

for coordination to the metal ion. Clearly, the steric preferences of sulfur in a ligand of this type are incompatible with the donor sites occupying three positions coplanar with a metal atom, as would be required for meridional coordination, for coordination around one square-planar center, or for a tetradentate mode of coordination in which the sulfur atom is bridging between two square-planar centers as found in  $\text{Pt}_2\text{Cl}_4(\mu\text{-SEt}_2)_2$ .<sup>24</sup>

We conclude that the diol **4** is a useful tridentate ligand for the preparation of complexes of first-row transition metals, requiring a facial mode of coordination that provides favorable geometry at the central sulfur atom. The total coordination

number of the resulting complex is limited to 5 by the bulk of the ligand.

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**Supplementary Material Available:** Tables of temperature factors (Table S-I), hydrogen atom coordinates and temperature factors (Table S-II), interatomic distances and angles associated with the  $\text{CF}_3$  groups (Table S-III), and  $10|F_o|$  and  $10|F_c|$  (Table S-IV) (14 pages). Ordering information is given on any current masthead page.

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## Synthesis, Characterization, and Photobehavior of *cis*- and *trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) and Some Related Compounds<sup>1</sup>

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The Cr(III) complexes *cis*- and *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>, where cyclam is the macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane, have been synthesized by the reaction of liquid ammonia with the corresponding bis(nitrato)-Cr(III) species. The photophysical and photochemical behaviors of these compounds have been examined in some detail. Both isomers exhibit strong <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> (O<sub>h</sub>) phosphorescence in room-temperature solution. The emission of the *trans* species is exceptionally intense and very long lived (136 μs, Me<sub>2</sub>SO, 20 °C). Both the intensity and lifetime of this *trans* emission display a remarkable 12-fold enhancement in Me<sub>2</sub>SO (20 °C) on N-H deuteration. This latter emission signal is in fact detectable with the naked eye and corresponds to a phosphorescence quantum yield at 20 °C of φ<sub>p</sub> = 2.3 × 10<sup>-2</sup> (comparable to Ru(bipyridine)<sub>2</sub><sup>2+</sup>). The corresponding *cis* species has a much shorter emission lifetime in room-temperature solution and displays only a weak deuterium isotope effect. Photochemically the two isomers also differ dramatically—the *trans* complex is photoinert, while the *cis* species exhibits facile NH<sub>3</sub> release (φ<sub>NH<sub>3</sub></sub> = 0.2, aqueous solution, room temperature). These contrasting photobehaviors are compared with those previously reported for Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Cr(en)<sub>3</sub><sup>3+</sup>, and the macrobicyclic sepulchrate ligand system Cr(sep)<sup>3+</sup>. Several different schemes for <sup>2</sup>E<sub>g</sub> excited-state decay are examined as possible rationalizations for these observations.

### Introduction

Considerable debate continues over the question as to which excited state(s) is (are) responsible for the observed photochemistry of octahedral Cr(III) complexes.<sup>2</sup> It has proven especially difficult to design experiments that identify unambiguously the state(s) responsible for the photoreaction component that is quenched on selective <sup>2</sup>E<sub>g</sub> (O<sub>h</sub>) excited-state quenching.<sup>2-7</sup> The relative merits of two alternative explanations for this reaction component—namely direct <sup>2</sup>E<sub>g</sub> reaction or “delayed” quartet reaction via <sup>2</sup>E<sub>g</sub> → <sup>4</sup>T<sub>2g</sub> back intersystem crossing (back-ISC)—have been argued for several years.<sup>2</sup> Both pathways have been advanced as rationalizations for the short lifetime and significant temperature dependence generally observed for <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> phosphorescence in room-temperature solutions. Very recently, Endicott and co-workers<sup>7</sup> have proposed a third model for <sup>2</sup>E<sub>g</sub> relaxation that involves vibrationally promoted surface crossing to a ground-state intermediate species, with subsequent partitioning between reaction and nonradiative relaxation to product and parent

ground-state surfaces, respectively.

As one approach to this problem we have recently examined the photobehavior of *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub>, where cyclam is the macrocyclic tetradentate amine ligand 1,4,8,11-tetraazacyclotetradecane.<sup>8</sup> The choice of this particular complex for investigation followed from consideration of current theoretical models for predicting Cr(III) photochemical reactivity<sup>2,9,10</sup> and recent experimental data<sup>11,12</sup> for the analogous nonmacrocyclic systems *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> and *trans*-Cr(en)<sub>2</sub>(CN)<sub>2</sub><sup>+</sup>. These latter complexes differ from most Cr(III) amine species in that the axial cyanide ligands have stronger ligand field (LF) strengths than the in-plane amine ligands, and theory predicts (as experimentally observed)<sup>11,12</sup> that photolabilization should be predominantly restricted to the in-plane amine positions. We were hopeful that for the cyclam analogue the presence of the macrocyclic ring would seriously restrict cleavage of an individual Cr-amine bond and render cyclam ligand loss highly improbable.

In keeping with this expectation, *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> displayed no discernible photochemical reactivity under LF excitation and exhibited an exceptionally intense, long-lived (340

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$\mu\text{s}$ ), essentially temperature-independent phosphorescence signal in aqueous solution.<sup>8</sup> Furthermore, deuteration of the cyclam N-H protons resulted in a 5-fold increase in the intensity and lifetime of the solution phosphorescence signal at 22 °C. Several alternative schemes were examined as rationalizations of the differences in photobehavior between *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> and the nonmacrocylic systems *trans*- and *cis*-Cr(en)<sub>2</sub>(CN)<sub>2</sub><sup>+</sup>. It was considered probable that back intersystem crossing was inefficient in both the en and cyclam complexes due to the large spectroscopic gap between the lowest excited quartet and lowest doublet level.<sup>13</sup> On this basis, direct reaction out of the <sup>2</sup>E<sub>g</sub> level was regarded as the most likely cause of the relatively short room-temperature lifetimes of *cis*- and *trans*-Cr(en)<sub>2</sub>(CN)<sub>2</sub><sup>+</sup> in room-temperature solution.<sup>8</sup>

The general objective of the present study has been to extend these photochemical studies to include other macrocyclic Cr(III) systems also expected to be photoinert in room-temperature solution. Unfortunately, the number of systems electronically similar to *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> is seriously restricted, since few ligands have stronger LF strengths than amines. A more productive approach may therefore be to extend such studies to the more common macrocyclic amine systems where the strongest LF strength resides in the amine plane. The photochemistry of nonmacrocylic complexes of the type *trans*-CrN<sub>4</sub>X<sub>2</sub><sup>+</sup> (where N = amine such as NH<sub>3</sub>; X = Cl<sup>-</sup>, Br<sup>-</sup>, NCS<sup>-</sup>) has been well documented<sup>2,15,16</sup> and involves exclusive loss of the X<sup>-</sup> ligands on the z axis (as theoretically predicted). For such systems displaying z-axis labilization, replacement of the in-plane amines by the macrocyclic amine cyclam might not appear to offer much promise with regard to developing a photoinert system. However, for all nonmacrocylic *trans*-CrN<sub>4</sub>X<sub>2</sub><sup>+</sup> complexes examined to date, X<sup>-</sup> ligand loss is accompanied by *trans* → *cis* isomerization.<sup>2,15,16</sup> Thus, the corresponding *trans*-Cr(cyclam)X<sub>2</sub><sup>+</sup> species may conceivably exhibit minimal X<sup>-</sup> photolabilization due to the macrocyclic ring presenting steric resistance to isomerization. Suppression of X<sup>-</sup> ligand loss has in fact been clearly demonstrated for the one cyclam species of this type previously investigated. In 1973 Kutal and Adamson<sup>17</sup> reported the quantum yield for Cl<sup>-</sup> release from *trans*-Cr(cyclam)Cl<sub>2</sub><sup>+</sup> was a factor of 1000 less than that for the NH<sub>3</sub> and en analogues and involved only *trans*-Cr(cyclam)(Cl)(H<sub>2</sub>O)<sup>2+</sup> product formation. It appears that the presence of the cyclam ring indirectly protects the molecule against Cl<sup>-</sup> ligand loss by introducing steric restraints against the *trans* → *cis* substitution reaction pathway normally favored energetically.

However, studies on *trans*-Cr(cyclam)Cl<sub>2</sub><sup>+</sup> were restricted by the absence of detectable phosphorescence under photochemically significant conditions. The specific objective of the present work has therefore been to synthesize the complex *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>. For this compound theory predicts preferential NH<sub>3</sub> ligand photolabilization, since NH<sub>3</sub> is lower in the spectrochemical series than cyclam (from a comparison of the visible absorption spectra of *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> and *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>3+</sup>).<sup>18</sup> However, in keeping with prior observations on the dichloro analogue,<sup>17</sup> a near-photoinert system is anticipated in fluid solution. In addition, the compound is expected to exhibit strong room-temperature solution phosphorescence since it contains a CrN<sub>6</sub> chromophore analogous to that present in the species Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Cr(en)<sub>3</sub><sup>3+</sup>. These last two species are known to display strong phosphorescence in fluid solution.<sup>4,18,19</sup> A detailed

comparison between the photobehavior of *trans*-Cr(cyclam)-(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> and that of the chromophorically similar Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Cr(en)<sub>3</sub><sup>3+</sup> complexes might help resolve some of the controversy concerning the actual photochemical role of the <sup>2</sup>E<sub>g</sub> excited state in these last two compounds. Deuterium isotope studies on the intensity and lifetime of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> phosphorescence in room-temperature solution may also prove valuable. If <sup>2</sup>E<sub>g</sub> excited-state relaxation is primarily via <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> decay (a weak coupled process), then the deuterium isotope effect observed may be significantly greater than that found for *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup>, since the *trans*-diamine complex contains six additional N-H bonds subject to deuteration.<sup>21-23</sup>

A related objective has been to synthesize and examine the photobehavior of the corresponding *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> species. Since, in general, *cis*-CrN<sub>4</sub>X<sub>2</sub><sup>+</sup> complexes undergo photosubstitution with little or no *cis* → *trans* isomerization,<sup>2,15,16</sup> then we anticipate some NH<sub>3</sub> loss for *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>. If this photoreactivity involves in part direct reaction out of the <sup>2</sup>E<sub>g</sub> level, then the emission lifetime and deuterium isotope effect for the *cis* complex could be substantially smaller than that for the *trans* compound. Many of these experimental expectations have in fact been confirmed during the course of the present study. The details and possible significance of these observations are discussed below.

### Experimental Section

**Reagents.** The free ligand cyclam and CrCl<sub>3</sub>·3THF were purchased from Strem Chemicals. Ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) was obtained from Alfa Products. D<sub>2</sub>O (99.8 atom % D) was purchased from Aldrich Chemicals. Anhydrous lithium perchlorate was purchased from G. Frederick Smith Co. All other reagents were of analytical grade quality (Fisher Scientific) and were used without further purification.

**Measurements.** All UV-vis absorption spectra were recorded with a Cary 118C spectrophotometer. A Perkin-Elmer 283 infrared spectrophotometer was used to obtain infrared spectra. KBr pellets were prepared in a Beckman KBr press (Model K-13) pressurized to 20 000 lb with a Carver Model K press.

A Markson Model 4403 Electromark Analyzer was used to measure conductance values. The elemental analyses for C, H, N, and F were performed by Midwest Microlabs. The equipment and procedures for obtaining steady-state emission spectra and emission lifetimes have been described elsewhere.<sup>8,24</sup> Photolysis procedures have also been described previously.<sup>24</sup>

**Syntheses.** The parent complexes *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub><sup>18</sup> and *cis*-[Cr(cyclam)Cl<sub>2</sub>]Cl<sup>25</sup> were prepared by literature methods.

***trans*-[Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>.** The preferred method of preparing the diaquo complex involves acid hydrolysis of *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub>.<sup>18</sup> A 0.34-g sample (8.5 × 10<sup>-4</sup> mol) of *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub> was dissolved in 20 mL of 0.1 M HClO<sub>4</sub> and heated to ~80 °C for 6-8 h while the solution was magnetically stirred. The solution was evaporated to near-dryness and then cooled in an ice bath for 20 min. The orange crystals were collected by suction filtration, washed with ether (40 mL), and air-dried; yield 0.29 g, 4.9 × 10<sup>-4</sup> mol (58%). The UV-vis spectrum agreed with literature values.<sup>25</sup>

**Caution!** ClO<sub>4</sub><sup>-</sup> salts are potentially explosive.

***trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·2H<sub>2</sub>O.** A 0.493-g sample (1.22 × 10<sup>-3</sup> mol) of *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub> was dissolved in 16.5 mL of 7.5 M HNO<sub>3</sub> and heated, while the solution was stirred, to near-dryness (to 2-3 mL of liquid). The solution was covered and allowed to cool to room temperature and crystallize. The crystals were collected by suction filtration, washed with 200 mL of acetone and 200 mL of ether, and then air-dried; yield 0.330 g, 6.70 × 10<sup>-4</sup> mol (55%). Anal. Calcd for CrC<sub>10</sub>H<sub>28</sub>N<sub>7</sub>O<sub>11</sub>: C, 25.32; H, 5.95; N, 20.67. Found: C, 25.02; H, 5.83; N, 21.21.

***cis*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O.** A 0.77-g sample (2.16 × 10<sup>-3</sup> mol) of *cis*-[Cr(cyclam)Cl<sub>2</sub>]Cl was added to 12 mL of water in a 50-mL beaker. AgNO<sub>3</sub> (1.14 g, 6.70 × 10<sup>-3</sup> mol) was dissolved in 12 mL of water, and 10 drops of concentrated HNO<sub>3</sub> was added. The two solutions

- (13) The actual energy barrier to back-ISC will be less than or equal to this spectroscopic energy gap. However, it is noteworthy that the spectral gap for *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> is significantly larger than that for Cr(bpy)<sub>3</sub><sup>3+</sup> (bpy = 2,2'-bipyridine), where back-ISC is considered highly unlikely.<sup>2,14</sup>
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were mixed together and heated at 90 °C for 2.5 h in order to remove both coordinated and ionic Cl<sup>-</sup> as insoluble AgCl. Celite filter aid was added to the solution, which was then filtered. Next, 15 mL of concentrated HNO<sub>3</sub> was added to the filtrate and the solution heated until the volume was reduced to ~5 mL. The solution was left at room temperature overnight, during which time copious crystallization of the bis-(nitrate) product occurred. The crystals were stirred with a small volume of acetone, collected by suction filtration, and washed with ether; yield 0.935 g, 2.13 × 10<sup>-3</sup> mol (98%). Anal. Calcd for CrC<sub>10</sub>H<sub>25</sub>N<sub>7</sub>O<sub>9.5</sub>: C, 26.85; H, 5.63; N, 21.92. Found: C, 26.99; H, 5.27; N, 21.83.

**trans-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>.** *Caution!* Initially, the crude *trans*-diammine complex was isolated as a ClO<sub>4</sub><sup>-</sup> salt. This ClO<sub>4</sub><sup>-</sup> salt was sent off for microanalysis, and we were subsequently informed that 2 mg of sample had exploded upon heating, destroying the quartz sample holder in the combustion chamber. Therefore, due to the possibly high explosive nature of the ClO<sub>4</sub><sup>-</sup> salt even at room temperature, all further isolations and crystallizations were carried out with NH<sub>4</sub>PF<sub>6</sub> to obtain the PF<sub>6</sub><sup>-</sup> salt.

**trans-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)(NO<sub>3</sub>)<sub>2</sub>·1/2H<sub>2</sub>O.** A 0.400-g sample (8.12 × 10<sup>-4</sup> mol) of *trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·3H<sub>2</sub>O was reacted with liquid NH<sub>3</sub> by condensing gaseous NH<sub>3</sub> with a liquid-N<sub>2</sub>-chloroform slush trap (-64 °C), which allowed the liquid NH<sub>3</sub> to drop down onto the solid *trans*-bis(nitrate) complex. Once enough liquid NH<sub>3</sub> had been collected to totally immerse the parent *trans*-bis(nitrate) solid, the NH<sub>3</sub> condensation was discontinued and the solution magnetically stirred for 15 min. Next, the liquid NH<sub>3</sub> was allowed to evaporate, leaving behind the bright yellow *trans*-diammine complex product. This solid *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> was dissolved in 3 mL of water, the solution was filtered to remove impurities, and the product was precipitated with excess NH<sub>4</sub>PF<sub>6</sub>. The PF<sub>6</sub><sup>-</sup> salt of the complex was collected by suction filtration and washed with acetone (20 mL) and ether (40 mL); yield 0.359 g, 6.36 × 10<sup>-4</sup> mol (78%). Anal. Calcd for CrC<sub>10</sub>H<sub>31</sub>N<sub>8</sub>F<sub>6</sub>PO<sub>6.5</sub>: C, 21.28; N, 5.54; N, 19.86. Found: C, 21.63; H, 5.78; N, 19.60.

**N-H-Deuterated trans-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>.** A 0.212-g sample (3.40 × 10<sup>-4</sup> mol) of *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)(NO<sub>3</sub>)<sub>2</sub>·1/2H<sub>2</sub>O was dissolved in 3 mL of D<sub>2</sub>O (99.8% deuterated), and the solution was left standing for 1 h in a stoppered glass vial. The ClO<sub>4</sub><sup>-</sup> salt of the deuterated sample was precipitated with excess anhydrous LiClO<sub>4</sub> and collected by suction filtration. In some early deuteration attempts this initial solid was washed with acetone and ether, but this procedure invariably led to inefficient deuteration (<70%) as determined from IR studies in the N-H and N-D stretch regions.<sup>8,20</sup> Subsequently, a high percent of deuteration (>90%) was obtained if the washing step was eliminated, and the ClO<sub>4</sub><sup>-</sup> solid product while still on the filter paper was dried on a vacuum line overnight; yield 0.058 g. *Caution!* This ClO<sub>4</sub><sup>-</sup> salt should be handled with extreme caution and only in very small quantities. It is strongly recommended that in future the deuterated complex be isolated as a PF<sub>6</sub><sup>-</sup> salt.

**cis-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)·H<sub>2</sub>O.** A 0.400-g sample (8.94 × 10<sup>-4</sup> mol) of *cis*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·1/2H<sub>2</sub>O was reacted with liquid NH<sub>3</sub> as previously described for the corresponding *trans*-diammine complex. The liquid NH<sub>3</sub> on evaporation left behind the yellow *cis*-diammine solid product. This solid was dissolved in ~5 mL of water, the solution was filtered, and excess NaBF<sub>4</sub> was added; but no product precipitated. The solution was then filtered again to remove impurities and placed in a refrigerator overnight. Yellow crystals of the BF<sub>4</sub><sup>-</sup> salt were collected the next day and were washed with a small volume of acetone; yield 0.105 g, 1.94 × 10<sup>-4</sup> mol (22%). Anal. Calcd for CrC<sub>10</sub>H<sub>32</sub>N<sub>7</sub>O<sub>6</sub>B<sub>2</sub>F<sub>8</sub>: C, 22.25; H, 5.97; N, 18.16. Found: C, 22.16; H, 5.73; N, 18.05.

**cis-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>).** A 0.400-g sample (8.94 × 10<sup>-6</sup> mol) of *cis*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·1/2H<sub>2</sub>O was reacted with liquid NH<sub>3</sub> as previously described for the corresponding *trans*-diammine complex. The liquid NH<sub>3</sub> was evaporated, leaving behind the yellow-orange NO<sub>3</sub><sup>-</sup> salt of the *cis*-diammine product. This solid was dissolved in 40 mL of 0.2 M HCl (50 °C), filtered, and precipitated with excess NH<sub>4</sub>PF<sub>6</sub>. (Note: Acid conditions were necessary to prevent possible base hydrolysis of an NH<sub>3</sub> ligand (vide infra).) The solid was collected by suction filtration and washed with a 4:1 ether-acetone solution (10 mL) and then ether; yield 0.32 g, 5.08 × 10<sup>-4</sup> mol (57%). Anal. Calcd for CrC<sub>10</sub>H<sub>30</sub>N<sub>7</sub>P<sub>2</sub>F<sub>12</sub>O<sub>3</sub>: C, 18.81; H, 4.75; N, 15.36; F, 35.72. Found: C, 18.84; H, 4.54; N, 15.58; F, 35.32.

**N-H-Deuterated cis-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>NO<sub>3</sub>.** A sample of *cis*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>) was deuterated by a procedure identical with that described earlier for the *trans* analogue, except that the complex was isolated as a PF<sub>6</sub><sup>-</sup> salt with use of NH<sub>4</sub>PF<sub>6</sub> for precipitation. Infrared analysis indicated the sample was 86% deuterated.

**trans-[Cr(cyclam)(H<sub>2</sub>O)(NH<sub>3</sub>)]Co(CN)<sub>6</sub>·2H<sub>2</sub>O.** A 0.079-g sample (1.4 × 10<sup>-4</sup> mol) of *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)(NO<sub>3</sub>)<sub>2</sub>·1/2H<sub>2</sub>O was

dissolved in 2 mL of 0.1 M NaOH for 5 min at room temperature. The solution was then acidified with 0.5 M HClO<sub>4</sub> and the volume increased to 5 mL with water. To this solution was added 0.044 g (1.32 × 10<sup>-4</sup> mol) of K<sub>3</sub>[Co(CN)<sub>6</sub>] in 4 mL of 0.01 M HClO<sub>4</sub> at room temperature. The yellow-orange crystals that formed upon scratching were collected by suction filtration and washed copiously with water, acetone, and then ether; yield 0.033 g, 6.13 × 10<sup>-5</sup> mol (46%). Anal. Calcd for CrCoC<sub>16</sub>H<sub>33</sub>N<sub>11</sub>O<sub>3</sub>: C, 35.69; H, 6.19; N, 28.62. Found: C, 35.97; H, 5.90; N, 28.23.

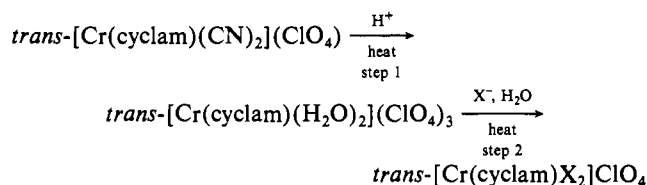
**cis-[Cr(cyclam)(H<sub>2</sub>O)(NH<sub>3</sub>)]Co(CN)<sub>6</sub>·3H<sub>2</sub>O.** A 0.100-g sample (1.57 × 10<sup>-4</sup> mol) of *cis*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>) was dissolved in 3 mL of 0.1 M NaOH for 5 min at room temperature. The solution was then acidified with 0.5 M HClO<sub>4</sub> and the volume increased to 5 mL with water. To this solution was added 0.056 g (1.69 × 10<sup>-4</sup> mol) of K<sub>3</sub>[Co(CN)<sub>6</sub>] in 5 mL of 0.01 M HClO<sub>4</sub> at room temperature. The red-orange crystals that formed upon scratching were collected by suction filtration and washed with a small volume of water and then copiously with acetone and ether; yield 0.046 g, 8.27 × 10<sup>-5</sup> mol (53%). Anal. Calcd for CrCoC<sub>16</sub>H<sub>33</sub>N<sub>11</sub>O<sub>4</sub>: C, 34.54; H, 6.35; N, 27.69. Found: C, 34.42; H, 6.38; N, 27.45.

**[Cr(cyclam)en](NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O.** A 0.200-g sample (4.47 × 10<sup>-4</sup> mol) of *cis*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·1/2H<sub>2</sub>O was added to 1.4 mL of anhydrous ethylenediamine (en) and the mixture stirred with a glass stirring rod for 10 min in a small vial. The resulting yellow solid was collected by suction filtration and washed with acetone (~30 mL) and ether (20 mL); yield 0.193 g, 3.61 × 10<sup>-4</sup> mol (81%). Anal. Calcd for CrC<sub>12</sub>H<sub>36</sub>N<sub>9</sub>O<sub>11</sub>: C, 26.97; H, 6.79; N, 23.59. Found: C, 27.12; H, 6.55; N, 23.54. The complex *cis*-[Cr(cyclam)en](NO<sub>3</sub>)<sub>3</sub> can also be made from the reaction of *trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> with en, but yields are lower (52%).

## Results and Discussion

**Syntheses. A. Trans Complexes.** The isolation of *trans*-Cr(cyclam)X<sub>2</sub><sup>+</sup> species (where X is a monodentate acido ligand) has generally proven to be difficult.<sup>25,26</sup> The traditional route to such complexes has been via the base hydrolysis of *trans*-Cr(cyclam)Cl<sub>2</sub><sup>+</sup> followed by anation with the appropriate anion. However, the parent *trans*-dichloro species is difficult to isolate in high yield. Our recent high-yield preparation of *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub> from readily available *cis/trans*-[Cr(cyclam)Cl<sub>2</sub>]ClO<sub>4</sub> suggests a potentially valuable general route to *trans*-Cr(cyclam)X<sub>2</sub><sup>+</sup> species (Scheme I).<sup>18</sup>

### Scheme I



We found<sup>18</sup> this synthetic route useful for the preparation of *trans*-Cr(cyclam)(NCS)<sub>2</sub><sup>+</sup> and in the present study have expanded this general approach to the *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> complex. Initially, we isolated a sample of solid *trans*-[Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, as shown in step 1 in Scheme I. This solid diaquo complex was then exposed to liquid NH<sub>3</sub> for 30–60 min. However, despite repeated efforts (including the addition in some instances of metallic Na) no samples of the desired *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> product were obtained. This procedure resulted instead in formation of what appeared to be the aquo-amine species *trans*-Cr(cyclam)(H<sub>2</sub>O)(NH<sub>3</sub>)<sup>3+</sup>. Similarly, a complex mixture of products was obtained when *trans*-Cr(cyclam)Cl<sub>2</sub><sup>+</sup> was employed as the parent complex. These results indicate that a better leaving group than coordinated H<sub>2</sub>O or Cl<sup>-</sup> is needed if the diammine product is to be readily obtained.

We subsequently found that the coordinated NO<sub>3</sub><sup>-</sup> group functions as an excellent leaving group in the presence of liquid NH<sub>3</sub>. A solid sample of the orange-red *trans*-[Cr(cyclam)-(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> complex immediately changes to the bright yellow color of *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> on addition of the first few drops of liquid NH<sub>3</sub>. We have also found that coordinated NO<sub>3</sub><sup>-</sup> is readily replaced by H<sub>2</sub>O, Me<sub>2</sub>SO, DMF, or CN<sup>-</sup>, which suggests that coordinated NO<sub>3</sub><sup>-</sup> may prove of general synthetic

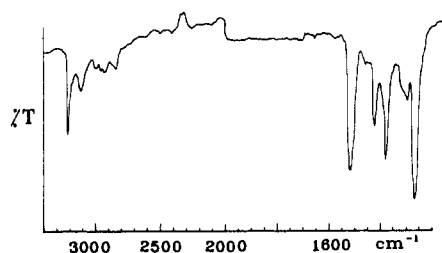
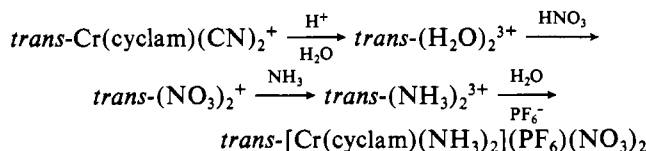


Figure 1. Infrared spectrum (KBr disk) of *trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]-NO<sub>3</sub>·2H<sub>2</sub>O.

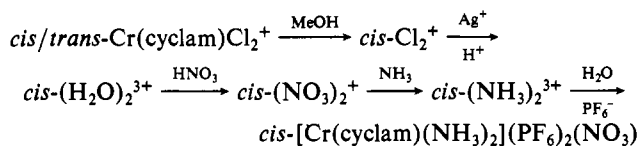
utility as a good leaving group for Cr(III) systems. The overall synthetic scheme finally adopted for the isolation of the *trans*-diammine complex is shown in Scheme II.

**Scheme II.** Synthesis of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>



**B. Cis Complexes.** In keeping with our prior observations on the analogous *trans* systems, the coordinated NO<sub>3</sub><sup>-</sup> group in *cis*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> has also proven to be an excellent leaving group in the presence of liquid NH<sub>3</sub>. In this case, it was necessary to obtain the precursor *cis*-Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> species from *cis*-Cr(cyclam)Cl<sub>2</sub><sup>+</sup>, since the complex *cis*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> has not as yet been reported. The overall synthetic route to *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is shown in Scheme III. It should be noted that Ferguson and Tobe<sup>25</sup> have previously reported the usefulness of *cis*-Cr(cyclam)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub><sup>+</sup> as a starting material for the synthesis of a variety of diacido species.

**Scheme III.** Synthesis of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>



**Characterizations. A. Bis(nitrato) Complexes.** Complexes containing the coordinated NO<sub>3</sub><sup>-</sup> group are known for a variety of transition-metal (TM) ions.<sup>27-30</sup> However, the *cis*- and *trans*-bis(nitrato) species described below are among the first Cr(III) complexes containing bound NO<sub>3</sub><sup>-</sup> (the species [Cr(NH<sub>3</sub>)<sub>5</sub>NO<sub>3</sub>]NO<sub>3</sub> has been reported previously<sup>31,32</sup> as has the complex *cis*-[Cr(cyclam)(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub><sup>25</sup>).

***trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·2H<sub>2</sub>O.** The microanalysis results for the isolated material are consistent with the formulation given above. However, these data are equally consistent with the structures *trans*-[Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>, *trans*-[Cr(cyclam)(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, and *trans*-[Cr(cyclam)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O. The question as to whether zero, one, or two NO<sub>3</sub><sup>-</sup> ions are coordinated may be addressed by examining the infrared absorption spectrum of the product. As summarized by Nakamoto,<sup>30</sup> there are characteristic bands for uni- and bidentate nitrate in the region between 1550 and 1000 cm<sup>-1</sup>. We assign two such bands observed for the solid product (KBr disk) at 1515 and 1270 cm<sup>-1</sup> to the presence of coordinated NO<sub>3</sub><sup>-</sup>. These assignments are essentially identical with those given by Ferguson

Table I. UV-Visible Spectral Data for Cr(III) Ammine Complexes and Related Species in Aqueous Solution

complex	λ <sub>max</sub> <sup>a</sup>	ref
Cr(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	463 (39), 351 (33)	36
Cr(en) <sub>3</sub> <sup>3+</sup>	456 (76), 350 (61)	36
<i>trans</i> -Cr(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	454 (47), 347 (37)	36
<i>cis</i> -Cr(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	460 (66), 351 (54)	36
<i>trans</i> -Cr(cyclam)(NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	445 sh (32), 420 (36), 334 (50)	this work
<i>cis</i> -Cr(cyclam)(NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	468 (115), 355 (80) <sup>b</sup>	this work
Cr(cyclam)(en) <sup>3+</sup>	465 (137), 355 (102)	this work
<i>trans</i> -Cr(cyclam)(H <sub>2</sub> O)(NH <sub>3</sub> ) <sup>3+</sup>	477 (23), 409 (28), 339 (41)	this work
<i>cis</i> -Cr(cyclam)(H <sub>2</sub> O)(NH <sub>3</sub> ) <sup>3+</sup>	476 (110), 362 (87)	this work
<i>trans</i> -Cr(cyclam)(H <sub>2</sub> O) <sub>2</sub> <sup>3+</sup>	510 (24), 405 (39), 350 (53)	25
<i>cis</i> -Cr(cyclam)(H <sub>2</sub> O) <sub>2</sub> <sup>3+</sup>	483 (126), 370 (38)	25

<sup>a</sup> Absorption wavelengths in nm. Values in parentheses are the molar absorptivities. <sup>b</sup> (PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>) salt.

and Tobe for the complex *cis*-[Cr(cyclam)(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> isolated under lower NO<sub>3</sub><sup>-</sup> concentration conditions.<sup>25</sup> These two bands are more intense than the corresponding N=O stretch of ionic nitrate, which is observed at 1380 cm<sup>-1</sup> (see Figure 1).

Three structures still require consideration: *trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·2H<sub>2</sub>O (A), *trans*-[Cr(cyclam)(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (B), and *cis*-[Cr(cyclam)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (C). Of these, the bidentate case C may be excluded on the basis of visible spectral evidence. When it is allowed to stand in acidified aqueous solution, the nitrate complex yields a Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> product whose visible spectrum matches closely that of a genuine sample<sup>25</sup> of *trans*-Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> (Table I). In view of the well-documented stereorrigidity of Cr(III) acid hydrolyses<sup>33</sup> and the marked differences<sup>25</sup> in the visible spectra of *cis*- and *trans*-Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>, it may be concluded that the parent nitrate compound has the *trans* configuration. Although a definitive distinction between the *trans* structures A and B is not possible from the infrared data alone, the relative intensities of the coordinated and ionic NO<sub>3</sub><sup>-</sup> stretches are more consistent with formulation A. In addition, the observation that this product converts rapidly and quantitatively to the *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> complex on the addition of liquid NH<sub>3</sub> argues against the presence of coordinated H<sub>2</sub>O.

***cis*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·1/2H<sub>2</sub>O.** The microanalysis data reported earlier are consistent with the formulation given above for the title complex. However, another structure also consistent with this analysis is *cis*-[Cr(cyclam)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>·1/2H<sub>2</sub>O (i.e. bidentate nitrate). An infrared spectrum of the *cis* product (KBr disk) contained the same two bands at approximately 1510 and 1280 cm<sup>-1</sup> as previously reported for *trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·2H<sub>2</sub>O. However, unlike the *trans* analogue the intensities of these two bands are less than that of the corresponding N=O stretch for ionic nitrate at 1380 cm<sup>-1</sup> (see Figure 1). The visible spectrum of the Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> product obtained when the parent nitrate complex is allowed to stand in acidified aqueous solution supports a *cis* geometry. However, this spectrum is not helpful in deciding between unidentate or bidentate NO<sub>3</sub><sup>-</sup> coordination, because a spectrum consistent with a *cis* geometry would result for both cases. However, the bidentate geometry is considered unlikely because the two IR bands characteristic of coordinated NO<sub>3</sub><sup>-</sup> are very similar in energy to the bands noted above for *trans*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·2H<sub>2</sub>O and those described earlier for *cis*-[Cr(cyclam)(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub>.<sup>25</sup>

**B. Diammine and Ethylenediamine Complexes. *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·1/2H<sub>2</sub>O.** The microanalysis data obtained for the yellow product isolated according to Scheme II are consistent with the formulation above, as is also the molar conductance. A 1 × 10<sup>-3</sup> M aqueous solution displayed a molar conductance of 425 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, which is in the range typical

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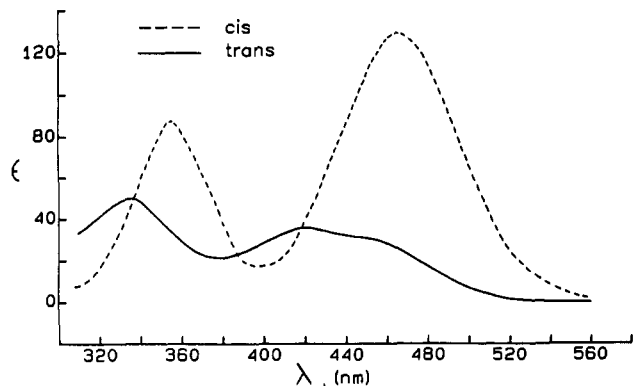
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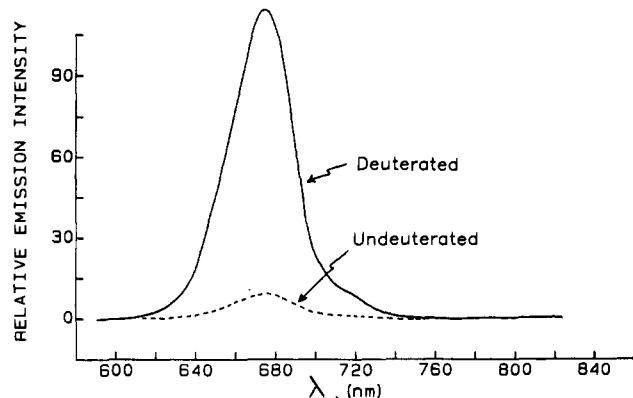
**Figure 2.** UV-visible absorption spectra of *cis*- and *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> in aqueous solution.

for a 3:1 electrolyte. The infrared spectrum (KBr disk) displayed N-H stretches from 3400 to 3000 cm<sup>-1</sup>, aliphatic C-H stretches from 2950 to 2850 cm<sup>-1</sup>, an ionic NO<sub>3</sub><sup>-</sup> band at 1380 cm<sup>-1</sup>, and a P-F stretch at 840 cm<sup>-1</sup>. Poon and co-workers<sup>26,34,35</sup> have explored the use of IR data for geometric configuration assignment and report bands that are characteristic of *trans* cyclam complexes, independent of the central metal, other ligands, and counterions. However, the strong P-F stretch observed in the present product overlaps this critical region so that the *trans* geometry cannot be confirmed by IR spectra.

The UV-visible spectrum of the title compound in aqueous solution is shown in Figure 2, and the data are compared with those for the analogous *cis* species (vide infra) and several related compounds in Table I. The title complex exhibits some splitting in the first LF band at approximately 440 nm (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub>; O<sub>h</sub> symmetry) but no observable splitting in the second LF band at 334 nm (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub>; O<sub>h</sub> symmetry). The splitting of the first d-d transition is not unusual for *trans* complexes due to their reduced symmetry (D<sub>4h</sub>).<sup>37</sup> Also consistent with this *trans* assignment,<sup>38</sup> the absorption bands of the title compound have significantly smaller molar absorptivities than those of the analogous *cis* species (Table I). It is noteworthy that the first d-d band for *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is at a higher energy than that for the ethylenediamine analogue *trans*-Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> (Table I). The macrocycle cyclam therefore lies *higher* in the spectrochemical series than en (or NH<sub>3</sub>), consistent with a higher σ-donor strength for cyclam. This LF strength is in accord with that previously found in the corresponding *trans*-dicyano series of complexes.<sup>18</sup>

Thermally, *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> appears to be inert to loss of coordinated NH<sub>3</sub> in room-temperature neutral or acidic aqueous solution even on prolonged standing. However, by comparison with Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Cr(en)<sub>3</sub><sup>3+</sup>, the complex is remarkably susceptible to base hydrolysis. Even in dilute basic solution, rapid UV-visible spectral changes occur consistent with the loss of one of the coordinated NH<sub>3</sub> ligands, i.e. *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> → *trans*-Cr(cyclam)(OH)(NH<sub>3</sub>)<sub>2</sub><sup>2+</sup>. Release of only one NH<sub>3</sub> was confirmed from analysis of a longstanding basic solution using an Orion ammonia-sensing combination electrode (Model 95-10). On reacidification, a solution of *trans*-Cr(cyclam)(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is obtained whose UV-visible spectrum is intermediate between those of the corresponding diammine and diaquo species (Table I). A solid derivative of the aquo-ammine complex is obtained on adding Co(CN)<sub>6</sub><sup>3-</sup> to this acidified solution (see Experimental Section).

The marked sensitivity of one NH<sub>3</sub> to base hydrolysis suggests that the other bound NH<sub>3</sub> ligand is unusually acidic, a situation that would also rationalize the difficulty encountered in obtaining



**Figure 3.** Steady-state emission spectra of absorbance-matched deuterated (—) and undeuterated (---) *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)(NO<sub>3</sub>)<sub>2</sub> in acidified Me<sub>2</sub>SO solution at 20 °C on 436-nm excitation.

a highly deuterated sample of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>. An X-ray crystallographic study of *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)(NO<sub>3</sub>)<sub>2</sub>/1/2H<sub>2</sub>O may help resolve this question.<sup>39</sup> It is of interest that Ferguson and Tobe have noted a considerable enhancement in the acidity of the coordinated aquo group in Cr(cyclam)(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> relative to that of the corresponding en complex.<sup>25</sup>

As anticipated, the title compound displays strong emission in room-temperature solution assigned to <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> (O<sub>h</sub> symmetry) phosphorescence. An emission maximum is observed at 680 nm (Figure 3), which is in agreement with the presence of an N<sub>6</sub> chromophore about Cr(III) (the corresponding Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Cr(en)<sub>3</sub><sup>3+</sup> species also have an emission maximum near 680 nm).<sup>4,19,20</sup>

**cis-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>)**. The microanalysis results obtained for the yellow product isolated via the procedure in Scheme III are consistent with the formulation above, as is also the molar conductance. A 1 × 10<sup>-3</sup> M aqueous solution displayed a molar conductance of 360 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, which is in the range found for complex 3:1 electrolytes. The IR spectrum displayed N-H stretches from 3560 to 3000 cm<sup>-1</sup>, C-H stretches from 2900 to 2780 cm<sup>-1</sup>, a strong ionic NO<sub>3</sub><sup>-</sup> band at 1360 cm<sup>-1</sup>, and an even stronger P-F stretch at 860 cm<sup>-1</sup>. The relative intensities of the NO<sub>3</sub><sup>-</sup> and P-F absorptions are the reverse of those observed for the *trans* analogue, in keeping with the respective anion compositions. Once again, the strong P-F stretch overlaps the critical region used by Poon and co-workers<sup>26,34,35</sup> to assign geometric configuration, so that the *cis* geometry cannot be confirmed on the basis of IR data.

The UV-visible spectrum of this species is compared with that of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> in Figure 2 and with several related compounds in Table I. The first LF band (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub>; O<sub>h</sub> symmetry) is observed at 468 nm, while the second LF band (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub>; O<sub>h</sub> symmetry) is centered at 355 nm. The molar absorptivities of the two d-d bands are substantially greater than those of the *trans* analogue, consistent with the given geometric assignment. In addition, no splitting is observed in either of these bands. However, the first d-d band for *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is at a lower energy than that for *cis*-Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> (Table I). This result indicates that, for these *cis* systems, cyclam is slightly *lower* in the spectrochemical series than en (or NH<sub>3</sub>). Some precedents for this reversal in LF strength order have been reported elsewhere.<sup>25</sup>

As previously noted for the *trans* complex, the species *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is highly susceptible to rapid base hydrolysis of one of the bound NH<sub>3</sub> ligands. The UV-visible spectrum of the *cis*-Cr(cyclam)(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> product obtained on reacidification is given in Table I. A solid derivative of this aquo-ammine species has been obtained as a Co(CN)<sub>6</sub><sup>3-</sup> salt (see Experimental Section). In interesting contrast to its base sensitivity, the diammine complex is very inert toward NH<sub>3</sub> ligand loss under acidic

(34) Poon, C. K. *Inorg. Chim. Acta* 1971, 5, 322.

(35) Poon, C. K.; Che, C. M. *Inorg. Chem.* 1981, 20, 1640.

(36) Wong, C. F. C.; Kirk, A. D. *Inorg. Chem.* 1978, 17, 1672.

(37) Baker, W. A.; Phillips, M. G. *Inorg. Chem.* 1966, 5, 1042.

(38) Cotton, F. A. "Chemical Applications of Group Theory", 2nd ed.; Wiley: New York, 1971.

(39) Butcher, R. T., work in progress (Howard University).

**Table II.** Phosphorescence Lifetimes (in  $\mu\text{s}$ ) for Various Deuterated and Undeuterated Cr(III) Complexes<sup>a</sup>

compd	T, K	$\tau_{\text{H}_2\text{O}}$	$\tau_{\text{Me}_2\text{SO}}$	$\tau_{\text{DMF}}$	$\tau_{\text{solid}}$
<i>trans</i> -Cr(cyclam)- (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	335	...	15		
	334	2.5	...		
	326	4.0	38		
	320	8.6	...		
	314	...	80		
	311	16	...		
	303	...	116		
	302	32	...		
	293	55	136	108	
	283	88	...		
	77	...	180	169	
deutd <i>trans</i> -Cr(cyclam)- (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	333	3.2			
	324	6.6			
	313	19			
	304	54			
	293	165	1620	810	
	283	468			
<i>cis</i> -Cr(cyclam)(NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	77		3720	3660	
	333	<1	<1		
	293	1.7	1.0	0.8	19 <sup>b</sup>
deutd <i>cis</i> -Cr(cyclam)- (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	77		116		73
	293	2.1	1.2		65 <sup>b</sup>
	77		1580		800
Cr(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup> 20	333		<1		
	297	2.2	4		
	77		70		
Cr(en) <sub>3</sub> <sup>3+</sup> 20	297	1.7	1.5		
	Cr(sep) <sup>3+</sup> 7	295	4.5		
		273			10

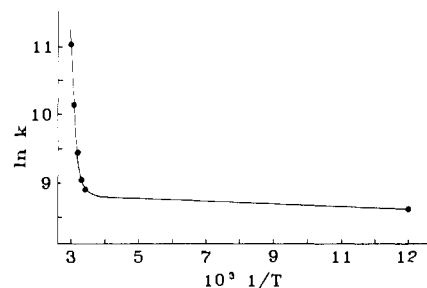
<sup>a</sup> All solutions were acidified to prevent base quenching.<sup>b</sup> (PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>) salt.

solution conditions. Consistent with the presence of a Cr–N<sub>6</sub> chromophore, *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> displays a strong emission signal in room-temperature solution centered at 680 nm.

**[Cr(cyclam)(en)](NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O.** The microanalysis data obtained for the yellow product from the reaction of *cis*-[Cr(cyclam)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> with en are in agreement with the structure given above. In addition, the molar conductance of a 1 × 10<sup>-3</sup> M aqueous solution (395 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) is consistent with the expected 3:1 electrolyte status of the complex. The UV–visible spectrum (Table I) is very similar to that of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>, which provides further support for the geometric assignment of the latter compound. Also as anticipated, the title compound displays strong room-temperature emission with a maximum at 680 nm.

**Photobehavior of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>.** **A. General Observations.** As noted in Characterizations, for *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> the z axis contains the weaker σ-donor ligands, and thus theory predicts preferential NH<sub>3</sub> photolabilization.<sup>10</sup> However, by analogy with the reported behavior of *trans*-Cr(cyclam)Cl<sub>2</sub><sup>+</sup>,<sup>17</sup> the cyclam ring could seriously restrict *trans* → *cis* isomerization, which may lead to an essentially photoinert complex in fluid solution. This expectation appears to have been realized, with no discernible photoreaction observed at 20 °C in acidic aqueous solution after 30 h of LF excitation (365 nm) with a 1000-W Hg–Xe lamp as irradiation source.<sup>24</sup>

Furthermore, the compound displays one of the most intense room-temperature d–d phosphorescence signals in aqueous or Me<sub>2</sub>SO solution of any Cr(III) complex previously reported. At 20 °C and 436-nm excitation, the steady-state emission intensity of an acidified aqueous solution of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> was 13.2 times that of a 436 nm absorbance matched 0.04 M HClO<sub>4</sub> solution of [Cr(en)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>. For the latter compound, Kirk and Porter<sup>40</sup> report a quantum yield for phosphorescence, φ<sub>p</sub>, of 6.2 × 10<sup>-5</sup> in aqueous solution at 20 °C. Thus, in aqueous solution *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> has a φ<sub>p</sub> value of 8.2 × 10<sup>-4</sup> (or an emission efficiency of 0.08%). The emission efficiency is ap-

**Figure 4.** Temperature-dependence plot of the <sup>2</sup>E<sub>g</sub> excited-state lifetime of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> in acidified Me<sub>2</sub>SO.

proximately 2.5 times greater in Me<sub>2</sub>SO solution at 20 °C (φ<sub>p</sub> = 1.9 × 10<sup>-3</sup>) and is also accompanied by a 2.5-fold increase in the emission lifetime (at 20 °C, 55 μs in H<sub>2</sub>O, 136 μs in Me<sub>2</sub>SO; see Table II). This latter observation argues strongly that the higher φ<sub>p</sub> value in Me<sub>2</sub>SO is primarily associated with a decrease in the net radiationless rate constant for <sup>2</sup>E<sub>g</sub> decay, rather than being due to an increase in the quantum yield for <sup>4</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub> ISC, φ<sub>isc</sub>.

The <sup>2</sup>E<sub>g</sub> excited-state lifetimes observed for *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> in room-temperature solution (Table II) are among the longest reported for a Cr(III) complex and are in marked contrast to the short lifetimes under comparable conditions for the analogous nonmacrocyclic systems Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Cr(en)<sub>3</sub><sup>3+</sup> and the hexamine species Cr(sep)<sup>3+</sup>, where sep is a macrobicyclic sepulchrate ligand<sup>7</sup> (Table II). Interestingly, the presence of dissolved O<sub>2</sub> does not decrease within experimental error the phosphorescence lifetime of *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>. This O<sub>2</sub> insensitivity was also noted<sup>8</sup> for *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> and contrasts with the strong O<sub>2</sub> quenching observed for other Cr(III) species known to have long <sup>2</sup>E<sub>g</sub> solution lifetimes, such as Cr(CN)<sub>6</sub><sup>3-</sup> and Cr(phen)<sub>3</sub><sup>3+</sup>.<sup>41-43</sup>

**B. Deuterium Studies.** Significantly, N–H deuteration of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> dramatically influences both the emission intensity and lifetime in fluid solution. The effect of deuteration in Me<sub>2</sub>SO, 0.01 M HClO<sub>4</sub>, and DMF solvent are discussed separately below.

**Me<sub>2</sub>SO Solvent.** In acidified DMSO a 12-fold enhancement in intensity is observed at 20 °C (Figure 3), and emission is in fact detectable with the naked eye. The quantum yield for phosphorescence for the deuterated sample (φ<sub>p</sub> = 2.3 × 10<sup>-2</sup>) is comparable to that for Ru(bpy)<sub>3</sub><sup>2+</sup> and is the largest yet reported for a Cr(III) species in room-temperature solution. In addition, the 12-fold increase in emission intensity on deuteration for *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is substantially larger than that for *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup>, which we had reported earlier<sup>8</sup> as the first example of a strong intramolecular deuterium isotope effect for a Cr(III) complex under these conditions. The larger effect observed in the *trans*-diammine case is consistent with the presence of an additional six N–H bonds subject to deuteration.<sup>21-23</sup>

Importantly, on N–H deuteration the emission lifetime of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> shows an enhancement essentially identical with that found for its emission intensity (from 136 to 1624 μs at 20 °C; Table II). It is therefore reasonable to conclude that φ<sub>isc</sub> remains effectively constant on deuteration and that the increase in phosphorescence intensity results primarily from a decrease in the nonradiative rate constants from the <sup>2</sup>E<sub>g</sub> level. Furthermore, the strong isotope effects observed are characteristic of a dominant weak-coupled deactivation mode for the <sup>2</sup>E<sub>g</sub> state,<sup>20-23</sup> in accord with <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> decay as the principal relaxation pathway; i.e., these observations indicate strong-coupled deactivation processes such as back-ISC and chemical reaction

(41) Wasgestan, H. F. *J. Phys. Chem.* **1972**, *76*, 1947.(42) Serpone, N.; Jamison, M. A.; Sriram, R.; Hoffman, M. Z. *Inorg. Chem.* **1981**, *20*, 3983.(43) The strong π-acceptor environment in Cr(CN)<sub>6</sub><sup>3-</sup> and Cr(phen)<sub>3</sub><sup>3+</sup> may provide more effective communication between dissolved O<sub>2</sub> and the metal-centered <sup>2</sup>E<sub>g</sub> excited state being quenched.(40) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.

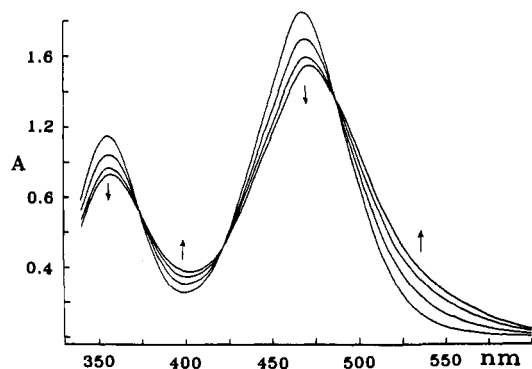


Figure 5. UV-visible spectral changes accompanying 365-nm photolysis of a  $3.20 \times 10^{-3}$  M solution of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> in 0.001 M HClO<sub>4</sub> (5-cm cell) at 22 °C.

are unimportant <sup>2</sup>E<sub>g</sub> relaxation modes in Me<sub>2</sub>SO solution at 20 °C.

In keeping with these conclusions, the emission lifetime and deuteration effect increase only marginally on decreasing the temperature to 77 K (Table II). However, as the temperature is raised above 20 °C, the phosphorescence lifetime and intensity of the undeuterated sample both decrease relatively rapidly with an apparent activation energy between 41 and 63 °C of  $16.0 \pm 1.0$  kcal mol<sup>-1</sup> (Table II and Figure 4). These results require that thermally activated processes play a key role in <sup>2</sup>E<sub>g</sub> deactivation for conditions above room temperature.

**Water Solvent.** In acidified solution at 10 °C the steady-state emission intensity of the deuterated complex is 5.3 times that of the undeuterated complex and an identical isotope effect is observed for the phosphorescence lifetime (Table II). These deuteration effects are significantly smaller than those in Me<sub>2</sub>SO solution at 20 °C and are even smaller in 20 °C aqueous solution (now only a factor of 3; Table II). These results indicate the presence in water of a more significant strong-coupled deactivation pathway at room temperature, which also accounts for the 2.5-fold difference noted earlier between Me<sub>2</sub>SO and H<sub>2</sub>O emission intensities and also lifetimes at 20 °C.

It is noteworthy that in acidic aqueous solution the deuterium isotope effect is virtually absent at temperatures above 60 °C (Table II), consistent with a now dominant role for strong-coupled relaxation processes for the <sup>2</sup>E<sub>g</sub> level. From the plots of  $\ln 1/\tau$  vs.  $1/T$  for the deuterated and undeuterated samples, apparent activation energies of  $19.0 \pm 0.4$  and  $17.5 \pm 1.3$  kcal mol<sup>-1</sup>, respectively, are obtained.<sup>44</sup>

Finally, the emission intensity and lifetime of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> display no discernible solvent isotope effect on changing from acidified H<sub>2</sub>O to acidified D<sub>2</sub>O as solvent at room temperature. The absence of a solvent isotope effect is in keeping with the results of prior studies on Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Cr(en)<sub>3</sub><sup>3+</sup>, and *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup>.<sup>4,8,20</sup>

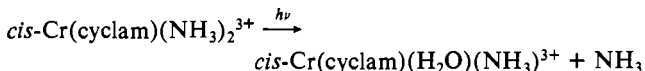
**DMF Solvent.** Only a limited study on the <sup>2</sup>E<sub>g</sub> excited-state lifetime of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> in acidified DMF was carried out, and the results are presented in Table II. At 20 °C, the lifetimes for both deuterated and undeuterated samples in DMF are intermediate between those obtained in H<sub>2</sub>O and Me<sub>2</sub>SO but are considerably closer to the Me<sub>2</sub>SO values. At 77 K, lifetimes are almost identical in DMF and Me<sub>2</sub>SO media (169 and 180 μs, respectively), which indicates that solvent influence on the <sup>2</sup>E<sub>g</sub>  $\omega \rightarrow \omega$  <sup>4</sup>A<sub>2g</sub> radiationless rate constant is minimal.

**Photobehavior of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>.** In marked contrast to the photoinertness of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> described above, we find *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> to be quite photoactive in room-temperature fluid solution. The UV-visible spectral changes accompanying 365-nm photolysis in acidified aqueous solution at 22 °C are shown in Figure 5. Three isosbestic points

Table III. Reaction Quantum Yields for Some Cr-N<sub>6</sub> Chromophore Systems in Room-Temperature Aqueous Solution

compd	φ <sub>NH<sub>3</sub></sub>	φ <sub>en</sub>	ref
Cr(en) <sub>3</sub> <sup>3+</sup>		0.33	2
Cr(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	0.46		2
<i>cis</i> -Cr(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	0.07	0.37	47
<i>trans</i> -Cr(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	0.06	0.40	47
<i>cis</i> -Cr(cyclam)(NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	0.2		this work
<i>trans</i> -Cr(cyclam)(NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	~0		this work

are observed, and the shifts in absorption maxima to longer wavelengths are consistent with replacement of coordinated NH<sub>3</sub> by solvent H<sub>2</sub>O:



Furthermore, the isosbestic point wavelengths are in agreement with those predicted for the net reaction shown, based on known spectral data for parent and presumed product. In addition to the spectral changes shown in Figure 5, 365-nm photolysis of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> results in a steady rise in the solution pH—as anticipated for NH<sub>3</sub> or cyclam ligand release. We have, therefore, been able to estimate a quantum yield for NH<sub>3</sub> release, φ<sub>NH<sub>3</sub></sub> (assuming φ<sub>cyclam</sub> = 0), from spectral changes and the well-known ΔpH method.<sup>45,46</sup> The results are recorded in Table III, along with those for related nonmacrocyclic systems. It is apparent that the LF photoreactivity of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is comparable to that of the nonmacrocyclic complexes listed and differs dramatically from that of the inert *trans* analogue.

In addition, the <sup>2</sup>E<sub>g</sub> excited state of the *cis* species in room-temperature solution is short-lived, with lifetimes similar to those reported for Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Cr(en)<sub>3</sub><sup>3+</sup>, and Cr(sep)<sup>3+</sup> (Table II). These *cis* emission lifetimes are markedly shorter than those for *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> (at 20 °C, τ<sub>trans</sub>/τ<sub>cis</sub> = 136 (Me<sub>2</sub>SO) and 32 (0.01 M HClO<sub>4</sub>)). The corresponding steady-state emission intensities at 20 °C also differ significantly for the *cis* and *trans* isomers, although the differences are not as great as they were for lifetimes (φ<sub>p</sub>(*trans*)/φ<sub>p</sub>(*cis*) = 19 (Me<sub>2</sub>SO) and 4.7 (0.01 M HClO<sub>4</sub>)). Trends in these emission lifetime and intensity ratios for *cis*- and *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> suggest that (i) the <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> (O<sub>h</sub>) radiative rate constant is smaller for the *trans* isomer and/or (ii) the quantum yield for ISC, φ<sub>isc</sub>, is smaller for the *trans* complex.

In keeping with our earlier observations on the *trans* analogue, the phosphorescence lifetime and intensity of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> both decrease relatively rapidly as the temperature is raised above 20 °C. The decrease in the steady-state emission intensity in 0.1 M HClO<sub>4</sub> solution over the temperature range 8–47 °C yields an apparent activation energy of  $10.3 \pm 0.2$  kcal mol<sup>-1</sup>. However, in further contrast to the *trans* species, the *cis* emission lifetimes also show a strong temperature dependence between 20 °C and 77 K (1 μs, 20 °C; 116 μs, 77 K (in Me<sub>2</sub>SO)). The *cis* complex also shows no evidence for a deuterium isotope effect at room temperature, whereas at 77 K a large isotope effect comparable to that of *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> is observed (Table II).

Interestingly, the short solution <sup>2</sup>E<sub>g</sub> lifetime at 20 °C (1.7 μs, H<sub>2</sub>O; 1.0 μs, Me<sub>2</sub>SO) increases by more than 1 order of magnitude for solid-state studies on the (PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>) salt of *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> (19 μs). The solid salt also displays no detectable photoreaction at 20 °C. Furthermore, the data in Table II reveal a substantial deuterium isotope effect on the phosphorescence lifetime for solid *cis*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>) at 20 °C

(44) For the deuterated sample the reported apparent activation energy of 17.5 kcal mol<sup>-1</sup> is for the temperature range 38.2–61.0 °C. Considerable curvature occurs in the plot at lower temperatures.

(45) Wasgestian, H. F.; Schlafer, H. L. *Z. Phys. Chem. (Wiesbaden)* 1968, 62, 127.

(46) Direct colorimetric or electrochemical detection of released NH<sub>3</sub> has not been possible, since both analytical methods require the use of basic conditions. As noted earlier, the parent *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> species undergoes rapid base hydrolytic loss of NH<sub>3</sub> at room temperature.

(47) Kirk, A. D.; Frederick, L. A.; Wong, C. F. C. *Inorg. Chem.* 1979, 18, 448.

Table IV. Spectroscopic  ${}^4T_{2g} \rightarrow {}^2E_g$  ( $O_h$ ) Energy Gap for Some Cr(III) Complexes

complex	$E({}^4T_{2g}) - E({}^2E_g),^a$ kcal mol $^{-1}$
Cr(NH $_3$ ) $_6^{3+}$	19.4
Cr(en) $_3^{3+}$	21.0
<i>cis</i> -Cr(cyclam)(NH $_3$ ) $_2^{3+}$	19.0
<i>trans</i> -Cr(cyclam)(NH $_3$ ) $_2^{3+}$	22.2
Cr(bpy) $_3^{3+}$	23.7
<i>trans</i> -Cr(cyclam)(CN) $_2^+$	29.2
Cr(CN) $_6^{3-}$	41.8

<sup>a</sup>  $E({}^4T_{2g})$  is the energy of the first spin-allowed quartet absorption band (Table I).  $E({}^2E_g)$  is the energy of the phosphorescence band maximum in room-temperature solution.

(19  $\mu$ s, undeuterated; 65  $\mu$ s, deuterated). The results are consistent with a more important role for  ${}^2E_g \rightsquigarrow {}^4A_{2g}$  relaxation in the solid than in solution.<sup>48</sup> However, solid lifetimes increase significantly on cooling to 77 K, and a more marked deuterium isotope effect is observed. These latter data suggest that solid-state room-temperature lifetimes are influenced by the presence of a strong-coupled relaxation process other than direct  ${}^2E_g$  reaction.

**Pathways for  ${}^2E_g$  Excited-State Deactivation. Pathway 1. Direct  ${}^2E_g$  Reaction.** As noted earlier, for *trans*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  at room temperature the  ${}^2E_g$  excited state decays predominantly (or significantly) via weak-coupled  ${}^2E_g \rightsquigarrow {}^4A_{2g}$  radiationless relaxation in Me $_2$ SO (or aqueous) solution. Furthermore, direct  ${}^2E_g$  reaction is improbable as the process responsible for the strong coupling observed above room temperature (although lifetimes are dramatically shortened, no net reaction is observed even at elevated temperatures).<sup>49</sup>

The corresponding room-temperature solution lifetime behavior of *cis*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  is consonant with a dominant strong-coupled radiationless process. Since the short  ${}^2E_g$  lifetimes are accompanied by the onset of photolability, it is tempting to assign the primary deactivation pathway to direct  ${}^2E_g$  reaction. The much shorter solution vs. solid-state lifetimes may also be associated in part with a direct  ${}^2E_g$  reaction path, which is absent in the solid. However, the solid-state data presented earlier indicated the additional presence at room temperature of a strong-coupled decay process other than direct  ${}^2E_g$  reaction.

**Pathway 2. Back-ISC.** The photoreactivity of *cis*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  may occur wholly out of the  ${}^4T_{2g}$  ( $O_h$ ) excited state and may involve contributions from both direct  ${}^4T_{2g}$  reaction and delayed  ${}^4T_{2g}$  reaction via back-ISC. The presence at room temperature of a prominent back-ISC process would then also account for the *cis* lifetime data. This explanation suggests, however, that back-ISC proceeds up to 140 times faster for *cis*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  than for the *trans* analogue in Me $_2$ SO solution at 20 °C (based on their relative lifetimes). Such rate differences are consistent with the spectral data in Figure 2 and Tables I and IV, which indicate that the spectroscopic  ${}^2E_g \rightarrow {}^4T_{2g}$  energy gap is larger for the *trans* complex. Following the argument of Magde, Linck, and co-workers<sup>6</sup> it may be concluded that the actual energy barrier to back-ISC is also larger for the *trans* compound. It should also be noted that on the basis of the relative size of the spectroscopic  ${}^2E_g \rightarrow {}^4T_{2g}$  energy gap (Table IV) back-ISC is more likely for *cis*- and *trans*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  than for *trans*-Cr(cyclam)(CN) $_2^+$ , where back-ISC was considered improbable.<sup>8</sup>

For both *cis*- and *trans*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  above room temperature the  ${}^2E_g$  level deactivates primarily via a strong-coupled process (based on the absence of a strong deuterium isotope effect). A substantially higher apparent activation energy is observed for  ${}^2E_g$  decay of the *trans* complex in acidic aqueous solution ( $E_a$ (*trans*) = 17.5 kcal mol $^{-1}$ ;  $E_a$ (*cis*) = 10.3 kcal mol $^{-1}$ ), consistent

with the strong-coupling process being back-ISC for both the *cis* and *trans* isomers. A higher activation energy for back-ISC for the *trans* species also accommodates the observation that its emission intensity and lifetime only become significantly temperature dependent above room temperature. However, the case for temperature-activated back-ISC for *trans*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  is difficult to reconcile with the absence of photoreaction at elevated temperatures.<sup>50</sup> According to the terminology employed by Porter<sup>51</sup>

$$k_{\text{bisc}} = (1 - \phi_{\text{isc}})k_{-4}$$

where  $k_{-4}$  is the intrinsic rate constant and  $k_{\text{bisc}}$  the effective rate constant for back-ISC. The lifetime of the  ${}^2E_g$  level is directly influenced by  $k_{\text{bisc}}$  rather than  $k_{-4}$ . If the  ${}^4T_{2g}$  level repopulated by back-ISC is photoinert, then  $\phi_{\text{isc}}$  may be close to unity, and thus  $k_{\text{bisc}}$  may have a relatively small value even at high temperatures.<sup>5,8</sup> One might then have also anticipated the observation of delayed fluorescence.

**Pathway 3.  ${}^2E_g \rightsquigarrow$  Ground-State Intermediate.** Endicott and co-workers<sup>7,52</sup> have recently proposed a strong-coupled  ${}^2E_g$  relaxation pathway for Cr(III) amine systems that involves temperature-activated crossing between the  ${}^2E_g$  surface and that of a ground-state substitutional intermediate (possibly seven-coordinate). The intermediate may subsequently relax to the ground-state parent (no net reaction) or proceed on to products. This model rationalizes their otherwise puzzling observation<sup>7</sup> that the macrobicyclic complex Cr(sep) $^{3+}$  has a solution phosphorescence lifetime and temperature dependence very similar to those of Cr(en) $_3^{3+}$  but yet is photoinert.

We feel Endicott's model also provides the most comprehensive explanation for the differences we observe in the photobehavior of *cis*- and *trans*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$ . In room-temperature solution,  ${}^2E_g$  excited-state relaxation is assigned to  ${}^2E_g \rightsquigarrow$  intermediate surface crossing for the *cis* species, while  ${}^2E_g \rightsquigarrow {}^4A_{2g}$  decay remains dominant for the *trans* analogue. The relative unimportance at room temperature of strong-coupled surface crossing for *trans*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  may be attributed to a larger activation barrier (for which there is some experimental lifetime data support) and/or a smaller preexponential term in the rate constant expression for surface crossing. Above room temperature this latter pathway becomes of increasing importance for the *trans* complex, which accounts for both the sharp drop in emission lifetimes and the continued absence of photoreaction. In fact, at high solution temperatures the photobehavior of *trans*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  is reminiscent of that reported for Cr(sep) $^{3+}$  (short lifetime, photoinert).<sup>7</sup> Finally, this model also accommodates the marked differences observed between the solid-state and solution photobehavior of *cis*-Cr(cyclam)(NH $_3$ ) $_2^{3+}$  at room temperature. In the solid state, crossing to a substitutional intermediate surface may be significantly impeded, and relaxation of any intermediate species formed will result only in parent complex regeneration. A greater role in the solid state for the weak-coupled  ${}^2E_g \rightsquigarrow {}^4A_{2g}$  process in  ${}^2E_g$  excited-state relaxation would therefore be anticipated, in accord with the relatively long emission lifetime and medium-strong deuterium isotope effect observed.

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**Registry No.** *trans*-[Cr(cyclam)(H $_2$ O) $_2$ ](ClO $_4$ ) $_3$ , 94484-05-6; *trans*-[Cr(cyclam)(CN) $_2$ ](ClO $_4$ ), 84277-87-2; *trans*-[Cr(cyclam)(NO $_3$ ) $_2$ ](NO $_3$ ) $_3$ ,

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(49) However, the possibility of direct  ${}^2E_g$  reaction as a relaxation mode involving Cr-cyclam bond cleavage cannot rigidly be excluded, since rapid ring closure could lead to no net observed reaction.

(50) A nondetected  ${}^4T_{2g}$  reaction involving Cr-cyclam bond cleavage is unlikely since theory predicts preferential NH $_3$  activation for this excited state<sup>9,10</sup> and no NH $_3$  loss was detected.

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*trans*-[Cr(cyclam)(H<sub>2</sub>O)(NH<sub>3</sub>)]Co(CN)<sub>6</sub>, 94484-14-7; *cis*-[Cr(cyclam)(H<sub>2</sub>O)(NH<sub>3</sub>)]Co(CN)<sub>6</sub>, 94536-67-1; *cis*-[Cr(cyclam)en](NO<sub>3</sub>)<sub>3</sub>, 94484-15-8; *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>, 94484-08-9; deud *trans*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>, 94484-11-4; *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>, 94536-68-2; deud *cis*-Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>, 94536-64-8; K<sub>3</sub>[Co(CN)<sub>6</sub>], 13963-58-1; D<sub>2</sub>, 7782-39-0.

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## Specific Sequestering Agents for the Actinides. 11. Complexation of Plutonium and Americium by Catecholate Ligands<sup>1</sup>

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The results of the first in vitro experiments regarding the complexation of plutonium and americium by catechol and tetracatechloylamide ligands are presented. Electrochemical techniques have allowed the elucidation of the protonation behavior of Pu(IV)- and Pu(III)-catecholate complexes. Above pH 12, the Pu(IV) complex is a tetrakis(catecholate) complex and the Pu(III) complex is a tetrakis- or tris(catecholate) complex, depending upon ligand concentration. At neutral pH, the Pu(IV) complex of the octadentate ligand 3,4,3-LICAMS appears to be a tris(catecholate) complex, indicating that the full denticity of the ligand is not utilized in vivo. Spectroscopic evidence is presented for the complexation of Am(III) by tetracatechloylamide ligands. The inability to observe the Am(IV)/Am(III)-catecholate reduction couple indicates that the free-ion Am(IV)/Am(III) reduction potential is greater than +2.6 V vs. NHE.

### Introduction

Although the wider use of nuclear fuel sources has increased the risk of exposure to actinide contamination (in particular exposure to plutonium and uranium), development of new complexing agents for decorporation of actinides has lain nearly dormant and those compounds presently used were not designed with this intent. As part of an ongoing research project to develop chelating agents to sequester actinide ions, a series of tetracatechloylamide ligands have been synthesized.<sup>2-4</sup> It was surmised that the catecholate dianion would be a good choice to bind and decorporate Pu(IV), the oxidation state most prevalent in vivo, because of this ion's similarity to Fe(III). Previous work has shown that catechloylamide ligands form extremely stable complexes with Fe(III) and other highly charged, hard cations.<sup>5-11</sup> Several comprehensive reviews have been published regarding the rationale of ligand design for these catecholate ligands.<sup>12-14</sup>

Test results of several catechloylamide ligands used to decorporate Pu(IV) from dogs and mice indicate that these ligands are exceptional in their ability to remove Pu(IV) from the body.<sup>4,15</sup> In fact, one derivative, 3,4,3-LICAMC (Figure 1), has been shown to be the most effective chelating agent for Pu(IV) tested to date that has no toxic side effects.<sup>13,14,16</sup>

Aside from the fact that tetrakis(catecholates) are known to complex effectively Pu(IV) in vivo, there has been no direct evidence about the nature of the complexes formed. Previous work demonstrated that catechols preferentially stabilize the higher oxidation states of metal ions such as Fe(III),<sup>8</sup> Ti(IV),<sup>11</sup> and Ce(IV)<sup>7</sup> to the extent that standard potentials of the uncomplexed ions shift negative in excess of 2.0 V upon complexation of catechol in basic solution. Since the Pu(IV)/Pu(III) reduction potential is +0.98 V vs. NHE,<sup>17,18</sup> complexation by catechol should shift it to about -1.0 V vs. NHE, well within the operating range of a hanging-mercury-drop electrode in basic solution.<sup>19</sup> When the ligand concentration and pH of Pu-catecholate solutions are varied, electrochemistry can be used not only to elucidate the relative stability of Pu(IV) vs. Pu(III) complexes but also to study the protonation behavior and stoichiometry of complexes.<sup>20</sup> These studies can be carried out in dilute solution (less than 0.2 mM in Pu) utilizing differential-pulse voltammetry,<sup>21</sup> allowing ex-

periments to be performed with relatively small amounts of ligand and radionuclide. Presented here is the electrochemistry of the Pu(IV)/Pu(III)-catecholate reduction couple studied as a function of pH and ligand concentration for catechol, 3,4,3-LICAMS, 3,4-LICAMS, and 3,4,3-LICAMC (Figure 1).

The study of americium-catecholate complexation was prompted by results of in vivo experiments in mice and dogs regarding americium removal by the tetracatechloylamides, 3,4,3-LICAMS and 3,4,3-LICAMC (Figure 1).<sup>16</sup> Originally it was thought that complexation of Am(III) in vivo by catecholate ligands would not be of sufficient stability to remove Am(III) from

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