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Effects of Steric Constraint on Chromium(III) Complexes of Tetraazamacrocycles. Chemistry and Excited-State Behavior of 1,4-C_2-Cyclam Complexes[†]

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The synthesis and characterization of several Cr(III) complexes of the constrained macrocyclic ligand 1,4-C_2-cyclam = 1,4,8,11-tetraazabicyclo[10.2.2]hexadecane is reported. The ligand appears to form only trans complexes, and the structure of *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]PF_6$ is presented. The constraint imposed by the additional C_2 linkage distorts the bond angles significantly away from the ideal values of 90 and 180°. The effect of the distortion is to enhance the aquation rate of *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]^+$ (k_{obs} for *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(H_2O)_2]^{3+}$ formation $= 6.5 \times 10^{-2}$ s^{-1}, 0.01M HNO_3, 25 °C) by over 5 orders of magnitude relative to *trans*-$[Cr(cyclam)Cl_2]^+$. The complexes *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]^+$ and *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(CN)_2]^+$ are found to have extinction coefficients four to five times higher than their cyclam analogues, owed to the lack of centrosymmetry caused by the steric constraint. The *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(CN)_2]^+$ complex is a very weak emitter in aqueous solution with a broad room-temperature emission centered at 735 nm ($\tau = 0.24$ μs). Extended photolysis (350 nm, 15 h) of *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(CN)_2]^+$ in aqueous solution results in CN^- ligand loss. This is in stark contrast to its unconstrained cyclam analogue, which is photoinert and has a room-temperature emission lifetime of 335 μs.

Introduction

Over the past several decades, complexes of Cr(III) have been studied extensively and have been of key importance in understanding general photochemical principles, particularly the relationship between excited-state behavior and molecular structure.[1] Cyclam complexes of Cr(III) have been of particular interest due to exceptionally long ^2E_g excited-state lifetimes and low photoreactivity, both of which have been attributed to the resistance of the tetradentate cyclam ligand to photolabilization. These complexes have also demonstrated a remarkable increase in their excited-state lifetimes upon N-deuteration.[2,3] Extensive studies of these types of complexes by Endicott and co-workers have been directed toward determining the effect that stereochemical alterations have on excited-state characteristics with the goal of being able to design ligand systems to produce desired excited-state behavior.[4,5] Several other groups have also taken advantage of the photobehavior of these types of complexes. Recently, we have shown that energy-transfer self-exchange rate constants can be measured or bracketed with the complexes *trans*-$[Cr(cyclam)(NH_3)_2]^{3+}$, *trans*-$[Cr(cyclam)(CN)_2]^+$, and *trans*-$[Cr(tet\ a)F_2]^+$ by monitoring exchange between the longer lived deuteriocomplex and the shorter

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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; tet a = *C-meso*-5,7,7,12,14,14- hexamethyl-1,4,8,11-tetraazacyclotetradecane; OTf = triflate = trifluoromethanesulfonate; DMF = dimethylformamide; THF = tetrahydrofuran.

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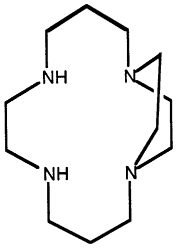

Figure 1. 1,4-C_2-Cyclam.

lived protiocomplex.[6] Additionally, Ford et al. have shown that the nitrito complexes of Cr(III) cyclam undergo reversible NO photolabilization,[7] a fact attributed to the suppressed amine labilization of cyclam.[8]

Because of the prominence of Cr(III) complexes in photophysical and photochemical studies, and our results that demonstrate that these systems allow the rare opportunity to study energy-transfer self-exchange dynamics, we have endeavored to prepare and study a new set of Cr(III) complexes of *constrained* cyclam ligands. In light of the aforementioned studies by Endicott,[4,5] we are particularly interested in the effect that ligand constraint has on the chemistry and excited-state behavior of the Cr(III) complexes, with the goal of finding additional systems with which we can measure self-exchange rate constants. Herein we present the synthesis and characterization of chromium complexes of 1,4,8,11-tetraazabicyclo[10.2.2]hexadecane (hereafter referred to as 1,4-C_2-cyclam; Figure 1), a constrained cyclam ligand first prepared by Wainwright,[9] and demonstrate the significant effect that the steric constraint of the ligand has on molecular geometry, substitution chemistry, electronic spectra, photophysics, and photochemistry.

Experimental Section

Materials and Methods. All materials were reagent grade and were purchased and used as received. All reactions were performed on the benchtop 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 and excitation 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 as the excitation source a Photon Technology International (PTI) GL-3300 pulsed nitrogen laser fed into a PTI GL-302 dye laser. The dye laser was operated at 440 nm, corresponding to $^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) excitation of *trans*-[Cr(1,4-C_2-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 $^4A_{2g} \rightarrow {}^4T_{1g}$ (O_h) excitation of *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]$^+$. Elemental analyses were performed by Atlantic Microlabs in Norcross, GA, or Midwest Microlabs in Indianapolis, IN.

Synthesis of 1,4-C_2-cyclam. The synthesis was carried out by a slight modification of the literature procedure.[9] A 250 mL round-bottom flask was charged with cyclam (4.47 g, 22.3 mmol), ethylene glycol di-*p*-tosylate (8.26 g, 22.3 mmol), ethanol (45 mL), and acetonitrile (53 mL). The mixture was refluxed with stirring under nitrogen for 72 h. The purification steps were performed as in the literature except that ether was used as the extraction solvent and sublimation performed for 20 h at 50 °C (30 mTorr). White crystals were washed from the sublimation probe at regular intervals using methylene chloride. Evaporation of the methylene chloride followed by drying in vacuo resulted in 1,4-C_2-cyclam as a white solid (1.33 g, 26%).

Synthesis of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl·H_2O. 1,4-C_2-cyclam (1.60 g, 7.07 mmol) was placed in a 25 mL round-bottom flask and dissolved in dry DMF (18 mL). $CrCl_3(THF)_3$ (2.21 g, 5.90 mmol) was added slowly with stirring and the mixture was refluxed under nitrogen for 15 min. The resulting thick green slurry was vacuum-filtered and washed with dry DMF (5 mL), acetone (2 × 5 mL), and Et_2O (2 × 8 mL). The crude solid (1.77 g) was redissolved in CH_3OH (57 mL) to which an equal volume of Et_2O was added. The solution was refrigerated overnight and gravity filtered, leaving behind a brownish purple residue. The filtrate was collected and the solvent removed by rotary evaporation until a saturated solution was obtained, and Et_2O was added to precipitate the product. The resulting green precipitate was collected by vacuum filtration, yielding *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl as a green powder (1.45 g, 53%). Anal. Calcd (found) for $C_{12}H_{28}Cl_3CrN_4O$: C, 35.79 (36.07); H, 7.01 (6.93); N, 13.91 (13.90); Cl, 26.41 (26.89).

Synthesis of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]PF_6. *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl (0.998 g, 2.59 mmol) was placed in a 50 mL beaker and dissolved in 3 M NaCl (4.0 mL). While the solution was stirred, a saturated aqueous solution of ammonium hexaflourophosphate (3.0 mL) was added slowly after which a green slurry formed immediately. The mixture was stirred for 5 min and then refrigerated for 15 min. The green solid was collected by vacuum filtration and washed with H_2O (3 × 5 mL), C_2H_5OH (2 × 4 mL), and Et_2O (2 × 5 mL) to yield *trans*-[Cr(1,4-C_2-cyclam)Cl_2]PF_6 as a green powder (1.09 g, 88%). X-ray quality crystals were grown by diffusion of ether into an acetonitrile solution of the complex. Anal. Calcd (found) for $C_{12}H_{26}Cl_2CrF_6N_4P$: C, 29.16 (28.78); H, 5.30 (5.29); N, 11.34 (11.15); Cl, 14.35 (14.06).

Synthesis of *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6. *trans*-[Cr(1,4-C_2-cyclam)Cl_2]PF_6 (0.304 g, 0.616 mmol) was added to a small vial and dissolved in dry DMF (2.2 mL). Finely ground sodium cyanide (0.094 g, 1.92 mmol) was added slowly with stirring. The mixture was stirred for 15 min followed by refrigeration at 0 °C for 15 min. The solids were removed using a medium fritted filter and discarded. To the red brown filtrate was added ether until precipitation of a brown yellow solid was complete. The solvent was decanted and the solid dissolved in CH_3CN (6 mL). Ether (30 mL) was added to precipitate the product. The resulting dark yellow solid was collected on a medium fritted filter and washed with ethanol until the washes ran clear (7 × 5 mL) yielding crude *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6 (0.163 g). The dark yellow solid was dissolved in a minimum amount of warm water (5 mL) and gravity filtered. To this yellow brown solution was added NH_4PF_6 (0.68 g). The mixture was refrigerated overnight, and the resulting bright yellow crystals were collected by vacuum filtration, washed with ice cold water (0.5 mL), ethanol (3 × 5 mL), and ether (5 mL) to yield pure *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6 as bright yellow crystals (0.071 g, 24%). Anal. Calcd (found) for $C_{14}H_{26}CrF_6N_4P$: C, 35.37 (35.15); H, 5.51 (5.52); N, 17.68 (17.40).

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(9) Wainwright, K. P. *Inorg. Chem.* **1980**, *19*, 1396−1398.

Table 1. Crystallographic Data for [Cr(1,4-C_2-cyclam)Cl_2]PF_6

formula	$C_{12}H_{26}Cl_2CrF_6N_4P$
fw	494.24
cryst syst	orthorhombic
space group	*Pbca*
a (Å)	12.389(4)
b (Å)	13.087(5)
c (Å)	24.520(6)
V (Å^3)	3975.7(23)
Z	8
D_{calc} (g/cm^3)	1.651
T (°C)	25
μ (mm^{-1})	0.984
R1[a] (F_o) ($I > 2\sigma(I)$)	0.0819
wR2[b] (F_o^2) ($I > 2\sigma(I)$)	0.2165

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$, $a = 0.1502$, and $b = 17.9193$.

Synthesis of *trans*-[Cr(1,4-C_2-cyclam)$(OTf)_2$]OTf. A flask fitted with a nitrogen bubbler was charged with *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl (0.453 g, 1.12 mmol) and 10 g of trifluoromethanesulfonic acid from a freshly opened ampule. Nitrogen was bubbled through the green solution for 40 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 = 0.70 g, 86%). The deliquescent solid slowly turns purple in contact with moisture and was immediately transferred to a drybox to avoid aquation. Anal. Calcd (found) for $C_{15}H_{26}CrF_9N_4O_9S_3$: C, 24.83 (24.58); H, 3.61 (3.63); N 7.72 (7.39).

X-ray Crystallography. X-ray data were acquired at ambient temperature using a Siemens/Bruker AXS P4 four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for absorption using the semiempirical method XABS2.[10] The structure was solved by direct methods[11] and Fourier difference maps.[11] Refinements were performed by full-matrix least-squares on F^2.[11] The hexafluorophosphate anion was highly disordered, so its bond lengths and angles were restrained to be the same in each orientation. The disorder was modeled with four orientations with site occupancies of 0.47, 0.26, 0.17, and 0.10. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in ideal positions (C−H, 0.97 Å; N−H, 0.91 Å; $U_H = 1.2U_{\text{attached C or N}}$) and were not refined. Crystallographic data are summarized in Tables 1 and 2, and a thermal ellipsoid plot[11] 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(1,4-C_2-cyclam)Cl_2]Cl. To a cuvette of water or 0.01 M HNO_3 (temperature = 25 °C) was added enough solid *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl to give a concentration of approximately 2×10^{-3} M. The cuvette was shaken to dissolve the material and placed in the UV−vis spectrophotometer. Spectral monitoring was begun within 5 s of mixing, and points were taken at 1 or 2 s intervals. Plots of $\ln[A(t)_{380} - A(\infty)_{380}]$ vs time were linear through four half-lives ($r \geq 0.998$).

Results and Discussion

Syntheses. The ligand 1,4-C_2-cyclam has been synthesized by a modification of the literature procedure.[9] Alhough our yields are no better than those reported by Wainwright,[9] in our hands we were able to obtain slightly higher yields when we substituted ethylene glycol di-*p*-tosylate for 1,2-dibromoethane and changed the reaction and extraction solvents. Metalation using $CrCl_3(THF)_3$ proceeded in good yield following the procedure used for cyclam by Ferguson and Tobe.[12] However, in contrast with the insertion of Cr(III) into cyclam, where the predominant isomer formed is *cis*-[Cr(cyclam)Cl_2]Cl, single-crystal X-ray diffraction of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]PF_6 demonstrates that the 1,4-C_2-cyclam ligand has adopted the trans configuration. This is in agreement with the suggestion by Wainwright that 1,4-C_2-cyclam might only adopt the trans conformation for steric reasons.[9] Indeed, the only previously published complex of this ligand, the Ni(II) complex, takes on a trans configuration.[9]

Table 2. Selected Distances (Å) and Angles (deg) for the Complex Cation of [Cr(1,4-C_2-cyclam)Cl_2]PF_6

Bond Lengths			
Cr−N(1)	2.069(6)	Cr−N(4)	2.058(8)
Cr−N(2)	2.091(7)	Cr−Cl(1)	2.353(2)
Cr−N(3)	2.076(7)	Cr−Cl(2)	2.364(2)
Deviation from Least Squares Plane[a]			
Cr	−0.004(3)	N(3)	0.175(3)
N(1)	0.200(4)	N(4)	−0.198(4)
N(2)	−0.173(4)		
Bond Angles			
N(1)−Cr−N(2)	102.7(3)	N(1)−Cr−N(3)	168.3(3)
N(2)−Cr−N(3)	83.2(3)	N(2)−Cr−N(4)	168.2(3)
N(3)−Cr−N(4)	103.8(3)	Cl(1)−Cr−Cl(2)	168.55(10)
N(4)−Cr−N(1)	72.2(3)		

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

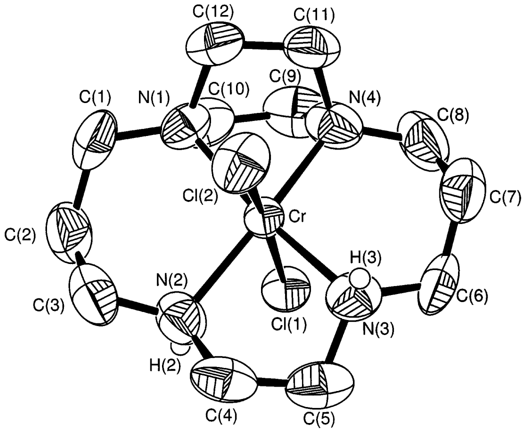

Figure 2. Thermal ellipsoid plot at the 50% probability level for the cation of [Cr(1,4-C_2-cyclam)Cl_2]PF_6. Key hydrogen atoms are shown at ideal positions.

To render the complex soluble in organic solvents for nonaqueous substitution reactions, the metathesis of the Cl^- counterion for PF_6^- was performed in aqueous solution. An excess of NaCl was required in order to suppress the aquation reaction (vide infra).

$$\textit{trans}\text{-}[\mathrm{Cr(1,4\text{-}C_2\text{-}cyclam)Cl_2}]\mathrm{Cl} + \mathrm{NH_4PF_6} \xrightarrow{\mathrm{NaCl}} \textit{trans}\text{-}[\mathrm{Cr(1,4\text{-}C_2\text{-}cyclam)Cl_2}]\mathrm{PF_6} + \mathrm{NH_4Cl} \quad (1)$$

We were particularly interested in preparing the dicyano

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(10) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Cyrstallogr.* **1995**, *28*, 53−56.

(11) *SHELXTL Software*, Version 5.03; (Siemens) Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1994.

complex because of the unique photochemical behavior of the corresponding cyclam complex.[2] Subsequent ligand exchange of Cl^- for CN^- (eq 2) using a modification of the literature scheme for the analogous cyclam complex[2a] gave the desired compound in moderate yield.

$$\textit{trans}\text{-}[\mathrm{Cr}(1,4\text{-}\mathrm{C_2}\text{-cyclam})\mathrm{Cl_2}]\mathrm{PF_6} + 2\mathrm{NaCN} \rightarrow \textit{trans}\text{-}[\mathrm{Cr}(1,4\text{-}\mathrm{C_2}\text{-cyclam})(\mathrm{CN})_2]\mathrm{PF_6} + 2\mathrm{NaCl} \quad (2)$$

In addition, we have prepared the trifluoromethanesulfonate salt, *trans*-[Cr(1,4-C_2-cyclam)(OTf)$_2$]OTf, by the metathesis of chlorides using trifluoromethanesulfonic acid (eq 3).[13] This salt is soluble in methylene chloride and should provide a route into many other trans-disubstituted Cr^{III}(1,4-C_2-cyclam) complexes.

$$\textit{trans}\text{-}[\mathrm{Cr}(1,4\text{-}\mathrm{C_2}\text{-cyclam})\mathrm{Cl_2}]\mathrm{Cl} + 3\mathrm{HOTf} \rightarrow \textit{trans}\text{-}[\mathrm{Cr}(1,4\text{-}\mathrm{C_2}\text{-cyclam})(\mathrm{OTf})_2]\mathrm{OTf} + 3\mathrm{HCl} \quad (3)$$

The following sections will demonstrate the effect of the additional C_2 linkage on the physical and chemical properties of these complexes, as well as on the excited-state behavior of the dicyanide complex.

Solid-State Structure of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]-PF_6. The X-ray structure (Figure 2) confirms the trans-configuration initially suggested as the most likely conformation for this macrocycle. To our knowledge, this is the first reported structure of a complex of this ligand. Several structures of the related $[Cr(cyclam)Cl_2]^+$ have been reported (each with a different counterion: nitrate,[14] tetrachlorozincate,[14] and bromide,[15]), which are internally consistent with respect to bond distances and bond angles, and provide an excellent basis for comparison with the 1,4-C_2-cyclam complex.[16] Comparison demonstrates that the average coordination sphere bond lengths of [Cr(1,4-C_2-cyclam)Cl_2]$^+$ have changed very little relative to the cyclam analogue. For example, the average Cr−N bond distance for each of the aforementioned cyclam complexes is 2.066 Å, whereas in the 1,4-C_2-cyclam complex that average is 2.074 Å. Furthermore, the Cr−Cl bond lengths in the cyclam complexes range from 2.332 to 2.347 Å, whereas the average Cr−Cl distance is 2.358 Å in the 1,4-C_2-cyclam complex. This slight bond lengthening is not terribly impressive and likely cannot account for the significant changes in physical and chemical properties we observe (vide infra).

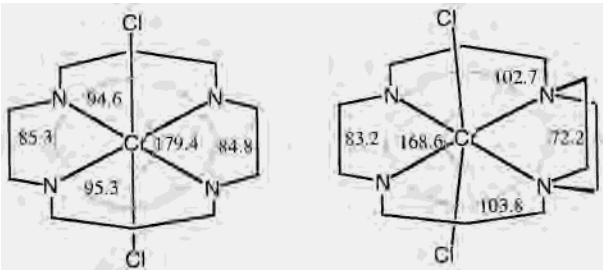

Figure 3. Comparison of coordination sphere bond angles (deg) between $[Cr(cyclam)Cl_2]NO_3$[14] and [Cr(1,4-C_2-cyclam)Cl_2]PF_6.

In contrast to the rather small bond length changes, there is a significant distortion in the coordination sphere bond angles which *could* account for the observed chemical and physical properties. This distortion is demonstrated by a comparison of the structure of $[Cr(cyclam)Cl_2]NO_3$[14] with the 1,4-C_2-cyclam complex (Figure 3). Note that the N−Cr−N bond angle subtended by the additional C_2 linkage has been reduced to 72° from approximately 85° in the cyclam complex, resulting in a distortion of the remaining N−Cr−N bond angles even further away from the ideal of 90°. The C_2 linkage also affects the Cl−Cr−Cl bond which is reduced to 168.6° from the value of 179.4° in the cyclam complex in Figure 3 (the Cl−Cr−Cl bond angle is in fact the expected value of 180° in the tetrachlorozincate and bromide cyclam complexes[14,15]). Another striking distortion caused by the constraint is a twisting of the CrN_4 surface away from planarity. This D_{2d} distortion is evidenced by the significant positive deviation of N(1) and N(3) together with the significant negative deviation of N(2) and N(4) from the least squares plane (Table 2). This results in N(1)−Cr−N(3) and N(2)−Cr−N(4) bond angles significantly lower than the ideal value of 180° (Table 2). This combination of a small bond lengthening and significant bond angle distortion reduces the degree of metal−ligand orbital overlap and has significant effects on the properties of this complex, as will be demonstrated in the following sections.

Substitution Chemistry. When the green *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl is dissolved in water, there is a color change from green to purple that is complete within 1 min. Presumably this is due to aquation (eqs 4 and 5).

$$\textit{trans}\text{-}[\mathrm{Cr}(\mathrm{N_4})\mathrm{Cl_2}]^{+} + \mathrm{H_2O} \rightleftharpoons \textit{trans}\text{-}[\mathrm{Cr}(\mathrm{N_4})(\mathrm{H_2O})\mathrm{Cl}]^{2+} + \mathrm{Cl}^{-} \quad (4)$$

$$\textit{trans}\text{-}[\mathrm{Cr}(\mathrm{N_4})(\mathrm{H_2O})\mathrm{Cl}]^{2+} + \mathrm{H_2O} \rightleftharpoons \textit{trans}\text{-}[\mathrm{Cr}(\mathrm{N_4})(\mathrm{H_2O})_2]^{3+} + \mathrm{Cl}^{-} \quad (5)$$

Conductivity and UV−vis absorption data support this hypothesis. Whereas a methanolic solution of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl remains green and demonstrates a conductivity consistent with two ions, purple aqueous solutions of the same compound have conductivities consistent with dissociation of both chloride ligands.[17] A UV−vis spectrum of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl in water closely resembles the UV−vis spectrum of *trans*-[Cr(1,4-C_2-cyclam)(H_2O)$_2$]-

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(12) Ferguson, J.; Tobe, M. L. *Inorg. Chim. Acta* **1969**, *4*, 109−112.

(13) For prior examples of this type of metathesis see: (a) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrence, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470−476. (b) Ryu, C. K.; Endicott, J. F. *Inorg. Chem.* **1988**, *27*, 2203−2214.

(14) Flores-Vélez, L. M.; Sosa-Rivadeneyra, J.; Sosa-Torres, M. E.; Rosales-Hoz, M. J.; Toscano, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3243−3247.

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(16) A complex with a thiocyanate counterion has several bond lengths and angles which are inconsistent with the others and is not included in this discussion. Bouckaert, J.; Maes, D.; Lisgarten, J. N.; Chattopadhyay, T. K., Palmer, R. A.; Mazid, M. A.; Gazi, D. M. *Acta Crystallogr.* **1993**, *C49*, 1361−1363.

(17) The molar conductivity, Λ_M, of aqueous solutions of the hydrolysis product is 566 cm^{-1} mol^{-1} Ω^{-1}, indicative of five ions. The high value is not unusual given that such complexes are acidic and the high mobility of the resulting proton increases the conductivity.

Table 3. UV−Vis Spectral Data for Cr(III) Tetraazamacrocycle Complexes

complex	λ_{max} (ϵ)[a]	ref
trans-$[Cr(cyclam)Cl_2]Cl$[b]	568 (20.0); 404 sh (29.0); 366 (32.8)	20
trans-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]Cl$[c]	604 (107); ∼447 sh (70); 388 (191)	this work
trans-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]PF_6$[d]	607 (103); ∼439 sh (80); 386 (185)	this work
trans-$[Cr(cyclam)(CN)_2]ClO_4$[b]	414 (62.5); 328 (62.5)	2a
trans-$[Cr(1,4\text{-}C_2\text{-cyclam})(CN)_2]PF_6$[b]	439 (236); 339 (233)	this work
trans-$[Cr(1,4\text{-}C_2\text{-cyclam})(OTf)_2]OTf$[e]	618 (75.0); ∼415 sh (115); 365 (265)	this work
trans-$[Cr(1,4\text{-}C_2\text{-cyclam})(H_2O)_2](OTf)_3$[f]	561 (85); ∼522 sh (82); ∼387 sh (112); 366 (119)	this work
trans-$[Cr(1,4\text{-}C_2\text{-cyclam})(H_2O)_2](OTf)_3$[g]	557 (111); 389 (130); 372 (128)	this work

[a] Absorption wavelengths in nm; extinction coefficients 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*-$[Cr(1,4\text{-}C_2\text{-cyclam})(OTf)_2]OTf$ in H_2O (9.2×10^{-3} M), peak shapes are slightly concentration dependent, which is likely due to the pH-dependent formation of *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(H_2O)(OH)]^{2+}$. [g] Obtained by dissolving *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(OTf)_2]OTf$ in 0.01 M HNO_3.

$(OTf)_3$ prepared by dissolving *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(OTf)_2]OTf$ in water (Table 3). Finally, addition of excess NaCl to an aqueous solution of the hydrolysis product results in a color shift from purple back to green, indicating that the aquation reactions are equilibria, a fact that was utilized synthetically in the counterion metathesis reaction (eq 1).

We have measured the pseudo-first-order rate constant for the formation of *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(H_2O)_2]^{3+}$ from *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]^{+}$ in 0.01 M HNO_3 to be 6.5×10^{-2} s^{-1}, indicating a half-life for the overall aquation of about 11 s. In the absence of added acid the rate constant is slightly faster, 8×10^{-2} s^{-1}, indicating a base-catalyzed mechanism as has been observed for the cyclam analogue.[18] Because the isosbestic points indicate a simple A → B process and because UV−vis data indicate that the final product under both sets of conditions is *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(H_2O)_2]^{3+}$, two possibilities for the identity of k_{obs} are indicated. Either (1) k_{obs} corresponds to the first step of aquation (eq 4) and the second step is too fast to observe or (2) the first step in aquation occurs rapidly, before the initial spectrum in the kinetic sequence is collected, and k_{obs} corresponds to the second step in aquation (eq 5). For the corresponding cyclam analogue, both steps are slow, but $k_1 > k_2$ so that the *trans*-$[Cr(cyclam)(H_2O)Cl]^{2+}$ can be observed spectroscopically.[12,18] This would suggest that case 2 may operate for the 1,4-C_2-cyclam aquation reported herein. However, this is inconsistent with the spectral data (see Supporting Information) which show that the first spectrum after mixing closely resembles the spectrum of *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]^{+}$ in methanol. Thus, for this reaction we favor the case 1 explanation, i.e., that $k_1 \ll k_2$, and therefore $k_{obs} = k_1$. Regardless, for the corresponding cyclam complex, the aquation is much slower and the room-temperature rate constant for the *first* step in its aquation has been estimated at 2×10^{-8} s^{-1} under acidic conditions, and the second step is presumably slower.[18]

The significant acceleration for the aquation rate of the 1,4-C_2-cyclam complex is likely due to a reduced bond strength of the axial chlorides, resulting from a bending of the Cl−Cr−Cl bond angle away from its ideal value of 180°.[19] Another example of the rate acceleration caused by the 1,4-C_2-cyclam ligand is that substitution of the Cl^- ligand by CN^- requires less forceful conditions for the 1,4-C_2-cyclam complex (room temperature) than for the corresponding cyclam complex (62 °C).[2a]

Electronic Spectroscopy. UV−vis absorption spectra (Table 3) for both $[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]Cl$ and $[Cr(1,4\text{-}C_2\text{-cyclam})(CN)_2]PF_6$ appear remarkably similar in shape to the corresponding cyclam complexes and show no additional splitting due to the reduced symmetry. (Noteworthy is that in order to obtain the spectrum of the dichloro complex, methanol was used as the solvent due to the rapid aquation that occurs in water.) However, both spectra are red-shifted relative to their cyclam analogues, indicative of a weaker ligand field due to poorer metal−ligand orbital overlap, as suggested in the structural discussion.

Another obvious difference from the cyclam analogues is the intensity of the d−d bands. The molar absorptivities for the d−d bands of the dichloro complex are more than five times greater than the corresponding cyclam complexes; the molar absorptivities for the dicyano complex have increased almost 4-fold vs the cyclam analogue (Table 3). We attribute this to the loss of centrosymmetry in these complexes and a concomitant relaxation of the Laporte selection rules. These complexes in fact belong to the noncentrosymmetric and chiral C_2 point group.

Particularly noteworthy are the sharp features on the low-energy side of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) absorption for the UV−vis spectra of *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})Cl_2]Cl$ in methanol and *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(OTf)_2]OTf$ in methylene chloride, as shown in Figure 4. These small sharp peaks ($0.5 < \epsilon < 2$ M^{-1} cm^{-1}) likely arise from the spin-forbidden transitions to the ${}^2T_{1g}$ (O_h) and ${}^2E_g$ (O_h) states, with the energy separation between the states being approximately the same for both complexes. For the triflate complex, the energy difference between the weak absorbances (653 and 691 nm) is 840 cm^{-1}. For the chloride complex, the weak absorbances appear to cluster as two pairs (661, 671 and 696, 709 nm). The difference between the lowest energy peak in each pair is about 800 cm^{-1}. This is consistent with other simple amine and ammine complexes of Cr(III), where the ${}^2T_{1g}$ (O_h) state typically appears 200 to 1000 cm^{-1} above the ${}^2E_g$ state.[21]

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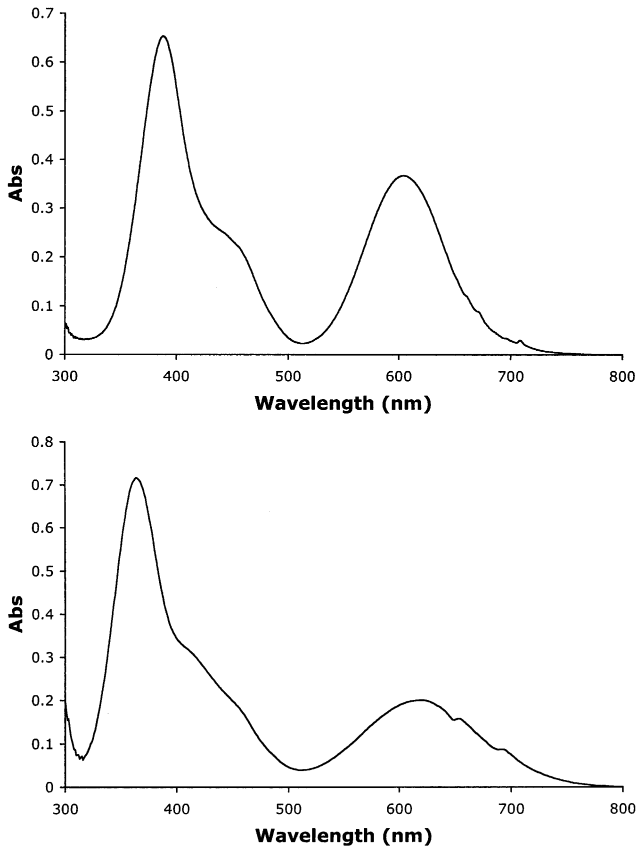

Figure 4. UV-vis absorption spectra of [Cr(1,4-C_2-cyclam)Cl_2]Cl (top) in CH_3OH and [Cr(1,4-C_2-cyclam)$(OTf)_2$](OTf) in CH_2Cl_2 (bottom).

These features are not apparent in the solution spectra of the dicyano or diaquo complexes.

Studies of Excited-State Behavior. The synthesis of the dicyano complex was undertaken due to the unique photobehavior of the corresponding cyclam complex[2] and the contention that one of the chief pathways for nonradiative relaxation of such Cr(III) cyclam complexes is through coupling with high-frequency N−H vibrations.[2,22] We had hoped that this new complex with fewer amine hydrogens would also have a long excited-state lifetime and be useful as a possible photosensitizer. Initial room-temperature studies of its luminescence in both aqueous and acidified (0.01 M HCl) aqueous environments reveal a very weak emission at 735 nm. The maxima of the excitation spectrum reasonably matched those of the absorption spectrum, indicating that the luminescence is from the dicyano complex and not an impurity. Because of the similarity in emission wavelength with the corresponding cyclam complex (720 nm),[2] this 735 nm emission is likely to be $^2E_g \rightarrow {}^4A_{2g}$ (O_h) phosphorescence, though emission from the $^2T_{1g}$ level cannot be ruled out at this time. A room-temperature emission lifetime of 0.24 μs was measured using a pulsed laser excitation source operating at 440 nm. The intensity and lifetime data markedly contrast that of the corresponding cyclam complex, which has a *strong* emission with a lifetime of 335 μs in room-temperature acidified aqueous solution.

The rather short lifetime led us to search for possible reactivity out of the excited state. Extended 350 nm photolysis (15 h) of a 1 mM acidified (0.01 M HCl) aqueous solution of [Cr(1,4-C_2-cyclam)$(CN)_2$](PF_6) resulted in significant spectral changes (from λ_{max} = 439 and 339 nm to λ_{max} = 558 and 370 nm), whereas a sample left in the dark for the same time period showed only a 2 nm shift, suggesting a much slower thermal reaction. The UV−vis spectrum of the final purple solution closely resembles the spectrum of [Cr(1,4-C_2-cyclam)$(H_2O)_2$]$(OTf)_3$ in acidic solution, indicating photochemical CN^- loss. Such reactivity is intriguing because the corresponding cyclam complex is photoinert under the same conditions,[2] but is perhaps not surprising considering the greatly enhanced ground-state lability of the *trans*-[Cr(1,4-C_2-cyclam)Cl_2]Cl relative to its cyclam counterpart. Kutal and Adamson[23] have noted a correlation of excited-state chloride loss in *trans*-[CrN_4Cl_2]$^+$ complexes with ground-state aquation rate constants. However, this slow photoreactivity may not be the chief reason for the short lifetimes. There have been several recent reports of short-lived ^2E excited states of macrocyclic polyamine complexes of Cr(III) where photoreaction was not the reason for the short lifetimes.[5, 24]

Conclusions

The effect of the additional C_2 linkage is to cause structural distortions which reduce the level of overlap between Cr(III) and the ligands. The resulting weakening of the bonds is evident in the UV−vis spectra and substitution chemistry, and also has a marked effect on the excited-state behavior. We are continuing our studies of the excited-state behavior of these complexes as well as making an effort to prepare and characterize the complexes of the recently reported 1,11-C_3-cyclam ligand,[25] which has a three-carbon bridge spanning the 1 and 11 nitrogens of the cyclam macrocycle.

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Supporting Information Available: UV−vis spectra of *trans*-[Cr(1,4-C_2-cyclam)$(OTf)_2$]OTf in water and 0.01 M HNO_3, UV−vis spectra as a function of time for the aquation of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]$^+$, and X-ray crystallographic files in CIF format for the structure determination of *trans*-[Cr(1,4-C_2-cyclam)Cl_2]PF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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