$Na[Cr(PDC)_2]\cdot1.5H_2O$ it is derived from the ^2E_g state. Certainly Dt is larger in the MIDA than in the PDC complex, since Dq for pyridine is much closer to that for carboxylate than is Dq for an imino nitrogen, and Dt is proportional to the difference between Dq(N) and Dq(O).

5. Summary. In interpreting the luminescence spectrum of $Na[Cr(PDC)_2]\cdot1.5H_2O$ we have also attempted to cast some light on the character of the vibrational modes involved. The validity of this approach depends on the assumption that vibrational modes involving the metal atom are most strongly coupled to the electronic transition. We have offered some evidence from infrared spectra that this is the case for the PDC complex. A structure determination and normal coordinate analysis would be required, however, to develop a more precise relationship.

Registry No. $Na[Cr(PDC)_2]$, 40354-84-5; $K[Cr(MIDA)_2]$, 29362-25-2.

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Mechanism of Photosubstitution in Chromium(III)-Acidoamine Complexes

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A detailed photochemical study of *cis*- and *trans*-$[Cr(cyclam)Cl_2]^+$ and *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$ (where cyclam is 1,4,8,11-tetraazacyclotetradecane and 2,3,2-tet is 1,4,8,11-tetraazaundecane) is reported. Phosphorescent emission maxima and lifetime data for the complexes are also included. The present results, in conjunction with those from earlier studies, are used to evaluate several alternative excited-state reaction mechanisms for chromium(III) acidoamines. The mechanism most consistent with the data involves a trans attack by an incoming solvent molecule; some degree of bond making in the rate-determining step is also indicated. For *trans*-$[CrN_4Cl_2]^+$ complexes (where $N_4 = 4NH_3$, 2en, 2,3,2-tet, or cyclam), a correlation between the quantum yields and thermal rate constants for chloride aquation is noted.

Introduction

The photochemistry of chromium(III)-acidoamine complexes on irradiation of the d-d or ligand field bands ($^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ in O_h symmetry, here designated $^4L_1$ and $^4L_2$, respectively) has generally been one of substitution by solvent.[1,2] Frequently, the predominant photochemical reaction does not occur thermally, indicating that the excited state involved possesses a chemistry distinct from that of the ground state. While considerable debate has centered on the identity of this reactive state, recent sensitization and luminescence quenching studies strongly suggest that the thermally equilibrated first quartet excited state, $^4L_1{}^0$, is the immediate precursor to photoreaction.[3,4]

The characteristics of quartet excited states which enhance their reactivity relative to the ground state have been discussed in detail elsewhere.[5-7] Briefly, irradiation in $^4L_1$ or $^4L_2$ promotes an electron from a nonbonding or weakly π-(anti)bonding t_{2g} orbital to a strongly σ-antibonding $e_g{}^*$ orbital.[8] This redistribution of electron density weakens the metal-ligand bonds (in some cases leading to considerable distortion from ground-state geometry)[9,10] and renders the complex susceptible to chemical reaction.

On a more detailed level, however, very little is known about the *mechanism* of the excited-state reaction; that is, the sequence of steps leading from $^4L_1{}^0$ to the final photoproduct. The importance of mechanistic considerations can be inferred from our recent study of *trans*-$[Cr(cyclam)Cl_2]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[11] Irradiation in the quartet region results in a quantum yield for chloride release $\sim10^3$ times smaller than found for the electronically and geometrically similar *trans*-$[Cr(en)_2Cl_2]^+$.[12] Further, the geometry of aquochloro product is predominantly trans for the former and cis for the latter compound. The imposition of the stereoretentive cyclam ring markedly affects the reactivity of the excited state, a result which would have been impossible to predict solely on the basis of ligand field strength considerations.

To gain further insight as to the nature of the excited-state reaction mechanism of chromium(III) acidoamines, we report here a detailed photochemical and photophysical study of *trans*- and *cis*-$[Cr(cyclam)Cl_2]^+$ and *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$ (2,3,2-tet = 1,4,8,11-tetraazaundecane). The 2,3,2-tet complex lies between those of cyclam and en in the degree of chelation or ring stricture about the metal atom and thus

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[1] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

[2] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[3] J. Martin and A. W. Adamson, *Theor. Chim. Acta*, **20**, 119 (1971).

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[5] A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

[6] G. B. Porter, S. Chen, H. L. Schlafer, and H. Gausmann, *Theor. Chim. Acta*, **20**, 81 (1971).

[7] J. I. Zink, *J. Amer. Chem. Soc.*, **94**, 8039 (1972).

[8] This description applies rigorously only to O_h complexes. For lower symmetries, specific axes in the molecule are preferentially labilized, depending upon the orbital splitting pattern (*cf.* ref 7).

[9] G. B. Porter and H. L. Schlafer, *Z. Phys. Chem.* (*Frankfurt am Main*), **37**, 109 (1963).

[10] S. Chen and G. B. Porter, *J. Amer. Chem. Soc.*, **92**, 2189 (1970).

[11] C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 5581 (1971).

[12] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1971).

serves as an important link between the photochemistry of the latter compounds.

Experimental Section

a. **Preparation and Characterization of Compounds.** The cyclam ligand was prepared by the method of Bounsall and Koprich.[13] *cis-* and *trans-*[Cr(cyclam)Cl$_2$]Cl were prepared and separated following the procedure of Ferguson and Tobe;[14] the compounds were characterized both spectrally and by elemental analysis. The cis isomer was dissolved in water and precipitated as the perchlorate salt on addition of cold, concentrated perchloric acid. The trans isomer was converted to the nitrate salt by ion exchange using Dowex 20-50 mesh, medium-porosity resin (converted from the chloride form by eluting with dilute nitric acid).

The 2,3,2-tet ligand is an intermediate product in the synthesis of cyclam. *trans-*[Cr(2,3,2-tet)Cl$_2$]Cl, whose preparation has not previously been reported, is present as a minor component in the synthesis of the corresponding cis isomer.[15] Separation was accomplished by extracting a portion of the latter compound with 5-10 ml of cold methanol, evaporating the solution to dryness, and washing the residue with small amounts of cold methanol. The resultant light green solid was dried under vacuum overnight. *Anal.* Calcd: C, 26.38; H, 6.34; N, 17.58. Found: C, 26.89; H, 6.56; N, 17.21.

Absorption spectra were recorded on a Cary 14 spectrophotometer and are shown for various *trans-*[CrN$_4$Cl$_2$]$^+$ complexes in Figure 1.[16]

b. **Photolysis Procedures.** Solutions (1-2) × 10^{-3} *M* in complex and acidified to pH ~3 with nitric acid were photolyzed in cylindrical cells of 2-, 5-, or 10-cm path length. Irradiations in the quartet bands (546 and 408 nm) were accomplished with a PEK 200-W high-pressure mercury lamp with quartz optics, using interference and blocking filters for wavelength selection. Irradiations at 254 nm were performed by immersing a quartz-jacketed pen ray lamp (UV Products, Inc.), whose output is >92% at this wavelength, into a cylindrical tube containing the sample solution.

Light intensity was measured with the reineckate[17] (546 nm) or ferrioxalate[18] (408 and 254 nm) actinometers. Released chloride ion was determined (1) potentiometrically with a Beckman silver electrode or an Orion specific ion electrode or (2) titrimetrically with mercuric nitrate using diphenylcarbazone as the indicator.[19] Upper limits to the quantum yields for proton uptake, ϕ_{H^+}, were estimated from the lack of any noticeable pH change following irradiation. Product stereochemistry was assigned from the observed spectral changes.

c. **Rate Studies.** A (1-2) × 10^{-3} *M* solution of *trans-*[Cr(2,3,2-tet)Cl$_2$]$^+$, acidified to pH 3 with nitric acid and contained in a spectrophotometer cell, was heated in a constant-temperature bath controlled to ±0.2°. At various times the cell was removed and cooled to room temperature, and the visible spectrum of the solution was recorded. The progress of the reaction was monitored by following the decrease in optical density at 378 nm. Two methods were utilized to calculate the rate constant: (1) plotting $(D_t - D_\infty)$ *vs.* time, where D_t and D_∞ are the optical densities at time *t* and at infinite time, and (2) plotting $(D_t - D_{t+\Delta})$ *vs.* time, where Δ is a constant increment of time. The two methods yielded rate constants agreeing to within ±10%.

Results

a. **Emission and Lifetime Studies.** Low-temperature emission spectral maxima and lifetimes for several [CrN$_4$Cl$_2$]$^+$ compounds are listed in Table I. From the band positions and narrow half-widths (~100 cm^{-1}), the spectra are assigned as chromium d-d phosphorescence ($^2E_g \rightarrow {}^4A_{2g}$, in O_h symmetry). The assignment is particularly straightforward for *cis-*[Cr(cyclam)Cl$_2$]$^+$, where the lowest energy feature (presumably the 0-0 transition) of its 14.24-kK emission overlaps with its doublet absorption band (14.37 kK, $\epsilon_{\max}$ 1.8 M^{-1} cm^{-1}). As noted previously,[11] the phosphorescence of *trans-*[Cr(cyclam)Cl$_2$]$^+$ appears in about normal intensity relative to its ethylenediamine analog. Likewise, the doublet lifetimes of the cyclam and 2,3,2-tet complexes are about as expected for [CrN$_4$Cl$_2$]$^+$ species.[20] There are thus no obvious indications of unusual photophysical processes for any of the compounds in this study.

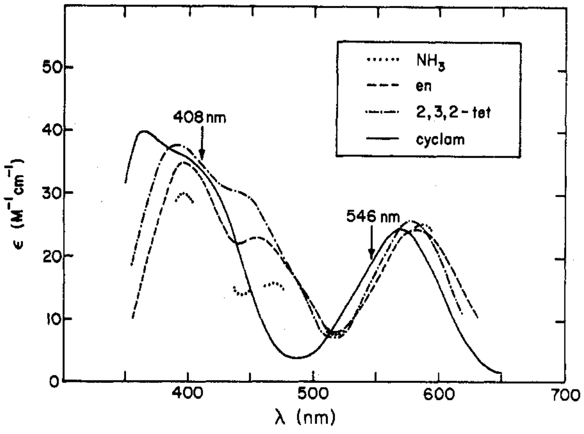

Figure 1. Spectra of various *trans-*[CrN$_4$Cl$_2$]$^+$ complexes. (NH$_3$ spectrum from ref 26.)

Table I. Emission Spectral Maxima and Lifetimes for Several [CrN$_4$Cl$_2$]$^+$ Complexes

Complex	Emission, kK	Lifetime,[a] μsec	Ref
trans-[Cr(en)$_2$Cl$_2$]$^+$	14.38		*d*
trans-[Cr(2,3,2-tet)Cl$_2$]$^+$	14.43[a]	56	*e*
trans-[Cr(cyclam)Cl$_2$]$^+$	13.97[b]	100	*e*
cis-[Cr(en)$_2$Cl$_2$]$^+$	14.49	33	*f*
cis-[Cr(cyclam)Cl$_2$]$^+$	14.24, 13.62[b]	50, 130, 3000[c]	*e*

[a] Measured in ethylene glycol-water (2:1 v/v) glass. [b] Spectrum of neat solid at 77°K. [c] Observed emission is nonexponential; there appear to be three components with the approximate lifetimes listed. [d] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, 70, 199 (1970). [e] This work. [f] K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, 20, 1603 (1964).

The only apparent anomaly occurs with *cis-*[Cr(cyclam)Cl$_2$]$^+$, where two distinct emission maxima and three lifetimes are observed.[21] As noted above, the higher energy peak closely overlaps the doublet absorption and corresponds to the expected phosphorescence; the origin of the second peak, however, is uncertain at present. The possibility of a chromium(III)-containing impurity exists, but, if present, it does not noticeably affect the elemental analysis. Alternatively, the second peak may arise from the phosphorescence of a different conformational isomer of the complex. Attempted isomer separations on alumina and silica gel columns, however, proved inconclusive.

b. **Direct Photolysis.** The product quantum yields for the trans and cis complexes studied are listed in Tables II and III. Where available, the results for the analogous ammonia and ethylenediamine compounds are included for comparison.

For the trans series, chloride aquation is the predominant reaction following d-d excitation, there being no measurable decoordination of an amine function. A significant observation is the decrease in photoreactivity as ring stricture about the metal atom increases. In the sequence NH$_3$ through

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(13) E. J. Bounsall and S. R. Koprich, *Can. J. Chem.*, 48, 1481 (1970).

(14) J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, 4, 109 (1970).

(15) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).

(16) The similarity of d-d transitions also occurs within the corresponding cis series (see ref 14).

(17) E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, 88, 394 (1966).

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(19) F. E. Clark, *Anal. Chem.*, 22, 553 (1950).

(20) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, 20, 1603 (1964).

(21) While the 50- and 130-μsec lifetimes are within the range normally observed for chromium(III) chloroamines, the 3000-μsec value is unusually large and is probably due to some minor contaminant.

Table II. Photolysis Quantum Yields for *trans*-$[CrN_4Cl_2]^+$ Complexes

N_4	Wavelength irradiated, nm	Temp, °C	Product yields[a]		Major product	Ref
			ϕ_{Cl^-}	ϕ_{H^+}		
$4NH_3$	L_1[b]	. . .[b]	0.37	$<2 \times 10^{-2}$[c]	*cis*-$[Cr(NH_3)_4OH_2Cl]^{2+}$	*e*
2en	540	0	0.32 ± 0.02	$<10^{-3}$	*cis*-$[Cr(en)_2OH_2Cl]^{2+}$	*f*
	400	0	0.35 ± 0.02	$<10^{-3}$	*cis*-$[Cr(en)_2OH_2Cl]^{2+}$	*f*
cyclam	546	25[d]	$(3.3 \pm 0.3) \times 10^{-4}$	$<2 \times 10^{-4}$	*trans*-$[Cr(cyclam)OH_2Cl]^{2+}$	*g*
	546	41	4.6×10^{-4}	$<10^{-4}$	*trans*-$[Cr(cyclam)OH_2Cl]^{2+}$	*g*
	408	25	$(2.3 \pm 0.1) \times 10^{-4}$	$<2 \times 10^{-4}$	*trans*-$[Cr(cyclam)OH_2Cl]^{2+}$	*g*
	254	24	6×10^{-2}			
2,3,2-tet	546	25	0.060 ± 0.003	$<7 \times 10^{-3}$	*cis*-$[Cr(2,3,2\text{-tet})OH_2Cl]^{2+}$	*g*

[a] Where quoted, error limits represent mean deviation of two or more runs. [b] Exact wavelength of irradiation and temperature not specified. [c] Upper limit for NH_3 aquation. [d] An Arrhenius type expression ($\phi_{Cl^-} = Ae^{-E_{app}/RT}$) yields an apparent activation energy for chloride release of 3.8 kcal/mol at 546 nm. [e] P. Riccieri and E. Zinato, *Proc. Int. Conf. Coord. Chem.*, 14, 252 (1972). [f] Reference 12. [g] This work.

Table III. Photolysis Quantum Yields for *cis*-$[CrN_4Cl_2]^+$ Complexes

N_4	Wavelength irradiated, nm	Temp, °C	Product yields[a]		Major product	Ref
			ϕ_{Cl^-}	ϕ_{H^+}		
2en	540	0	$(2 \pm 1) \times 10^{-2}$	0.12 ± 0.02	$[Cr(en)(enH)OH_2Cl_2]^+$	*d*
	400	0	$(1.1 \pm 0.5) \times 10^{-2}$	0.13 ± 0.02	$[Cr(en)(enH)OH_2Cl_2]^+$	*d*
cyclam	546	24[b]	$(8.0 \pm 0.8) \times 10^{-3}$	$<2 \times 10^{-3}$	*cis*-$[Cr(cyclam)OH_2Cl]^{2+}$	*e*
	546	3	$(4.3 \pm 0.3) \times 10^{-4}$	$<5 \times 10^{-4}$	*cis*-$[Cr(cyclam)OH_2Cl]^{2+}$	*e*
	408	24[b]	$(8.0 \pm 1.1) \times 10^{-3}$	$<2 \times 10^{-3}$	*cis*-$[Cr(cyclam)OH_2Cl]^{2+}$	*e*
	408	3	$(3.8 \pm 0.8) \times 10^{-3}$	$<5 \times 10^{-4}$	*cis*-$[Cr(cyclam)OH_2Cl]^{2+}$	*e*
	254	24	$(9.4 \pm 0.6) \times 10^{-2}$[c]			

[a] Where quoted, error limits represent mean deviation of two or more runs. [b] E_{app} is 4.8 kcal/mol (546 nm) and 5.8 kcal/mol (408 nm); see footnote *d* in Table II. [c] ϕ_{Cl^-} is $(8.0 \pm 0.7) \times 10^{-2}$ and $(5.7 \pm 0.4) \times 10^{-2}$ for photolyses in 10^{-3} *N* $HClO_4$ and H_2SO_4, respectively. [d] Reference 12. [e] This work.

cyclam, decreasing the number of open edges in the plane perpendicular to the Cl-Cl axis causes an overall reduction in ϕ_{Cl^-} by ~10^3.

In contrast, the corresponding cis compounds show comparable reactivity for chloride release following ligand field irradiation. However, Cr-N bond breaking is now the predominant reaction mode for *cis*-$[Cr(en)_2Cl_2]^+$. The low ϕ_{H^+} value for the cyclam complex undoubtedly reflects the "anchoring" effect on any single Cr-N bond by the remainder of the macrocyclic ligand, in that the components of the labilized bond are not allowed to separate to the point where protonation can occur.

Irradiation in the Cl→Cr charge-transfer band (254 nm) causes a marked increase in ϕ_{Cl^-} for both the cis and trans cyclam complexes. A similar effect has been reported for $[Cr(NH_3)_5X]^{2+}$ (X = Cl, Br).[22,23]

The major photoproducts are listed in Tables II and III. For *trans*-$[Cr(cyclam)Cl_2]^+$, the absence of significant reaction even after extended ligand field irradiation renders a quantitative assignment difficult. However, the spectral changes observed parallel those found (initially) in thermal aquation and are consistent with the predominant (≥80%) formation of the *trans*-aquochloro complex. The identity of the 254-nm photoproduct, on the other hand, is unknown at present. Irradiation results in a general increase in absorbance similar to that reported for prolonged thermal aquation of the complex.[24] *cis*-$[Cr(cyclam)Cl_2]^+$ undergoes photolysis to the corresponding *cis*-aquochloro product at all wavelengths studied, as evidenced by the spectral similarity to the thermal process. The spectral changes on irradiation of *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$ are shown in Figure 2 (note differences from Figure 3) and are consistent with those computed for the formation of ≥80% *cis*-$[Cr(2,3,2\text{-tet})OH_2Cl]^{2+}$ (an authentic sample of which is formed by thermal aquation

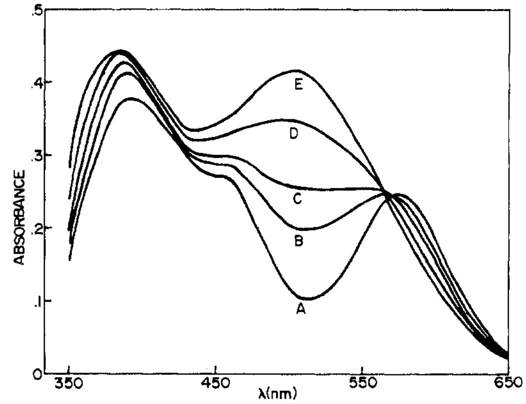

Figure 2. Spectral changes upon irradiation of *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$: A taken at time zero; B, C, D, and E at successively longer times.

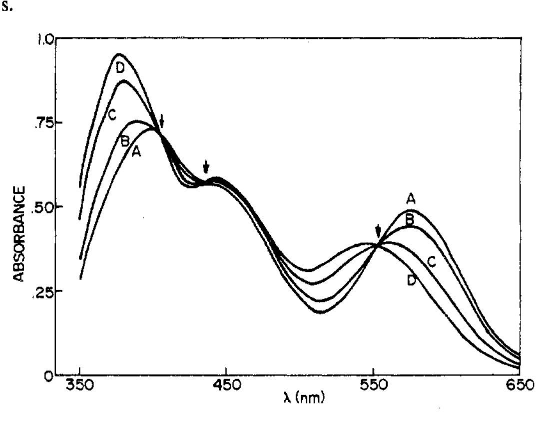

Figure 3. Spectral changes upon thermal aquation of *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$: A taken at time zero; B, C, and D at successively longer times. Arrows indicate isosbestic points in the aquation of *trans*-$[Cr(en)_2Cl_2]^+$ (from ref 25).

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(22) H. F. Wasgestian and H. L. Schlafer, *Z. Phys. Chem.* (*Frankfurt am Main*), 62, 127 (1968).

(23) P. Riccieri and H. L. Schlafer, *Inorg. Chem.*, 9, 727 (1970).

(24) E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, 9, 1781 (1970).

of the dichloro complex). Thus a change in configuration has occurred, similar to that observed for the corresponding NH_3 and en complexes.

c. **Thermal Studies.** *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$ undergoes thermal aquation to the corresponding *trans*-aquochloro complex. The reaction follows first-order kinetics over several half-lives, indicating that the release of the second chloride is a much slower process. The rate constants and activation parameters are listed in Table IV. The assignment of product geometry is made by analogy to *trans*-$[Cr(en)_2Cl_2]^+$;[25] as shown in Figure 3, both compounds exhibit virtually identical spectral changes during aquation. Retention of geometric configuration is a feature common to the thermal reactions of chromium(III)-amine complexes.[26]

A correlation was noted between the rate constant (at 25°) for thermal aquation and the quantum yield of the corresponding photochemical reaction for *trans*-$[CrN_4Cl_2]^+$ complexes. As illustrated in Figure 4, a plot of log $k_{25°}$ *vs.* ϕ_{Cl^-} yields a straight line with slope near unity. Thus, factors which influence the reactivity of the ground state appear to have a proportional effect in the excited state.

Discussion

The d-d photochemistry of chromium(III) acidoamines conforms in a general way to the predictions of Adamson's rules.[6,27,28] However, it seems clear that ligand field strength (while often dominant) cannot be the sole factor determining overall photoreactivity. Within the series of electronically similar *trans*-$[CrN_4Cl_2]^+$ complexes (Table II), for example, ϕ_{Cl^-} drops drastically with increasing ring stricture about the metal atom. We have previously considered the mechanistic implications of this effect from several viewpoints,[11] namely (1) the complex undergoes more efficient photophysical deactivation, (2) prompt dissociation of a chloride occurs without a concomitant reorganization of the basic octahedral framework, (3) dissociation of a chloride is concerted with rearrangement of the remaining complex to a trigonal bipyramid, and (4) a solvent molecule attacks the complex to form a seven-coordinate transition state (or intermediate) with the consequent expulsion of a chloride and possible rearrangement. In view of the present study, each of these possibilities can be reexamined in more detail.

Alternative 1 cannot be completely discounted, since chromium(III) acidoamines rarely exhibit detectable fluorescence emission.[29] Thus no direct measurement of the rates of radiative or nonradiative deactivation of $^4L_1{}^0$ is possible. However, the phosphorescent intensities of the cyclam complexes and the lifetimes listed in Table I appear normal, suggesting that the deactivation processes of the doublet state and the rate of intersystem crossing from the quartet are relatively constant within the series. Further, it is not immediately apparent that a relationship between the efficiency of deactivation and increasing ring stricture *should* exist. If one assumes that N-H vibrations play an important role in the deactivation process,[30,31] for example, the importance of this pathway would diminish within the ligand series from NH_3 to cyclam (as the number of N-H bonds decreases). The prediction is one of increasing ϕ_{Cl^-} which is opposite to the observed trend. Subject to the limitation noted earlier, an explanation based solely on changes in photophysical deactivation appears unlikely.

Table IV. First-Order Rate Constants and Activation Parameters for the Aquation of *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$

Temp, °C	$10^5 k$,[a] sec^{-1}	Activation parameters[b]
47.8	6.9	$\Delta H^{\ddagger} = 24.8 \pm 0.5$ kcal/mol
55.5	17.0	$\Delta S^{\ddagger} = 1 \pm 1$ cal/deg mol
56.3	20.0	
64.0	47.0	

[a] Average value obtained from the two methods described in section c of the Experimental Section. [b] Error limits are estimated.

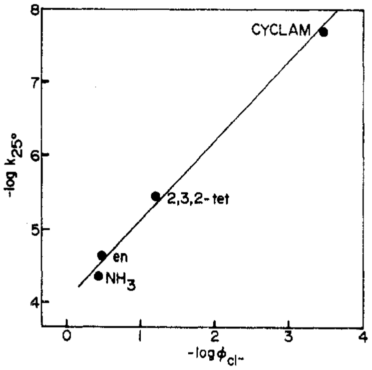

Figure 4. Correlation of ϕ_{Cl^-} with $k_{25°}$ for *trans*-$[CrN_4Cl_2]^+$ complexes.

Alternative 2 is eliminated on grounds that a simple dissociation of a chloride should be equally facile for each member of the trans series. The reaction would be localized mainly along the Cl-Cr-Cl axis and thus largely independent of the belt ligand(s). This type of mechanism, however, is probable for the charge-transfer photochemistry of chromium(III) acidoamines; it has also been postulated for a series of rhodium(III) chloroamines.[32]

Alternatives 3 and 4 appear to explain the photolysis results equally well. Considering the trans series, increasing ring stricture should retard the motion required to generate a trigonal bipyramid as well as hinder the approach of a seventh ligand. While it is difficult to choose solely on the basis of trends in ϕ_{Cl^-}, a further clue is provided by the stereochemistry of the photoproduct. For NH_3, en, and 2,3,2-tet, the aquochloro product is predominantly (if not exclusively) the cis isomer. This stereospecificity argues against the formation of a trigonal bipyramid, where a 2:1 mixture of cis to trans products is expected on statistical grounds. The results are consistent, on the other hand, with alternative 4 in terms of a backside attack or edge displacement mechanism.[33] This assignment accommodates both the drop in ϕ_{Cl^-} as the number of free edges decreases and the configuration change in the photoproduct. Likewise, the high chloride yield (relative to the en analog) of *cis*-$[Cr(cyclam)Cl_2]^+$ agrees with its possessing an open edge accessible to solvent attack.

The degree of bond making *vs.* bond breaking in the transition state of the excited-state reaction is difficult to access from the data available. It might be supposed that a dissociative mechanism would be favored, since the metal-ligand

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[29] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

[30] G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962).

[31] M. Wrighton, G. S. Hammond, and H. B. Gray, *Inorg. Chem.*, **11**, 3122 (1972).

[32] C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1454 (1973).

[33] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 4.

bonds are weakened in $^4L_1{}^0$. On the other hand, bond weakening also renders the complex more susceptible to attack by an incoming ligand. While this question remains largely unanswered, we feel that some degree of participation by the incoming solvent molecule in the expulsion of a chloride is at least suggested by the trend in ϕ_{Cl^-} shown by the trans complexes.

The correlation between $k_{25°}$ and ϕ_{Cl^-} shown in Figure 4 is unexpected. Seemingly, factors which influence reactivity in the ground state exert a proportional (if not equal) effect in the excited state. One might suppose that similar mechanisms are operative in the thermal and photochemical reactions. The analogy cannot be carried too far, however, since obvious differences exist between the two processes. The thermal aquation of the NH_3, en, and 2,3,2-tet complexes occurs with retention of configuration, while the opposite is true photochemically. Further, there is a fortuitous similarity in the two types of reaction for *trans*-$[CrN_4Cl_2]^+$ complexes. No correlation exists for the $[CrN_5X]^{n+}$ series, for example, since the predominant thermal and photochemical reactions differ. Thus the significance of the correlation is uncertain at present.[34]

Registry No. *trans*-[Cr(2,3,2-tet)Cl_2]Cl, 40813-71-6; *trans*-[Cr(cyclam)Cl_2]Cl, 27385-72-4; *cis*-[Cr(cyclam)Cl_2]Cl, 27435-95-6; *trans*-$[Cr(NH_3)_4Cl_2]^+$, 22452-49-9; *trans*-[Cl-$(en)_2Cl_2]^+$, 14403-88-4; *trans*-$[Cr(cyclam)OH_2Cl]^{2+}$, 41156-37-0; *cis*-$[Cr(2,3,2\text{-tet})OH_2Cl]^{2+}$, 40901-23-3; *cis*-$[Cr(en)_2Cl_2]^+$, 14482-74-7; *cis*-$[Cr(cyclam)OH_2Cl]^{2+}$, 41139-30-4.

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(34) We can suggest one rationalization of the observed behavior; namely, both processes involve a rate-determining attack by a solvent molecule (essentially alternative 4), whose approach is hindered by increasing ring stricture. Subsequent rearrangement (or lack of it) then leads to the difference in product stereochemistries.

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Infrared Spectra of Isotopically Substituted Metal Carbonyls. III. Evidence for Conformational Isomerism in π-Cyclopentadienyldicarbonyl(dialkyl sulfide)manganese(I) Complexes[1]

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The *n*-hexane solution ir spectra of the organosulfide complexes π-$C_5H_5Mn(CO)_2SR_2$ (R = Me, Et, *n*-Pr, *n*-Bu) and π-$C_5H_5Mn(CO)_2$THT (THT = tetrahydrothiophene) have been studied under high resolution in the CO stretching region. Each of the complexes exhibits four CO absorptions instead of the two expected. This "CO frequency doubling" is attributed to the first examples of conformational isomerism about the manganese–sulfur bonds. This conclusion is supported by approximate force constant calculations for the CO modes of the two conformers of π-$C_5H_5Mn(CO)_2S(n\text{-Bu})_2$ and their $C^{18}O$-substituted derivatives and by ir data for all of the complexes in the 4000–3700-cm^{-1} overtone and combination region.

Introduction

Recently, the ir spectra of various π-cyclopentadienylmetal carbonyl complexes in nonpolar solvents have been found to exhibit twice the number of CO stretching frequencies expected. More specifically, these are complexes of iron,[2-4] ruthenium,[3] manganese,[3] and molybdenum[3] containing certain silicon, tin, and phosphorus ligands, *e.g.*, π-$C_5H_5Fe(CO)_2SiCl_2Me$, π-$C_5H_5Ru(CO)[P(OMe)_3]I$, and π-$MeC_5H_4Mn(CO)_2[P(OPh)_3]$. This phenomenon has been attributed to conformational isomerism either about the metal–ligand bonds or within the ligands themselves.

We now report the first examples of π-cyclopentadienylmetal carbonyl complexes containing organosulfide ligands displaying this type of "CO frequency doubling." In particular, the ir spectra of π-$C_5H_5Mn(CO)_2SR_2$ (R = Me, Et, *n*-Pr, *n*-Bu) and π-$C_5H_5Mn(CO)_2$THT (THT = tetrahydrothiophene) in *n*-hexane solution exhibit four CO stretching frequencies instead of the two expected. We attribute this to conformational isomerism about the manganese-sulfur bonds. This conclusion is supported by approximate force constant calculations for the CO stretching modes of π-$C_5H_5Mn(CO)_2S(n\text{-Bu})_2$ and its $C^{18}O$-substituted derivatives and by ir data for all of the organosulfide complexes in the 4000-3700-cm^{-1} overtone and combination region. To the best of our knowledge, conformational isomerism about metal-sulfur bonds has not been reported previously.

Experimental Section

The organosulfide complexes, π-$C_5H_5Mn(CO)_2SEt_2$ and π-$C_5H_5Mn(CO)_2$THT, were prepared photochemically from π-$C_5H_5Mn(CO)_3$ (a gift from Ethyl Corp.) by the literature methods.[5] Similar methods were used to prepare the previously unknown π-$C_5H_5Mn(CO)_2SR_2$ complexes; these new complexes were fully characterized by elemental analysis and by ir, nmr, and mass spectroscopy.[6] All the complexes were recrystallized from *n*-hexane solution at −78° immediately prior to use.

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