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Effects of Steric Constraint on Chromium(III) Complexes of Tetraazamacrocycles, 2. Comparison of the Chemistry and Photobehavior of the *trans*-Dichloro- and *trans*-Dicyano- Complexes of Cyclam, 1,4-C_2-Cyclam, and 1,11-C_3-Cyclam[†]

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The synthesis and characterization of several Cr(III) complexes of the constrained macrocyclic ligand 1,11-C_3-cyclam (1,4,8,11-tetraazabicyclo[9.3.3]heptadecane) is reported. Only trans complexes are formed, and the structure of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]PF_6 is presented. The chemical and photophysical behavior of the 1,11-C_3-cyclam complexes are compared with those of the corresponding cyclam (1,4,8,11 tetraazacyclotetradecane) and 1,4-C_2-cyclam (1,4,8,11-tetraazabicyclo[10.2.2]hexadecane) complexes. The aquation rate of *trans*-[Cr(1,11-C_3-cyclam)-Cl_2]$^+$ is similar to that of the corresponding 1,4-C_2-cyclam complex and is more than 5 orders of magnitude faster than the cyclam counterpart. A monotonic increase in the extinction coefficient is observed on going from the cyclam complexes to the 1,11-C_3-cyclam complexes to the 1,4-C_2-cyclam complexes, and this is related to the degree of centrosymmetry in each complex. The *trans*-[Cr(1,11-C_3-cyclam)$(CN)_2$]$^+$ complex is a weak emitter in aqueous solution with a room-temperature emission maximum at 724 nm ($\tau = 23\ \mu$s). Like the corresponding 1,4-C_2-cyclam complex ($\tau = 0.24\ \mu$s), the 1,11-C_3-cyclam complex shows no deuterium-isotope effect in room-temperature solution. This is in marked contrast to the corresponding cyclam complex which has an emission lifetime of 335 μs and a significant deuterium isotope effect in room-temperature solution. Low temperature (77K) data are also presented in an attempt to understand the differences in photophysical behavior.

Introduction

Complexes of the *trans*-[Cr(N_4)X_2]$^{n+}$ (where N_4 = ammine or polydentate amine ligands or their combination and X = Cl^-,[1] F^-,[2] CN^-,[3−5] or NH_3[6]) type have a rich photochemistry, and the study of these complexes has offered insights into photochemical mechanisms.[7] Of particular interest are studies that demonstrate the effect of geometric distortion and constraint on the photobehavior of the complex.[4,5,8−12] We recently reported the chemistry and photobehavior of a

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[†] Abbreviations used in this paper: cyclam = 1,4,8,11 tetraazacyclotetradecane; 1,4-C_2-cyclam = 1,4,8,11-tetraazabicyclo[10.2.2]hexadecane; 1,11-C_3-cyclam = 1,4,8,11-tetraazabicyclo[9.3.3]heptadecane; OTf = triflate = trifluoromethanesulfonate; DMF = dimethylformamide; THF = tetrahydrofuran.

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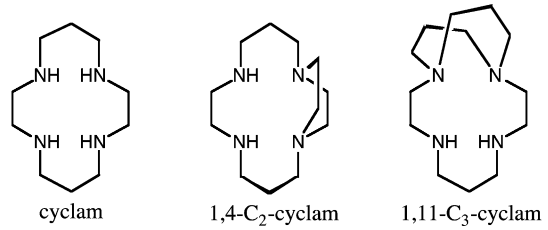

Figure 1. Macrocyclic ligands discussed in this paper.

complex of the constrained ligand 1,4-C_2-cyclam (Figure 1).[13] The presence of the additional C_2 strap significantly distorts the coordination environment of Cr(III) and has significant effects on the chemistry and photobehavior of its complexes when compared with the analogous cyclam complexes. In an effort to further understand the effect of this type of steric constraint on the behavior of these types of complexes, we have prepared and studied the analogous complexes of 1,11-C_3-cyclam. Herein, we report the chemistry and photobehavior of these new 1,11-C_3-cyclam complexes, as well as a more detailed study of the 1,4-C_2-cyclam complexes.

Experimental Section

Materials and Methods. All materials were reagent grade and were used as received. *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6[13] and 1,11-C_3-cyclam[14] were prepared according to literature procedures. All reactions were performed under a nitrogen atmosphere unless otherwise noted. UV−vis absorption spectra were recorded using a Cary 50 spectrophotometer. Conductivity measurements were performed on 0.001 M solutions using an Accumet AB30 conductivity meter. Emission spectra were carried out in a 1 cm quartz cell using a SPEX Fluorolog 2 with a Xenon excitation source. Emission lifetimes were measured at room temperature using a Photon Technology International (PTI) GL-3300 pulsed nitrogen laser fed into a PTI GL-302 dye laser as the excitation source. The dye laser was operated at 440 nm, corresponding to a $^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) excitation of *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]$^+$ and *trans*-[Cr(1,11-C_3-cyclam)$(CN)_2$]$^+$. Emission was monitored at right angles using a Hamamatsu R928 photomultiplier tube. The signal from the photomultiplier was fed into a LeCroy 9350A digital oscilliscope and stored for further analysis. Extended photolyses were carried out in a 1 cm glass emission cell using a Rayonet Photochemical Reactor operating at 350 nm, corresponding to a $^4A_{2g} \rightarrow {}^4T_{1g}$ (O_h) excitation of *trans*-[Cr$(N_4)(CN)_2$]$^+$. Elemental analyses were performed by Atlantic Microlabs in Norcross, GA.

Synthesis of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]Cl·$2H_2O$. In a drybox, 1,11-C_3-cyclam (0.76 g, 3.18 mmol) and $CrCl_3(THF)_3$ (1.13 g, 3.00 mmol) were placed in a 25 mL round-bottom flask and dissolved in dry DMF (7 mL). The mixture was stirred for 5 min, brought out, and then refluxed for 10 min under nitrogen. When the mixture had cooled, acetone (7 mL) was added to further precipitate the product. The solid was filtered and washed with acetone (2 × 7 mL) and Et_2O (2 × 7 mL) to yield *trans*-[Cr(1,11-C_3-cyclam)Cl_2]Cl as a green powder (1.16 g, 86%). Anal. Calcd (found) for $C_{13}H_{28}Cl_3CrN_4$: C, 35.91 (36.40); H, 7.42 (7.38); N, 12.89 (12.88); Cl, 24.46 (24.64).

Synthesis of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]PF_6. [Cr(1,11-C_3-cyclam)Cl_2]Cl (0.28 g, 0.64 mmol) was dissolved in a 3 M NaCl solution (1 mL). Saturated aqueous NH_4PF_6 (1 mL) was added to the above solution resulting in a green slurry. The green precipitate was filtered, washed with water (3 × 2 mL), ethanol (3 × 2 mL), and diethyl ether (3 × 2 mL), and dried under vacuum to yield 0.33 g (93%). X-ray quality crystals were grown by diffusion of ether into an acetonitrile solution. Anal. Calcd (found) for $C_{13}H_{30}N_4CrCl_2PF_6$: C, 30.72 (30.83); H, 5.55 (5.54); N, 11.02 (10.87); Cl, 13.95 (13.68).

Synthesis of *trans*-[Cr(1,11-C_3-cyclam)$(CN)_2$]PF_6·$0.5CH_3CN$. [Cr(1,11-C_3-cyclam)Cl_2]PF_6 (0.67 g) and NaCN (0.24 g) were stirred in dry acetonitrile (8 mL) in a drybox. The solution changed from green to brown-red, then to yellow. After 4 h, the flask was moved out of the drybox, and the solution was filtered. The yellow solid was dissolved in CH_3CN (40 mL) leaving behind a white solid, which was removed by filtration. Ether (100 mL) was added to the acetonitrile solution, and the resulting precipitate was filtered and washed with water (4 mL), ethanol (10 mL), and ether (10 mL). The yellow solid (0.50 g, 77%) was recrystallized by diffusion of ether into an acetonitrile solution of the complex. Yield: 0.40 g (62%). Anal. Calcd (found) for $C_{15}H_{28}CrN_6PF_6$·$0.5CH_3CN$: C, 37.69 (37.84); H, 5.83 (5.92); N 17.85 (17.95).

Synthesis of *trans*-[Cr(1,11-C_3-cyclam)$(OTf)_2$]OTf. A flask fitted with a nitrogen bubbler was charged with *trans*-[Cr(1,11-C_3-cyclam)Cl_2]Cl·$2H_2O$ (0.480 g, 1.10 mmol) and 10 g of trifluoromethanesulfonic acid from a freshly opened ampule. Nitrogen was bubbled through the green solution for 24 h. The green solution was transferred to a large beaker and anhydrous ether (400 mL) was added. Upon stirring and scratching, a green powder formed which was filtered and washed with anhydrous ether (yield = 0.76 g, 92%). The light green solid is stable under normal atmospheric conditions. Anal. Calcd (found) for $C_{16}H_{28}CrF_9N_4O_9S_3$: C, 25.98 (25.95); H, 3.82 (3.99); N, 7.58 (7.44).

N−H Deuteration of *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6. A suspension of *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6 (105 mg) in D_2O (4 mL) was heated to 45 °C for 30 min and then evaporated to dryness. This was repeated four times; the resulting yellow powder was taken up in 3 mL of D_2O at 45 °C, and KPF_6 (112 mg) was added. The mixture was stirred for 2 min and refrigerated overnight. The product was filtered, washed with acetone/ether (1:2, 20 mL), 1 mL of ethanol, and then 10 mL of ether. The product was dried under vacuum to yield 67 mg (64%). Deuteration was determined to be >95% by IR spectroscopy.

N−H Deuteration of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]PF_6. A suspension of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]PF_6 (67 mg) in D_2O (4 mL) was heated to 45 °C for 30 min and then evaporated to dryness. This was repeated three times; the yellow powder was then taken up in 2 mL of D_2O at 45 °C, and KPF_6 (79 mg) was

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Table 1. Crystallographic Data for $[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]PF_6\cdot CH_3CN$

formula	$C_{15}H_{31}Cl_2CrF_6N_5P$
fw	549.32
cryst syst	monoclinic
space group	*C*2/*c*
a	25.762(6) Å
b	7.557(3)Å
c	25.693(7) Å
β	116.99(2)°
V	4457.3(26) Å^3
Z	8
D_{calcd}	1.637 g/cm^3
T	−80 °C
μ	0.888 mm^{-1}
R1[a] (F_o) ($I > 2\sigma(I)$)	0.0914
wR2[a] (F_o^2) ($I > 2\sigma(I)$)	0.2580

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$, $a = 0.2376$, and $b = 0.0000$.

added. The mixture was stirred for 5 min and refrigerated overnight. The product was filtered, washed with acetone/ether (1:2, 10 mL), and then washed with 10 mL of ether. It was dried under a vacuum to yield 34 mg (51%). Deuteration was determined to be >95% by IR spectroscopy.

X-ray Crystallography. X-ray data for *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]PF_6\cdot CH_3CN$ were acquired at −80 °C using a Siemens/Bruker AXS P4 four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and were corrected for absorption using the semiempirical method XABS2.[15] The structure was solved by direct methods[16] and Fourier difference maps.[16] Refinements were performed by full-matrix least-squares on F^2.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in ideal positions (C−H, 0.99 Å; N−H, 0.93 Å; $U_H = 1.2U_{\text{attached C or N}}$) and were not refined. The methyl group of the acetonitrile solvent was modeled as freely rotating. Crystallographic data are summarized in Tables 1 and 2, and a thermal ellipsoid plot[16] of the cation at the 50% probability level is shown in Figure 2. Additional details are available via Supporting Information.

Aquation Kinetics of *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]Cl$. Enough solid *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]Cl$ to give a concentration of approximately 2×10^{-3} M was added to a cuvette of water or 0.01 M HNO_3 (temp = 25 °C). The cuvette was shaken to dissolve the material and immediately placed in the UV−vis spectrophotometer. Spectral monitoring was begun within five seconds of mixing, and scans were taken at six second intervals. Because of a slow decomposition process (vide infra), overall isosbestic points are not evident. However, isosbestic points for the slow decomposition are evident at 393 and 537 nm (Supporting Information). Thus, the first reaction is followed (0.1 s intervals) at an isosbestic point for the decomposition. Plots of $\ln[A(t)_{393} - A(\infty)_{393}]$ versus time were linear through four half-lives ($r \geq 0.998$).

Results and Discussion

Syntheses and Substitution Chemistry. The syntheses of the Cr(III) complexes of 1,11-C_3-cyclam were performed by only slight modifications of the procedures for the corresponding complexes of 1,4-C_2-cyclam.[13] However, the resulting complexes have some notable solubility differences. For example, *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(CN)_2]PF_6$ is significantly more water-soluble than the corresponding 1,11-C_3-cyclam complex reported herein. Likewise, though *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(OTf)_2]OTf$ is very soluble in methylene chloride, the analogous complex of 1,11-C_3-cyclam has a substantially lower solubility (<2 mM).

Table 2. Selected Distances (Å) and Angles (deg) for the Complex Cation of $[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]PF_6$

bond lengths	
Cr−N(1)	2.039(6)
Cr−N(2)	2.072(6)
Cr−N(3)	2.071(6)
Cr−N(4)	2.050(6)
Cr−Cl(1)	2.351(2)
Cr−Cl(2)	2.342(2)
angles	
N(1)−Cr−N(2)	88.0(2)
N(2)−Cr−N(3)	85.4(2)
N(3)−Cr−N(4)	87.8(2)
N(4)−Cr−N(1)	98.9(2)
N(1)−Cr−N(3)	173.3(2)
N(2)−Cr−N(4)	173.1(2)
Cl(1)−Cr−Cl(2)	167.62(8)
N(2)−C(5)−C(6)	116.8(7)
C(5)−C(6)−C(7)	116.2(7)
C(6)−C(7)−N(3)	115.7(6)
N(2)−C(11)−C(12)	118.2(6)
C(11)−C(12)−C(13)	123.0(6)
C(12)−C(13)−N(3)	116.3(7)
deviation from least squares plane[a]	
Cr	0.005(3)
N(1)	−0.001(3)
N(2)	−0.002(3)
N(3)	−0.001(3)
N(4)	−0.002(3)

[a] Least squares reference plane defined by the atoms Cr, N(1), N(2), N(3), and N(4).

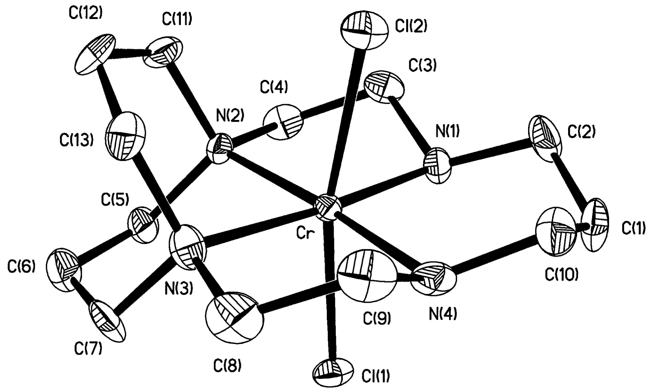

Figure 2. Thermal ellipsoid plot at the 50% level for the cation of *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]^+$. Hydrogen atoms have been omitted for clarity.

Like $[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]Cl$, the corresponding 1,11-C_3-cyclam complex undergoes aquation (eqs 1 and 2) much more rapidly than the corresponding cyclam analogue.

$$trans\text{-}[Cr(N_4)Cl_2]^+ + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Cr(N_4)(H_2O)Cl]^{2+} + Cl^- \quad (1)$$

$$trans\text{-}[Cr(N_4)(H_2O)Cl]^{2+} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} trans\text{-}[Cr(N_4)(H_2O)_2]^{3+} + Cl^- \quad (2)$$

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Table 3. UV-vis Spectral Data for Cr(III) Tetraazamacrocycle Complexes

complex	λ_{max} (ϵ)[a]	ref
trans-[Cr(1,11-C_3-cyclam)Cl_2]Cl[c]	589 (52.0), 427 (71.1), ∼380 sh (39.7)	this work
trans-[Cr(1,11-C_3-cyclam)Cl_2]PF_6[d]	592 (51.6), 433 (70.7), 373 (41.8)	this work
trans-[Cr(1,4-C_2-cyclam)Cl_2]Cl[c]	604 (107), ∼447 sh (70), 388 (191)	13
trans-[Cr(cyclam)Cl_2]Cl[b]	568 (20.0), 404 sh (29.0), 366 (32.8)	29
trans-[Cr(1,11-C_3-cyclam)$(CN)_2$]PF_6[b]	424 (99.4), 335 (90.0)	this work
trans-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6[b]	439 (236), 339 (233)	13
trans-[Cr(cyclam)$(CN)_2$]ClO_4[b]	414 (62.5), 328 (62.5)	4a
trans-[Cr(1,11-C_3-cyclam)$(OTf)_2$]OTf[e]	599 (26.2), ∼451 sh (44), 404 (82.1), 344 (51.4)	this work
trans-[Cr(1,11-C_3-cyclam)$(H_2O)_2$]$(OTf)_3$[f]	490 (sh) (28.2), 410 (sh) (58.6), 363 (64.9)	this work
trans-[Cr(1,11-C_3-cyclam)$(H_2O)_2$]$(OTf)_3$[g]	493 (25.8), 413 (61.8), 365 (62.1)	this work

[a] Absorption wavelengths are in nm, and the extinction coefficients are in units of M^{-1} cm^{-1}. [b] Aqueous solution. [c] Methanol solution. [d] Acetonitrile solution. [e] Methylene chloride solution. [f] Obtained by dissolving *trans*-[Cr(1,11-C_3-cyclam)$(OTf)_2$]OTf in H_2O (1.7 × 10^{-2} M); the peak shapes are slightly concentration dependent which is likely to be the result of the pH-dependent formation of *trans*-[Cr(1,11-C_3-cyclam)(H_2O)(OH)]$^{2+}$. [g] Obtained by dissolving *trans*-[Cr(1,11-C_3-cyclam)$(OTf)_2$]OTf in 0.01 M HNO_3.

Thus, when the green *trans*-[Cr(1,11-C_3-cyclam)Cl_2]Cl is dissolved in water there is a color change from green to peach that appears complete within a few minutes. Conductivity and UV−vis absorption data support the hypothesis that this color change is the result of aquation. Whereas a methanolic solution of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]Cl remains green and demonstrates a conductivity consistent with two ions, the peach aqueous solutions of the same compound have conductivities consistent with dissociation of both chloride ligands.[17] A UV−vis spectrum of *trans*-[Cr(1,11-C_3-cyclam)-Cl_2]Cl in water resembles the UV−vis spectrum of *trans*-[Cr(1,11-C_3-cyclam)$(H_2O)_2$]$(OTf)_3$ prepared by dissolving *trans*-[Cr(1,4-C_2-cyclam)$(OTf)_2$]OTf in water (Table 3). An exact match between the spectrum of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]Cl in water and the spectrum of *trans*-[Cr(1,11-C_3-cyclam)$(OTf)_2$]OTf in water can be obtained via the addition of 3 equiv of chloride to the latter, an indication that the aquation reaches an equilibrium with chloride. Furthermore, the addition of excess NaCl to an aqueous solution of the hydrolysis product results in a color shift from peach back to green/olive, offering additional evidence of this equilibrium. As was the case for the 1,4-C_2-cyclam complex, this equilibrium was used synthetically in the counterion metathesis reaction.[13]

There is another much slower reaction following aquation, which results in color changes imperceptible to the eye but which are evident as slight differences in the UV−vis spectrum over the course of an hour. This reaction is irreversible in that subsequent addition of chloride does not shift the equilibrium back toward the green dichloro complex. Although we do not know the nature of this slow step, the possibility that aquation is complicated by competing unidentified side reactions is precedented for the case of the solvolysis of *trans*-[Cr(cyclam)Cl_2]$^+$.[18]

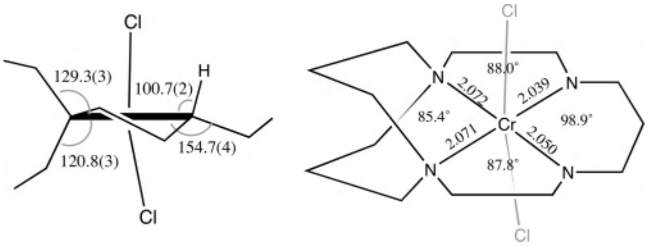

Figure 3. Two views of [Cr(1,11-C_3-cyclam)Cl_2]$^+$ showing bond angles, dihedral angles, and coordination-sphere bond lengths (Å).

Solid State Structure of *trans*-[Cr(1,11-C_3-cyclam)Cl_2]-PF_6. The X-ray structure (Figure 2) confirms the trans arrangement of the 1,11-C_3-cyclam ligand found for the other two known structures of complexes of this ligand.[14] Of additional interest is that the two six-membered rings that the diazacyclooctane (daco) subunit makes with the metal are both in the chair conformation (referred to as the chair−chair conformation). Such was the case for the previously reported [Co(1,11-C_3-cyclam)$(NCS)_2$]OTf.[14] There are very strong structural similarities between the Cr(III) complex reported herein and the previously reported Co(III) complex. First, the dihedral angles between the coordination plane and the selected molecular planes of the Cr(III) complex (Figure 3) are all within 1° of the analogous angles in the Co(III) complex. Second, the angles within the daco subunit of the Cr(III) complex (Table 2) show very similar strain (deviations from tetrahedral) to that of the Co(III) complex. Previous research suggests this is caused by steric repulsions between the β-CH_2 groups.[14] Third, the axial ligands bend away from the daco subunit. Finally, the N−Cr−N bond angle subtended by the daco subunit is significantly smaller than the same angle subtended by the single C_3 linkage opposite the daco subunit. Thus, it seems that the details of the chair−chair conformation for the 1,11-C_3-cyclam ligand architecture are largely independent of whether the metal is Cr(III) or the smaller Co(III). Perhaps the most significant difference is that the M−N bond lengths are almost 0.1 Å longer for Cr(III) than those of Co(III), not surprising given that Cr(III) is slightly larger than low-spin Co(III).

Another interesting comparison is with the corresponding complex of the 1,4-C_2-cyclam ligand, [Cr(1,4-C_2-cyclam)-Cl_2]$^+$.[13] The average coordination-sphere bond lengths for both complexes are quite similar, namely, the average Cr−N and Cr−Cl bond lengths for the C_3-cyclam complex are 2.058 Å and 2.347 Å, respectively, compared with 2.074 Å and 2.358 Å, respectively, for the C_2-cyclam complex. Another strong similarity between these complexes is the

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(17) The molar conductivity, Λ_M, of aqueous solutions of the hydrolysis product is 476 cm^{-1} mol^{-1} Ω^{-1}, indicative of between 4 and 5 ions. The high value is not unusual given that such complexes are acidic and the high mobility of the resulting proton increases the conductivity. A similar phenomenon occurred with the 1,4-C_2-cyclam complex.[13]

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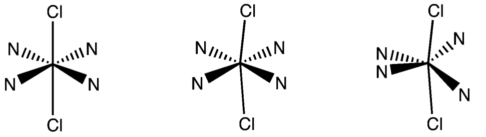

cyclam 1,11-C_3-cyclam 1,4-C_2-cyclam

Figure 4. Effect of ligand structure on the coordination-sphere geometry for the dichlorochromium(III) complexes of tetraazamacrocycles.

Table 4. Orbital Energies in Terms of e_σ for Several $[Cr(N_4)Cl_2]^+$ Geometries

	O_h	cyclam	1,11-C_3-cyclam	1,4-C_2-cyclam
$d(z^2)$	3	3.00	2.93	2.88
$d(x^2 - y^2)$	3	2.98	2.96	2.78
Σ(e_g orbitals)	6	5.98	5.89	5.66

Cl−Cr−Cl bond angle, which is 167.6° for the 1,11-C_3-cyclam complex and 168.6° for the 1,4-C_2-cyclam complex. Not surprisingly, there are also significant bond-angle *differences* between the 1,11-C_3-cyclam complex and the 1,4-C_2-cyclam complex (N−Cr−N bond angles for the 1,4-C_2-cyclam complex range from 72.2° to 103.8°) as a result of the differential constraint imposed by the two ligands. Perhaps most significant is the difference in the amount of distortion from planarity in the coordination plane. Whereas for the 1,11-C_3-cyclam complex reported herein the Cr and all four nitrogens are nearly coplanar, in the 1,4-C_2-complex previously reported there is a substantial D_{2d} twist of the N_4 plane with deviations of the four nitrogens of approximately 0.2 Å from the best-fit coordination plane. Thus, there appears to be a significant effect of the ligand constraint on the overall symmetry of the complexes. Because symmetry is often invoked in discussions of photophysical parameters, a quantification of the symmetry differences is in order here.

As demonstrated in Figure 4, the cyclam complex has both a flat coordination plane and linear Cl−Cr−Cl bond; the 1,11-C_3-cyclam complex has a flat coordination plane but a bent Cl−Cr−Cl bond, and the 1,4-C_2-cyclam complex has both a bent Cl−Cr−Cl bond and a coordination plane with a D_{2d} twist.

It is probable that such distortions are driven by the constraint of the macrocycle (vide supra*)* and thus that similar distortions exist with axial ligands other than chloride. The reduction of symmetry evident across Figure 4 can be quantified in the following ways. The maximum symmetry for $[Cr(cyclam)X_2]^+$ is C_{2h}, whereas for the corresponding 1,-11-C_3-cyclam complex, it is C_s, and for the corresponding 1,4-C_2-cyclam complex, it is C_2. However, it is more often the microsymmetry about the central metal that affects selection rules for electronic transitions and band splitting. The reduction in microsymmetry from O_h can be examined using a simple AOM model and calculating the overall increase in energy (in terms of e_σ) of the e_g orbitals for each complex using angular overlap factors (Table 4).[19] Table 4 demonstrates the departure from maximum overlap for each of the complexes using $3e_\sigma$ as the benchmark for maximum octahedral overlap, and this is an indication of departure from O_h symmetry as one moves from left to right through Figure 4.

It is useful also to quantify departures from centrosymmetry. Because the loss of O_h symmetry is not necessarily a departure from centrosymmetry, mean deviations of the trans N−Cr−N angles from 180° have previously been used to quantify losses in centrosymmetry.[20,21] From the crystal structures for the *trans*-$[Cr(N_4)Cl_2]^+$ complexes, the mean deviations from 180° for the three pairs of trans ligands are 0.3° for cyclam,[22] 8.7° for 1,11-C_3-cyclam, and 11.7° for 1,4-C_2-cyclam, indicating a definite loss of centrosymmetry through this series as well.

Aquation Kinetics. We have followed the aquation (eqs 1 and 2) of *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]^+$ in 0.01 M HNO_3 by UV−vis spectroscopy. To simplify the data analysis, the absorbance during aquation was monitored at an isosbestic point (393 nm) for the slower subsequent reaction (vide supra). Plots of $\ln(A_\infty - A_t)$ versus t (measured through at least three half-lives) are linear ($r > 0.998$) and yield a pseudo-first-order rate constant of 1.0×10^{-1} s^{-1}, indicating a half-life for the overall aquation of about 7 s. In the absence of added acid, the rate constant is 9.1×10^{-2} s^{-1}, indicating little effect of pH or a slight base-catalyzed mechanism, as has been observed for the cyclam[18] and 1,4-C_2-cyclam analogues.[13] Because the UV−vis data demonstrate that the first spectrum most closely matches the dichloro complex and that the product (before the subsequent slow decomposition is substantial) resembles *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})(H_2O)_2]^{3+}$, the most likely kinetic explanation is that the first aquation (eq 1) is rate limiting; thus, the observed rate constant is the rate of this first step. A more complete kinetic analysis (Supporting Information) with consideration that this is not an irreversible aquation but an approach to equilibrium yields the same conclusion; the measured rate constant is simply k_1.

It is noteworthy that the rate constant measured here for aquation of *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})Cl_2]Cl$ is of the same order of magnitude as that reported for *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]Cl$ (6.5×10^{-2} s^{-1}),[13] but it is over 6 orders of magnitude greater than that for the corresponding cyclam complex[18] and at least 3 orders of magnitude greater than that for a range of *trans*-$[Cr(RNH_2)_4Cl_2]^+$ complexes.[24] In an earlier manuscript, we attributed this rate acceleration for *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]Cl$ to the bending of the Cl−Cr−Cl bond angle away from linearity and a likely dissociative nature to the aquation mechanism.[13] Molecular modeling supports this theory.

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Table 5. Energies of $[Cr(N_4)Cl_2]^+$ Complexes and 5- and 7-coordinate Reaction Intermediates, Calculated Using the MM2 Force Field[a]

complex	CSD code	MM energy (kcal mol^{-1})	$\Delta E^{\ddagger}$ relative to the cyclam complex	
			5-coordinate	7-coordinate
$[Cr(cyclam)Cl_2]^+$	JOFYIM	18.89		
$[Cr(cyclam)Cl]^{2+}$		15.20	0	
$[Cr(cyclam)Cl_2(H_2O)]^+$		63.91		0
$[Cr(1,4\text{-}C_2\text{-}cyclam)Cl_2]^+$	EKOCEM	53.24		
$[Cr(1,4\text{-}C_2\text{-}cyclam)Cl]^{2+}$		38.49	−11.06	
$[Cr(1,4\text{-}C_2\text{-}cyclam)Cl_2(H_2O)]^+$		101.06		+2.80
$[Cr(1,11\text{-}C_3\text{-}cyclam)Cl_2]^+$	this work	55.49		
$[Cr(1,11\text{-}C_3\text{-}cyclam)Cl]^{2+}$		41.59	−10.21	
$[Cr(1,11\text{-}C_3\text{-}cyclam)Cl_2(H_2O)]^+$		109.73		+9.22

[a] Cr−N metal-based MM2 parameters: strain-free Cr−N length = 2.045 Å, and Cr−Cl length = 2.24 Å. *K*(Cr−N) = 1.00 and *K*(Cr−Cl) = 1.00 (mdyne Å^{-1}). MM calculations were carried out using the program Hyperchem.

Molecular Modeling. Molecular modeling (MM2 force field[25] and PM3 semiempirical method[26] using HyperChem[27]) was performed on the *trans*-$[Cr(N_4)Cl_2]^+$ complexes and their possible associative and dissociative intermediates (Table 5 and Supporting Information) to investigate the likelihood of various mechanisms in both the thermal aquation discussed above and the excited-state relaxation rates discussed later. MM2 calculations using the force constants of Bernhardt and Comba[28] give a very adequate account of the three $[Cr(N_4)Cl_2]^+$ complexes studied here, with root-mean-square deviations of 0.13−0.15 Å between the calculated and observed atomic positions. Cr−N and Cr−Cl bond lengths were reproduced to within 0.03 Å. The increase in strain energy in the MM calculations upon adding a water to give a seven-coordinate intermediate suggests that the rate of hydrolysis for these complexes is cyclam > 1,4-C_2-cyclam ≫ 1,11-C_3-cyclam. On the other hand, for a dissociative mechanism where a Cl^- is lost first to give a five-coordinate intermediate, the rate of hydrolysis is suggested to be cyclam ≪ 1,4-C_2-cyclam ≈ 1,11-C_3-cyclam. The latter certainly resembles the observed order of rate constants more closely, supporting the idea that the mechanism is dissociative.

PM3 calculations also reproduce the structures of the four $[Cr(N_4)Cl_2]^+$ complexes quite well, except that the Cr−L bonds tend to be too short. In attempts to model the seven-coordinate intermediates, it was found that with a large number of different starting structures, the water always moved away from the Cr and became hydrogen bonded to a Cl. Thus, it was not possible to maintain a 7-coordinate intermediate. From calculations on the 5-coordinate intermediates (Supporting Information), the calculated activation energies support the dissociative mechanism indicated by the MM calculations, with a predicted order of cyclam < 1,11-C_3-cyclam < 1,4-C_2-cyclam. In summary, the results here suggest that the aquation mechanism is dissociative and that the faster aquation reaction for the bridged cyclams relative to cyclam is the result of steric repulsion on the coordinated Cl^- ions, which is relieved upon the formation of a five-coordinate intermediate.

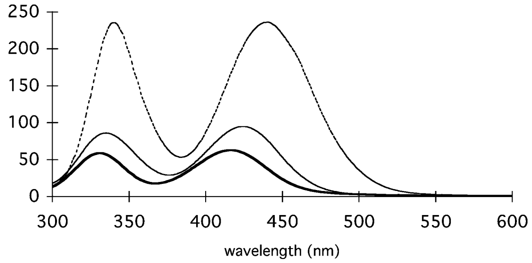

Figure 5. A comparison of the aqueous UV−vis spectra of *trans*-$[Cr(cyclam)(CN)_2]ClO_4$ (—), *trans*-$[Cr(1,11\text{-}C_3\text{-}cyclam)(CN)_2]PF_6$ (—), and *trans*-$[Cr(1,4\text{-}C_2\text{-}cyclam)(CN)_2]PF_6$ (- - -).

Photobehavior. UV−vis Absorption Spectra. One of the more striking observations from the UV−vis data is the monotonic increase in the molar absorptivity on going from the complexes of cyclam to those of 1,11-C_3-cyclam to those of 1,4-C_2-cyclam. This is evident from a comparison within the *trans*-dichloro analogues and within the *trans*-dicyano analogues (Table 3) and is demonstrated graphically for the *trans*-dicyano complexes (Figure 5). There is a strong empirical relationship between the extinction coefficient and the degree of centrosymmetry discussed previously. That is, as one proceeds from the cyclam complex to the 1,11-C_3-cyclam complex to the 1,4-C_2-cyclam complex, there is a loss of centrosymmetry, and one finds a concomitant increase in the molar absorptivity of the complexes. Alhough this is a well-documented relationship,[30] the set of closely related complexes reported herein stands as a clear example of the relaxation of the Laporte selection rule with respect to the loss of centrosymmetry.

There appears also to be a general increase in λ_{max} values as the distortion increases, indicating that the ligand field strength decreases with increased distortion. This can be explained by considering the aforementioned AOM parameters (Table 4) which show a net lowering of the energy of the e_g orbitals for the bridged cyclam complexes versus the cyclam complex. In fact, there is a very strong agreement between the relative band energies and the summed e_σ orbital energies shown in the bottom row of Table 4.

As with the corresponding 1,4-C_2-cyclam complexes,[13] both *trans*-$[Cr(1,11\text{-}C_3\text{-}cyclam)Cl_2]Cl$ and *trans*-$[Cr(1,11\text{-}C_3\text{-}cyclam)(OTf)_2]OTf$ show sharp features ($0.5 < \epsilon < 2$) on the low-energy side of their $^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) absorptions

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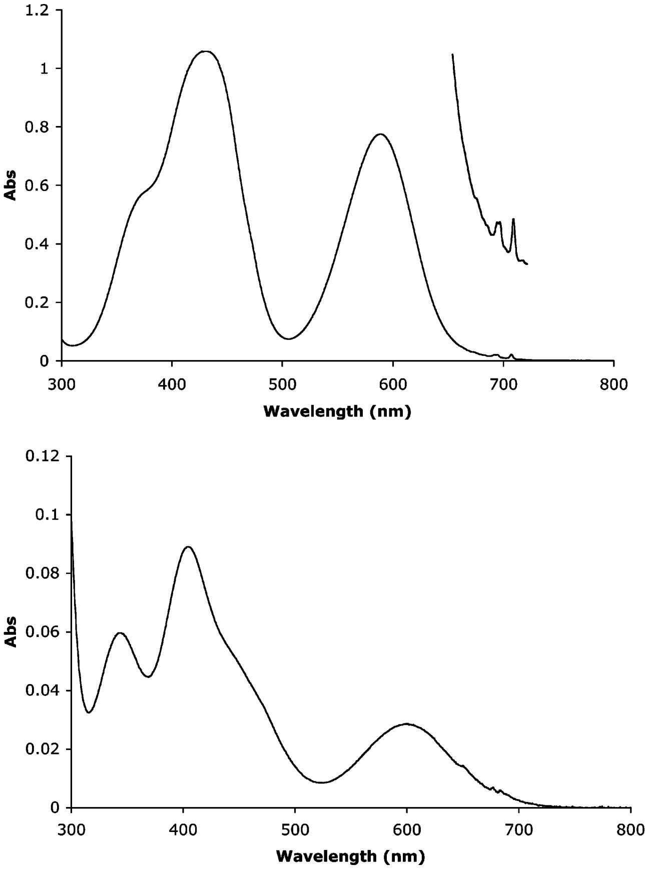

Figure 6. UV-vis spectra of [Cr(1,11-C_3-cyclam)Cl_2]Cl in methanol (top) and [Cr(1,11-C_3-cyclam)$(OTf)_2$]OTf in CH_2Cl_2 (bottom). The solubility limits of the latter preclude spectra with higher absorbances.

(Figure 6). For the ditriflato complex, there is a low-energy pair at 677 and 683 nm and a higher-energy feature at 647 nm. The corresponding C_2-cyclam complex showed nosplitting for the lower-energy feature.[13] For the dichloro complex, there is a low-energy pair at 693 and 707 nm and a higher-energy feature at 672 nm. It is unclear whether the higher-energy feature is unsplit or if only one of the two lines is observed since for the corresponding 1,4-C_2-cyclam complex each of the features is split. Regardless, the difference between the low-energy and high-energy features, as previously discussed for the 1,4-C_2-cyclam complexes,[13] is consistent with the lower-energy features in each case resulting from the spin-forbidden ^2E_g (O_h) state and the high-energy feature resulting from the spin-forbidden $^2T_{1g}$ (O_h) state.[31,32]

Excited-State Behavior. Photophysical data for the *trans*-$[Cr(N_4)(CN)_2]^+$ complexes (where N_4 = cyclam, 1,4-C_2-cyclam, or 1,11-C_3-cyclam) are summarized in Table 6 and Figure 7. As demonstrated in Figure 7, the 1,4-C_2-cyclam and 1,11-C_3-cyclam complexes are dominated by the 0−0 band in contrast to the cyclam complex,[4,5] which shows substantial vibronic structure. This probably reflects the lower symmetry of these complexes as discussed above. The lower-symmetry complexes also exhibit quite broad emissions. It is possible that this breadth reflects a splitting of the ^2E_g energy level which is unresolved.[20,33]

Table 6. Photophysical Data for $[Cr(N_4)(CN)_2]^+$ Complexes

compound	0→0 transition[a] (nm)	τ^b (μs)	τ^c (μs)
[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6	733.1	0.24 E_a = 26 kJ/mol[d]	322
(N-deuterated)		(0.24)	(450)
[Cr(1,11-C_3-cyclam)$(CN)_2$]PF_6	723.6	23 E_a = 33 kJ/mol[e]	535
(N-deuterated)		(23)	(2100)
[Cr(cyclam)$(CN)_2$]ClO_4	716.9[5]	335[4b]	355[4b]
(N-deuterated)		(1500)	(3060)

[a] 77 K in glass dmso/water. [b] Room temperature in solution, H_2O (0.01 M HCl). [c] 77 K in glass dmso/water. [d] Determined by emission intensity vs *T* from 5 to 45 °C. [e] Determined by both emission intensity and lifetime vs *T* from 5 to 65 °C.

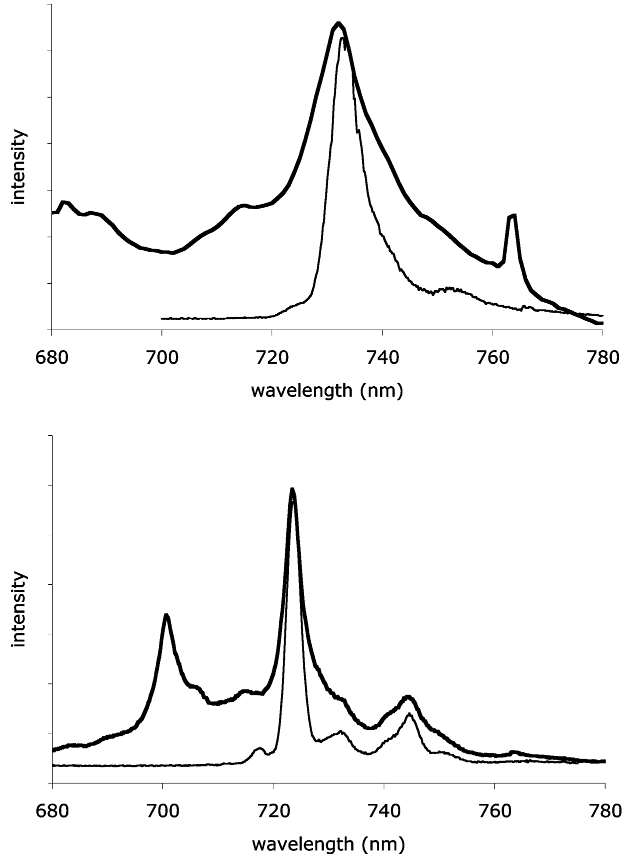

Figure 7. Emission spectra of [Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6, excitation = 440 nm (top) and [Cr(1,11-C_3-cyclam)$(CN)_2$]PF_6, excitation = 425 nm (bottom): solid state at ambient temperature (—) and dmso/water glass at 77 K (—). Room-temperature solution spectra are available in the Supporting Information.

The excited-state decay rates also vary significantly for the macrocyclic complexes discussed herein. At this point, it is helpful to adopt an operationally useful formalism,

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extensively discussed for Cr(III) complexes, whereby the excited-state decay rate constant is broken down into temperature-dependent and temperature-independent components (eq 3).[5,7d,11]

$$\tau^{-1} = k = k(T) + k^{\circ} \tag{3}$$

Here, τ is the observed lifetime, k° is the nearly temperature-independent limiting rate constant for relaxation, and $k(T)$ represents the temperature-dependent term. The term k° can be further broken down into a radiative term, k_r°, and a nonradiative term, k_{nr}°, and $k(T)$ takes into account all temperature-dependent terms.[7d]

Let us begin with a discussion of the 77 K lifetimes for the complexes in Table 6. The inverse of these lifetimes approximates k°. For complexes of the type discussed herein, where the ^2E_g (O_h) excited state and $^4A_{2g}$ (O_h) ground state have very similar geometries, the nonradiative relaxation involves tunneling from the excited state to the ground state and is significantly affected by high-frequency vibrations. Typically, the more N−H oscillators in a complex, the lower the lifetime.[11,34] Deuteration of these N−H bonds increases the lifetime. A comparison of the cyclam complex with the 1,11-C_3-cyclam complex reveals that the lifetime of the 1,11-C_3-cyclam complex (two N−H bonds) is noticeably longer than that of the corresponding cyclam complex (four N−H bonds) as expected from the total number of high-frequency oscillators in each. In addition, upon deuteration, the lifetime increases by a factor of 2 for each N−H available for isotopic substitution, that is, the lifetime of the cyclam complex increases just over 8-fold, whereas the 1,11-C_3-cyclam complex increases almost 4-fold. Thus, the comparison of these two complexes is consistent with expectations based on the number of N−H bonds.

The lifetime data for the 1,4-C_2-cyclam complex, on the other hand, does not fit with this explanation. Although it also has only two N−H oscillators, just like the corresponding 1,11-C_3-cyclam complex, its 77 K lifetime is *less* than that of the cyclam complex, and it shows a very modest deuterium isotope effect. One possible explanation is that k_r° is large enough for this complex to compete with k°_{nr}. Why might this effect show up for the 1,4-C_2-cyclam complex and not the cyclam complex or the 1,11-C_3-cyclam complex? The value of k_r should increase with a decrease in the centrosymmetry of the complex[10] because of the direct dependence of k_r on the oscillator strength.[35] Given the effect of the Laporte selection rule on the molar absorptivities of the *trans*-$[Cr(N_4)(CN)_2]^+$ discussed above, it is likely that the oscillator strength of the lower-symmetry 1,4-C_2-cyclam complex will be the largest, and thus, k_r will be the largest.

The most significant differences in photobehavior are evident in the $k(T)$ term. Whereas the excited-state lifetime of the cyclam complex is essentially identical at 77 K and room temperature, there is an approximately 20-fold reduction in lifetime for the 1,11-C_3-cyclam complex and a greater than 1000-fold reduction for the 1,4-C_2-cyclam complex over the same temperature range. Thus, there exists a thermally activated decay mechanism with the constrained complexes herein, whereas such a process is only of very minor significance with the cyclam complex.

One possibility for the thermally activated relaxation processes is photoreaction. Although the complexes mentioned here do undergo long-term photoaquation in a Rayonet photolyzer (mM acidified aqueous samples in quartz cuvettes with the Rayonet operating at 350 nm), this reactivity is barely perceptible by UV−vis after 30 min and requires several hours to be significant. Using UV−vis, we can estimate the quantum yields to be well below 0.05. These results suggest that it is unlikely that productive photoreaction is the primary source of the decreased lifetimes. It is worth noting here that the possibility of a nonproductive chemical reaction cannot be precluded. The association of water to give a seven-coordinate intermediate followed by rapid relaxation has been previously invoked.[7a,9b,36] The MM2 calculations discussed earlier suggest this is an unlikely mechanism because association should be most facile for the cyclam complex, which in fact has the longest lifetime.[37] Another possibility is photodissociation of one of the Cr−N bonds, followed by rapid recoordination. This is a very credible hypothesis as the topologically constrained $[Cr(N_4)(CN)_2]^+$ complexes are much easier to N-deuterate than their cyclam counterpart (hours stirring in D_2O compared with days). The fact that this thermal reactivity may proceed through making a lone pair available through dissociation may also imply a facile photodissociation.

A second possibility is back-intersystem crossing (bisc) to the $^4T_{2g}$ excited state. The bisc process would certainly have an activation barrier associated with it, but using the 5% absorption procedure[38] to estimate the doublet/quartet energy gap suggests minimum barriers in excess of 80 kJ/mol for each complex. Given that these are more than twice the measured activation barriers (Table 4), bisc seems implausible, in agreement with previous work on cyano-am(m)ine complexes.[5]

A third possibility is the facilitation of nonradiative return to the ground state by symmetry-lowering molecular deformations, a mechanism extensively studied by Endicott and others.[9−11,39] Often, a more rigid environment leads to longer room-temperature lifetimes, for example $Cr(NH_3)_6^{3+}$ doped into the crystal lattice of an inert matrix effectively quenches $k(T)$.[40] This led some to postulate that ligands capable of restricting excited-state distortions would have longer-lived excited states, a suggestion which proved to be correct for

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Table 7. Energies (kcal mol^{-1}) of $[Cr(N_4)Cl_2]^+$ Complexes in the "Flat" Configuration and the 16° "Twisted" Configuration, Calculated Using the MM2 Force Field

complex	flat[a]	16° twisted[a]	difference
$[Cr(cyclam)Cl_2]^+$	18.89[b]	25.04	+6.15
$[Cr(1,11\text{-}C_3\text{-}cyclam)Cl_2]^+$	55.49[b]	65.78	+10.29
$[Cr(1,4\text{-}C_2\text{-}cyclam)Cl_2]^+$	65.40	53.24[b]	−12.16

[a] The equilibrium geometry of the 1,4-C_2-cyclam complex has a N−N−N−N improper torsion angle (improper because the nitrogens are not connected by bonds) of 16°. In the other two complexes, it is very close to 0°. It is this torsion angle that is constrained in the calculations. [b] Indicates equilibrium geometry.

several ligand systems.[9−11,39] For this reason, we had initially considered that the topologically constrained ligand systems discussed herein would lead to long-lived ^2E_g excited states. However, this is not the case. Consequently, it seemed prudent to determine if these ligands indeed imposed a more rigid environment on the complex than the cyclam ligand or if they instead might *facilitate* excited-state distortion. The static distortion observed in the crystal structure of $[Cr(1,4\text{-}C_2\text{-}cyclam)Cl_2]^+$ seemed to be a good candidate for a possible excited-state distortion mode. Using molecular mechanics, we have calculated the energy required for the *trans*-dichlorochromium(III) complexes of cyclam and 1,11-C_3-cyclam to undergo a D_{2d} distortion of the same magnitude as the static structure of 1,4-C_2-cyclam (Table 7). For the cyclam complex, this twist is uphill by 6.15 kcal/mol, whereas for the 1,11-C_3-cyclam complex, it is uphill by 10.29 kcal/mol. Flattening the 1,4-C_2-cyclam complex from its equilibrium-twisted geometry costs 12.16 kcal/mol. Thus, the topologically constrained ligands indeed appear to impart more structural rigidity to the complex, and consequently, it is unlikely that excited-state distortions are the cause of the differences in the $k(T)$ term. Although the above evidence does not rule out dynamic distortion as a means of promoting nonradiative relaxation, it seems unlikely that the more topologically constrained ligands, the complexes of which demonstrate shorter lifetimes, would facilitate such a process.

Conclusions

The ligand set presented herein poses a unique opportunity to study the effects of topological constraint on a set of complexes of octahedral geometry. When the topological constraint imposes a steric repulsion on the coordinated chloride ligands there is an effect on the aquation rates. To the extent that topological constraint affects centrosymmetry, there is an effect on the transition-selection rules as demonstrated by the intensities of the absorption bands and the possible effect on k_r for the *trans*-$[Cr(1,4\text{-}C_2\text{-}cyclam)(CN)_2]^+$ complex. In addition, the effect of topological constraint on the emission behavior, although not completely understood, is evident in the extreme differences in excited-state lifetimes of the chromium(III) complexes discussed; this may be the result of facilitating a nonproductive photoreaction such as the photodissociation of a macrocyclic nitrogen.

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Supporting Information Available: UV−vis spectra as a function of time for the aquation of *trans*-$[Cr(1,11\text{-}C_3\text{-}cyclam)Cl_2]^+$, the derivation of the approach to equilibrium for the aquation reaction, results of PM3 semiempirical calculations on the *trans*-$[Cr(N_4)Cl_2]^+$ complexes, results of MM2 calculations on the *trans*-$[Cr(N_4)(CN)_2]^+$ complexes, room-temperature solution emission spectra for *trans*-$[Cr(1,11\text{-}C_3\text{-}cyclam)(CN)_2]^+$ and *trans*-$[Cr(1,14\text{-}C_2\text{-}cyclam)(CN)_2]^+$, and X-ray crystallographic files in CIF format for the structure determination of *trans*-$[Cr(1,11\text{-}C_3\text{-}cyclam)Cl_2]PF_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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