclear distortion would, this mechanism has many features that are qualitatively consistent with the observations. In its simplest form this mechanism cannot accommodate the solvent dependence of $k(T)$.

The third is relaxation of the (^{2}E)Cr(III) excited state to form a highly distorted (e.g., 7- or 5-coordinate) intermediate in its ground electronic configuration. In a simple classical surface crossing, the ^{2}E-intermediate energy gap would modify the activation energy for the relaxation channel. This energy gap would also result in a net driving force for the accompanying nuclear displacements.

A complete description of the relaxation behavior of any one of the (^{2}E)Cr(III) complexes could involve some contribution from all the mechanisms listed above, and it is unlikely that a single, unique pathway is common to all the complexes.

B. ^{2}E Excited-State Relaxation Behavior in Cr(III) Complexes with Macrocyclic Ligands. The Effect of "Heavy" Atoms. Kane-Maguire and co-workers made the very important observation that the *trans*-Cr([14]aneN$_4$)(CN)$_2^{+}$[3] and *trans*-Cr([14]aneN$_4$)(NH$_3$)$_2^{3+}$[6] complexes have exceptionally long ^{2}E lifetimes in fluid solutions under ambient conditions. In fact, the ambient-temperature lifetimes are either the same (for the dicyano complex) or only slightly smaller (for the diammine) than the 77 K lifetimes. Similar behavior has been found in other *trans*-Cr(N$_4$)(CN)$_2^+$ complexes[2g,h,4,5] where N$_4$ is a macrocyclic tetraamine. In contrast with this, the cis complexes with macrocyclic ligands have much shorter, temperature-dependent ^{2}E lifetimes in fluid solutions. This contrasting behavior has been postulated to be consistent with fewer stereochemical constraints in the cis complexes on the nuclear motions necessary for relaxation to form

Table IV. (^2E)Cr(III) Lifetimes and Their Temperature Dependences

complex[a]	τ_{298}, μs	τ_{77}, μs	T_{tr}, K	E_a, kcal/mol	A, s^{-1}
trans-Cr(ms-(5,12)-Me$_6$[14]aneN$_4$)Br$_2$$^+$ [b]	$(20 \times 10^{-6})^c$	122	156	9.2	9×10^{16}
Cr(NH$_3$)$_5$Cl^{2+} [d]	$(2 \times 10^{-6})^c$	41^f	170^f	13.0^f	2×10^{21} ^{f}
[Cr(NH$_3$)$_5$Cl]Cl$_2$/[Rh(NH$_3$)$_5$Cl]Cl$_2$ [g]	3.12^h	43.4^f	225^f	6.9^f	1×10^{11}
cis-Cr([14]aneN$_4$)Cl$_2$$^+$ [d]	$(10 \times 10^3)^c$	52^f	164^f	6.5^f	1×10^{13} ^{f}
trans-Cr([14]aneN$_4$)Cl$_2$$^+$ [d]	$(8 \times 10^{-4})^c$	88^f	168^f	11.9^f	4×10^{19} ^{f}
trans-Cr([15]aneN$_4$)Cl$_2$$^+$ [d]	$(1 \times 10^{-7})^c$	68	170	14.3	3×10^{22}
Cr([14]aneN$_3$S)Cl$_2$$^+$ [d]	$(2 \times 10^{-7})^c$	66	171	14.7	3×10^{23}
trans-Cr([14]aneN$_4$)(NH$_3$)Cl^{2+} [d]	$(31 \times 10^{-3})^c$	104	192	8.6	7×10^{13}
Cr([14]aneN$_3$S)(NH$_3$)$_2$$^{3+}$	0.27	116	215	8.4	6×10^{12}
Cr(NH$_3$)$_6$$^{3+}$ [i]	2.2	78^{f,i,j}	244	11.2	1×10^{12}
trans-Cr(ms-(5,12)-Me$_6$[14]aneN$_4$)(NH$_3$)$_2$$^{3+}$	31.2	186	264	7.5	8×10^9
cis-Cr([14]aneN$_4$)(NH$_3$)$_2$$^{3+}$ [k]	1.0^l	116	235	10.3	4×10^{13}
trans-Cr([14]aneN$_4$)(NH$_3$)$_2$$^{3+}$ [k]	136^l	180^m	308	16.0	6×10^{15}
cis-Cr(Me$_2$pyo[14]eneN$_4$)(NH$_3$)$_2$$^{3+}$ [n]	1.42	101			
Cr([14]aneN$_4$)(en)$^{3+}$	3.0^o	136^p	243^{f,o}	10.5^{f,o}	2×10^{13} ^{f,o}
Cr(sen)$^{3+}$	$(24 \times 10^{-3})^c$	96	202^f	10.0^f	9×10^{14} ^{f}
Cr(NH$_3$)$_5$CN^{2+} [f]	14	79	290	12.4	9×10^{13}
Cr(NH$_3$)$_5$NCS^{2+}	0.27	90	217	8.1	3×10^{12}
cis-Cr([14]aneN$_4$)(NCS)$_2$$^+$	4.4	96	242	7.5	7×10^{10}
trans-Cr([14]aneN$_4$)(NCS)$_2$$^+$		184			
Cr(NH$_3$)$_5$H$_2$O^{3+}	$(40 \times 10^{-3})^c$	56.8	189	7.7	2×10^{13}
Cr(NH$_3$)$_5$ONO^{2+}	$(6 \times 10^{-3})^c$	62.0	160	6.4	8×10^{12}
cis-Cr[(14]aneN$_4$)(H$_2$O)$_2$$^{3+}$		92			
trans-Cr([14]aneN$_4$)(H$_2$O)$_2$$^{3+}$ [q]	$(50 \times 10^{-3})^c$	106	202	7.6	3×10^{13}
cis-Cr([14]aneN$_4$)F$_2$$^+$		80^{r,s}			
trans-Cr(ms-(5,12)-Me$_6$[14]aneN$_4$)F$_2$$^+$	30^{l,r}	49^{r,s}			
Cr(NH$_3$)$_5$F^{2+}	$(2 \times 10^{-3})^c$	50.0	167	7.2	6×10^{13}

^{a} Measured in DMSO/H$_2$O (1:1, v/v). ^{b} Measured in DMSO/1 M HBr (1:1, v/v). ^{c} Value extrapolated from thermally activated behavior at very low temperatures. Actual lifetime may be longer, see text. ^{d} Measured in DMSO/1 M HCl (1:1, v/v). ^{e} Forster, L. S.; Rund, J. V.; Fucalaro, A. F.; Lin, S. H. *J. Phys. Chem.* **1984**, *88*, 5017. Fucalaro, A. F.; Forster, L. S.; Rund, S.; Lin, S. H. *J. Phys. Chem.* **1983**, *87*, 1796. ^{f} Reference 2g. ^{g} 30:1, Rh/Cr doped solid. ^{h} T = 273 K; extrapolated τ_{298} = 1.0 μs. ^{i} Reference 5a. ^{j} Forster, L. S.; Rund, J. V.; Castelli, F.; Adams, P. *J. Phys. Chem.* **1982**, *86*, 2395. Flint, C. D.; Mathews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 419. ^{k} Reference 6. ^{l} Measured in H$_2$O at 293 K. ^{m} Measured in DMSO. ^{n} Reference 25. ^{o} Reference 4. ^{p} Kuhn, K.; Wasgestian, H. F.; Kupka, H. *J. Phys. Chem.* **1981**, *85*, 665. ^{q} Reference 3. ^{r} Kane-Maguire, N. A. P.; Wallace, K. C.; Speece, D. G. *Inorg. Chem.* **1986**, *25*, 4650. ^{s} Measured in ethylene glycol/H$_2$O (2:1, v/v).

an intermediate chemical species.[2g,h] Waltz and co-workers have presented evidence for solvent quenching of cis-(^2E)Cr([14]-aneN$_4$)(NH$_3$)$_2$$^{3+}$ to form a 7-coordinate intermediate.[8] Interestingly, the X-ray crystal structure of [cis-Cr(rac-(5,12)-Me$_6$-[14]aneN$_4$)(CN)$_2$]Cl shows the chloride to be situated opposite the cyanides (along a C_2 axis), "positioned" as if for nucleophilic substitution on Cr through the "pocket" formed by the folded macrocycle.[4,28] One might be inclined to generalize these few observations into some allegedly general description of "the mechanism" for quenching of the (^2E)Cr(III) excited states under ambient conditions. The work reported here indicates that such generalizations would be inappropriate.

Many years ago Kutal and Adamson[10] invoked a stereochemical argument to account for the smaller photochemical product yields from irradiations of trans-Cr([14]aneN$_4$)Cl$_2$$^+$ than found in similar studies of chloroam(m)ine complexes containing no macrocyclic ligands. This might suggest similar stereochemical influences of the macrocyclic ligand on the ^2E excited state for all trans-Cr^{III}(N$_4$)X$_2$ complexes. In fact the heavier halo complexes (X = Cl, Br) all contrast markedly from their ammine and cyano analogues in photophysical behavior: (a) the ^2E excited-state lifetimes become temperature dependent in the low-temperature, glassy regime; (b) there is no marked contrast in lifetime behavior of the cis and trans isomers of the complexes examined. Even the decay of trans-(^2E)Cr([14]aneN$_4$)(NH$_3$)Cl^{2+} becomes thermally activated in the glassy (DMSO/0.1 M HCl) regime. It is difficult to avoid the conclusion that the relaxation channel that is so sensitive to macrocyclic ligand stereochemistry in the cyano and ammine complexes is overwhelmed by a different, more facile relaxation channel available to most of the chloro and bromo complexes. Zinato and co-workers[29] have very recently reported an interesting variation on the points raised above by demonstrating that the very low-temperature, thermally activated re-

laxation channel characteristic of most chloro complexes is apparently repressed in trans-Cr(NH$_3$)$_4$(CN)Cl$^+$.

If there is a different relaxation channel operating among the chloro and bromo complexes, the most likely origin of such a facile relaxation pathway would be either (1) enhanced doublet–quartet mixing due to greater spin–orbit coupling or (2) efficient BISC to the relatively low-energy quartet levels. We have synthesized and examined the photophysical behavior of Cr([14]aneN$_3$S)-(NH$_3$)$_2$$^{3+}$ as a test of the spin–orbit coupling hypothesis. We do not know at this time whether we isolated the cis or the trans isomer of this complex; however, its photophysical behavior is much more similar to that of cis-Cr([14]aneN$_4$)(NH$_3$)$_2$$^{3+}$ than to any of the chloro complexes since the thermally activated decay is found only in fluid solution ($T_{tr} \approx 215$ K for the N$_3$S complex and ≈ 235 K for the N$_4$ complex). It seems unlikely that variations in spin–orbit coupling constants play a major role in determining the contrasts in behavior observed for chloro and ammine complexes. On the other hand, the vertical energy differences between the ^2E and $^4T_2$ excited states of the N$_3$S and N$_4$ diammines are comparable, so our observations do not preclude significant spin–orbit coupling contributions to $k(T)$.

In order to assess the BISC hypothesis, we have had to make estimates of the ^2E–quartet excited-state energy gap. To estimate $E(^4T_2{}^{00})$ we have used a procedure proposed by Fleischauer et al.[2b] This method appears to underestimate $E(^4T_2{}^{00})$;[2h,4,30] consequently, it is useful as an estimate of the smallest value possible for the $^4T_2$–^2E energy gap. The simplest BISC model involves thermal equilibrium (K_{DQ}) between the ^2E and the nearest quartet excited states and rapid reaction (k_Q) from the quartet state. Thus, the apparent activation energy, E_a(obsd), for $k(T) \cong K_{DQ}k_Q$ ($K_{DQ} \ll 1$) should contain a contribution from the doublet–quartet energy gap, ΔE_{DQ}; i.e.

$$E_a(\text{obsd}) \cong \Delta E_{DQ} + E_{a,Q}$$

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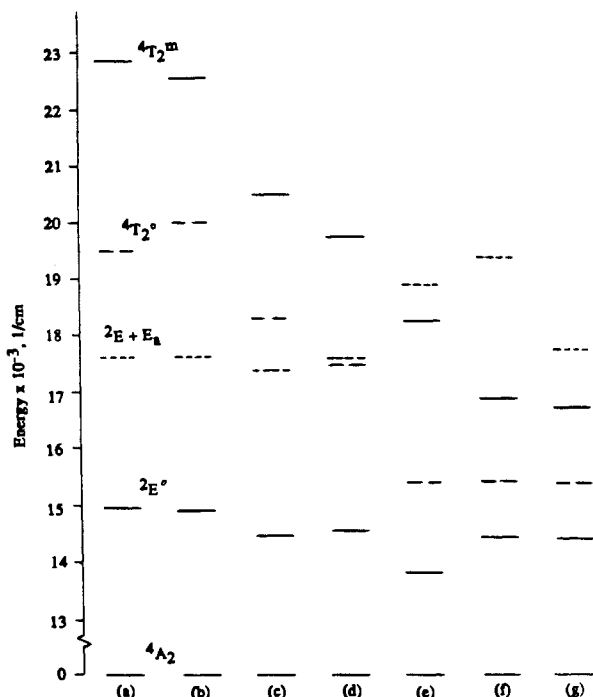(30) Ryu, C. K. Ph.D. Dissertation, Wayne State University, 1987.

Figure 10. Comparison of excited state and activation energies for several macrocyclic complexes of Cr(III): (a) *trans*-Cr(*ms*-(5,12)-Me$_6$[14]-aneN$_4$)(NH$_3$)$_2$$^{3+}$; (b) *trans*-Cr([14]aneN$_4$)(NH$_3$)$_2$$^{3+}$; (c) Cr([14]-aneN$_3$S)(NH$_3$)$_2$$^{3+}$; (d) *trans*-Cr([14]aneN$_4$)(NH$_3$)Cl^{2+}; (e) Cr([14]-aneN$_3$S)Cl$_2$$^+$; (f) *trans*-Cr([15]aneN$_4$)Cl$_2$$^+$; (g) *trans*-Cr(*ms*-(5,12)-Me$_6$[14]aneN$_4$)Br$_2$$^+$. Solid lines designate the 0–0 energy of ^{2}E excited state (lower) or the lowest energy quartet absorption maximums (upper); estimates of the quartet band origins are indicated with a dashed line (--); the sum of $E(^2$E$^0) + E_a$ is indicated with a dotted line (⋯) for each complex.

where $E_{a,Q}$ is the effective activation energy for quartet relaxation pathways that do not regenerate the doublet state. The BISC model is only possible, in this limit, if E_a(obsd) $\geq \Delta E_{DQ}$. Among the pentaammines this condition is met only for the haloam(m)ine complexes: E_a(obsd) $\gg \Delta E_{DQ}$(estd) for Cr(NH$_3$)$_5$Cl^{2+} and E_a-(obsd) $\cong \Delta E_{DQ}$(estd) for Cr(NH$_3$)$_5$F^{2+}. Clearly, BISC could be a contributing or dominant mechanism for Cr(NH$_3$)$_5$Cl^{2+}. Since ΔE_{DQ}(estd) is probably an underestimate for Cr(NH$_3$)$_5$F^{2+}, BISC may not be feasible for this complex.

It is again the chloro (and bromo) complexes, among those with macrocyclic ligands, for which E_a(obsd) $\gg \Delta E_{DQ}$(estd). This is graphically illustrated in Figure 10. Thus, the simplest explanation for the observation that the chloro complexes are not very sensitive to variations in macrocyclic ligand stereochemistry is that ΔE_{DQ} is small enough that the BISC pathway becomes the most facile relaxation channel in these complexes. This argument would require that ΔE_{DQ} is too large for the BISC pathway to be dominant in the relaxation of *trans*-(^{2}E)Cr(NH$_3$)$_4$(CN)Cl$^+$, and thus seems to be consistent with the recent report on this complex.[29]

If BISC is indeed an important relaxation pathway, thermally activated, or "delayed" fluorescence (^{4}T$_2$ → ^{4}A$_2$) should be observable in those systems where it dominates. We have examined the emission spectra of the [Rh(NH$_3$)$_5$Cl]Cl$_2$/[Cr(NH$_3$)$_5$Cl]-Cl$_2$-doped solid in the 77–250 K temperature range. We did not observe any features attributable to fluorescence in this temperature range. The fluorescence should have about 10^3 times the doublet (phosphorescence) emission rate, and we should have been able to detect a fluorescence with 1–10% of the intensity of the doublet phosphorescence. As a consequence, these observations imply that $\Delta E_{DQ} \geq 1.8 \times 10^3$ cm^{-1} for Cr(NH$_3$)$_5$Cl^{2+}, consistent with the above estimates.

The very simple BISC mechanism described above could imply that the ^{2}E lifetime becomes relatively weakly temperature dependent at high temperatures if the quartet excited state is a bound state; i.e., at sufficiently high temperature $K_{DQ} \sim 1$ and $\Delta E_{a(obsd)} \cong E_{a,Q}$. To our knowledge, there is one report of such a situation:

Cr(urea)$_6$$^{3+}$ has a 0.7 ns, approximately temperature-independent lifetime in the ambient-temperature region,[12] while its lifetime at 77 K is 150 μs.[31] This complex also exhibits a thermally promoted fluorescence.[12] In the simplest BISC model, a strongly temperature-dependent lifetime at low temperature and a nearly temperature-independent lifetime at high temperatures suggest the saturation of the doublet–quartet equilibrium; i.e.

$$[\tau(^2\text{E})]^{-1} \cong k_Q/(1 + K_{DQ}^{-1}) = k_Q/[1 + \exp(\Delta E_{DQ}/RT)]$$

Thus, the observations of Rojas and Magde[12] on Cr(urea)$_6$$^{3+}$ are most simply consistent with a bound quartet state that has an ambient-temperature rate of relaxation, by pathways not leading to the ^{2}E state, of $k_Q \cong 1.4 \times 10^7$ s^{-1}. Our observations indicate that similar behavior might be expected of most chloro and bromo complexes. However, it is possible that the quartet excited states of some of these complexes are not well-defined, bound states and that limiting rates might not always be observed. Of course, the accessibility of alternate relaxation channels would greatly complicate this analysis. Furthermore, k_Q would generally be expected to be temperature dependent, and $E_{a,Q}$ might vary appreciably from one complex to another.

C. Macrocyclic Ligand Effect and (^{2}E)Cr(III) Relaxation Pathways. While the thermal insensitivity of $\tau(^2$E) for the *trans*-(^{2}E)Cr^{III}(N$_4$)X$_2$ complexes (X = CN$^-$ or NH$_3$) cannot yet be explained in detail, there is little doubt that this effect is fundamentally stereochemical. Thus, it is clear that the relatively facile, thermally activated relaxation of the corresponding *cis*-(^{2}E)Cr^{III}(N$_4$)X$_2$ complexes indicates the availability of a relaxation pathway that is stereochemically blocked in the trans complexes. The stereochemistry of the macrocyclic ligands severely restricts the possible coupled nuclear motions. In terms of relaxation mechanisms along trajectories leading to chemical intermediates, there are two limiting possibilities for such complexes.

(1) Formation of a 5-Coordinate Species. This is an attractive pathway for *cis*-macrocyclic complexes, especially for those with Me$_6$[14]aneN$_4$ ligands, since the lower coordination number would allow the macrocycle to relax some of the internal repulsions by expanding the equatorial N–Cr–N angle (forming a quasi-trigonal-bipyramidal intermediate).

(2) Formation of a 7-Coordinate Intermediate. The work of Waltz and co-workers[8] suggests this as a likely possibility.

Some of the details of these possible pathways are being explored in further studies.[28] It is important to note that different kinds of ligands can impose different stereochemical constraints, quite likely promoting (^{2}E)Cr(III) relaxation along trajectories involving different kinds of intermediate structures. For example, and in contrast to the stereochemical effects observed in complexes with tetraaza macrocyclic ligands, some of the ligands derived from 1,4,7-triazacyclononane ([9]aneN$_3$ or TACN) form trigonally strained Cr(III) complexes that have some of the shortest lived ^{2}E excited states reported.[2g,2h,5b,18,32] The very facile, thermally activated relaxation of these complexes is likely to involve a trigonal distortion. Trigonal distortions mix the d-orbital wave functions[32] and could promote ^{2}E → intermediate surface crossings. Our studies of such systems will be reported in detail elsewhere.[33]

D. Some Consequences of Multiple Decay Channels. This study and the related work summarized above indicate that there may be several channels that could contribute to the thermally activated relaxation of (^{2}E)Cr(III), e.g., (1) formation of 7-coordinate intermediates in certain complexes with macrocyclic ligands, (2) trigonal distortions in certain stereochemically strained complexes, and (3) BISC. There are no doubt other possible relaxation channels. The channel that dominates is no doubt different in different classes of complexes, and there are undoubtedly some complexes in which two or more pathways contribute.

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One simple explanation of the extreme matrix dependence of $k(T)$ for $Cr(NH_3)_5Cl^{2+}$ is that more relaxation channels are available in the DMSO/0.1 M HCl glass than in the doped crystalline solid (alternatively, the BISC channel would have to involve a large solvent contribution). If only the BISC channel were available in the doped solid, our estimate of $\Delta E_{DQ} \geq 6.8$ kcal mol⁻¹ (or 2.4×10^3 cm⁻¹ as in Table III) suggests that, in the solid, $E_a(estd) \geq 6.8$ kcal mol⁻¹ + $E_{a,Q}$. This can be compared to $E_a(obsd) = 6.9$ kcal mol⁻¹.

If several (N_c) channels do contribute to (^2E)Cr(III) relaxation in solution, then

$$k(T) = \sum_{i=1}^{N_c} k_i(T) = \sum_{i=1}^{N_c} A_i \exp(-\Delta G_i^*/RT)$$

where the sum extends over all possible relaxation channels. In such an event, "average" values of $E_a(obsd)$ and $A(obsd)$ would be obtained from the data fits. If the temperature independent component of $k(T)$ is represented by an effective entropy of activation, ΔS^*_{eff} will be larger in the multiple channel situation than the average of the entropies of activation (ΔS_i^* for the individual channels: $\Delta S^*_{eff} > (\sum_{i=1}^{N_c} \Delta S_i^*)/N_c$). This effect could be one factor contributing to exceptionally large preexponential factors characteristic of the compounds with $T_{tr} < 200$ K.

We have long been concerned with the very large Arrhenius preexponential factors (10^{15}–10^{22} s⁻¹) of $k(T)$ found for many of these compounds.[2d,g,h] Somewhat smaller but still large values (10^{13}–10^{15} s⁻¹) are commonly found for many compounds in fluid solution. These preexponential factors do vary with the solvent matrix.[2d,g,h] The exceptionally large values, $A > 10^{18}$ s⁻¹ are nearly all obtained in glassy matrices, and they are very likely related to a distribution of solvation environments, each with a different fluidity, melting range, etc. In such a situation the inferred values of ΔS^*_{eff} must be large, partly for reasons described in the previous paragraph.

Summary and Conclusions

We have compared the photophysical behavior of several stereochemically constrained chromium(III)–macrocyclic ligand complexes to that of simpler ammine complexes. The results indicate that several relaxation mechanisms are important among these complexes. In particular, the relaxation channel, which is sensitive to macrocyclic ligand stereochemistry in ammine and cyano complexes, does not appear to dominate the ^2E excited-state relaxation of complexes containing the chloride or bromide ligands. Rather these halo complexes relax by means of a stereochemically insensitive pathway that may involve back intersystem crossing to populate the lowest energy quartet excited state.

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Ab Initio MO Study of CO₂ Insertion into a Cu(I)-H Bond. Semiquantitative Understanding of Changes in Geometry, Bonding, and Electron Distribution during the Reaction

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An ab initio MO study was carried out on CO_2 insertion into a Cu(I)-H bond of $CuH(PH_3)_n$ ($n = 2, 3$). $Cu(PH_3)_2(\eta^2\text{-}O_2CH)$ is predicted to be a final product in the reaction of $CuH(PH_3)_2$, while in the reaction of $CuH(PH_3)_3$, $Cu(PH_3)_3(\eta^1\text{-}OCOH)$ is predicted to be a final product. In both reaction systems, the CO_2 insertion is calculated to be significantly exothermic and its activation barrier is estimated to be rather small, which suggests the CO_2 insertion into the Cu(I)-H bond is facile. Around the transition state, the $CuH(PH_3)_2$ moiety is distorted little but the CO_2 moiety is somewhat distorted. The origin of the activation barrier is the destabilization due to the CO_2 distortion and the exchange repulsion between $CuH(PH_3)_2$ and CO_2. The destabilization arising from these factors is compensated by a strong charge-transfer interaction from $CuH(PH_3)_2$ to CO_2 and an electrostatic attraction between $Cu^{\delta+}$ and $O^{\delta-}$ of CO_2. This is the reason that the activation barrier is rather small. Through this theoretical study, we obtained a useful guideline to finding a metal complex that easily causes the CO_2 insertion.

Introduction

There has been much current interest in the interaction of CO₂ with transition-metal complexes, since formation of transition-metal complexes is one of the most powerful and universal ways of activating inert molecules.[1] Several transition-metal complexes capable of reacting with CO₂ have been known.[1] For instance, CO₂ easily coordinates with $IrCl(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$), by which electrophilic attack on the O atom is significantly accelerated.[2] Also, CO₂ inserts into an M–X bond (X = H⁻, CH_3^-, OR⁻) of metal complexes, such as Co(I),[3] Cu(I),[4,5]

Chart I
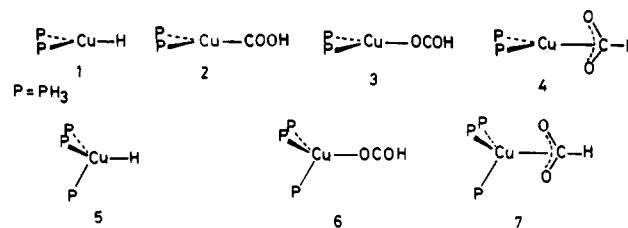
Rh(I),[6] Ru(II),[7] Ru(0),[8] Al(III),[9] Cr(0), Mo(0), and W(0),[10,11] Ni(II),[12] Mo(VI),[13] Zn(II),[14] and In(III)[15] complexes. However,

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