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Synthesis and Photophysical Properties of New Chromium(III) Complexes of N-Derivatized 1,4,8,11-Tetraazacyclotetradecane Ligands *cis*-[Cr(1,8-R_2cyclam)Cl_2]Cl, Where R Is a Pendant Chromophore. Exclusive Formation of the *cis* Isomer

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Several new chromium(III) complexes have been synthesized utilizing derivatives of the macrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane) with various N-substituted chromophores in the 1 and 8 positions (1,8-R_2cyclam) where R = CH_3, CH_2Ph, CH_2Nph (Nph = naphthyl), and CH_2Anth (Anth = anthracyl). X-ray crystal structures were determined for all four complexes, and these are formed exclusively in the *cis* configuration with the two tertiary amines in the “hinge” positions (i.e., along the folding axis) of the coordinated ligand. As a result, the *cis* isomers appear to be inert to isomerization under conditions dramatically more forcing than needed to effect the *cis* to *trans* isomerization of the unsubstituted Cr(cyclam)Cl_2^+ ion. Photophysical studies demonstrated that emission occurs solely from the metal-centered ligand field doublet excited states regardless of whether initial excitation is into the quartet ligand field bands or into the π–π^* bands of the pendant chromophore. Thus, excitation of the pendant chromophore results in efficient intramolecular energy transfer to the metal centered ligand field excited states.

Introduction

Ongoing studies in this laboratory and others have been concerned with the synthesis and photochemical characterizations of new metal based compounds having possible applications as photochemically activated drugs.[1−7] Among the materials of interest in this regard have been chromium(III) complexes of macrocyclic tetraamine ligands, such as cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane).[8−10] Although such Cr(III) complexes display visible range quartet and doublet ligand field absorption bands, these are symmetry (and in the case of the doublet, spin) forbidden, so extinction coefficients are small. Therefore, it would be desirable to build new systems with ligand based chromophores with higher extinction coefficients that can be used as internal sensitizers of photoreactions initiated by excitation into ligand field (LF) states. In this context, we have extended synthetic schemes first described by Guilard et al.[11] to prepare cyclam ligands (1,8-R_2cyclam) with substituents R = CH_3, CH_2Ph, CH_2Nph (Nph = naphthyl), and CH_2Anth (Anth = anthracyl) covalently linked to the 1- and 8-nitrogens and have used these to prepare the new Cr(III) complexes. These syntheses are described as are the X-ray crystal structures and spectroscopic characterizations for each complex. Also described are certain photophysical properties of these new compounds which demonstrate efficient energy transfer from

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the pendant ligands to metal centered ligand field excited states as well as unsuccessful attempts to isomerize these complexes to the *trans* analogues.

Experimental Section

1. Materials, Procedures, and Instrumentation. All syntheses were carried out in the presence of air with the exception of the halide exchange reaction.[12] 1,4,8,11-Tetraazacyclotetradecane, 1-chloromethylnaphthalene, and 9-chloromethylanthracene were purchased from Aldrich and used without further purification. CrCl$_3$·3THF was purchased from the Strem Chemical Company. Dimethylformamide (DMF) was dried over 3 Å molecular sieves before use. Tetrahydrofuran (THF) and 2-methyl-tetrahydrofuran (2-MeTHF) were dried and distilled over sodium and benzophenone. All other solvents were used as received. Electronic spectra were recorded using a Hewlett-Packard model HP8452A diode array spectrophotometer. Low resolution mass spectra were obtained using a VG Fisons Platform II single quadrupole mass spectrometer with an electrospray ionization source run with a Fisons Masslinks data system. NMR spectra were obtained on Varian 200 and 400 MHz spectrometers in CDCl$_3$ (CHCl$_3$ at 7.26 ppm) or D$_2$O (H$_2$O at 4.81 ppm). Infrared spectra were recorded with a Bio-Rad FTS-60 SPC 3200 FTIR spectrophotometer using KBr pellets. Elemental analysis was obtained via thermal conductivity experiments using a Control Equipment Corporation 440 elemental analyzer.

Emission and excitation spectra were recorded utilizing a SPEX Fluorolog 2 spectrofluorimeter equipped with a Hamamatsu R928-A water-cooled PMT configured for photon counting and interfaced with a computer running Spex DM3000f software. Emission spectra were corrected for PMT response as well as for lamp intensity variation by the ratio method with a Rhodamine-6G reference. A cutoff filter was placed in front of the emission monochromator to block scattered excitation light. All emissions were obtained in a front-face configuration at 77 K using 2-MeTHF glass matrixes (**4a**−**c**) or a 2:1 (v/v) 2-Me THF/MeOH glass matrix (**4d**). All solutions were 500 μM. A second sample of **4c** was diluted to 4.3 μM.

Lifetime data were recorded using the second (532 nm) and third (355 nm) harmonics of a Nd:YAG pulsed laser system (Continuum NY61). The samples were placed in a quartz dewar filled with liquid nitrogen. Emission lifetimes at 77 K were monitored by a PMT (RCA 8852) coupled to a digitalizing oscilloscope (Tektronix TDS 540), and data were transferred to a computer for subsequent analysis.

2. Synthesis of Ligands and Chromium(III) Complexes. 1,4,8,11-Tetraazatricyclo[9.3.1.1^{4,8}] hexadecane (1) was prepared from cyclam according to a published procedure.[11] Yield: 0.789 g (70.5%). MS (EI): 224 (calcd), 224 (found). ^{1}H NMR (CDCl$_3$): δ −1.05−1.20 (m, 2H, β-CH$_2$), 2.1−2.48 (m, 2H, β-CH$_2$), 2.35 (d, 4H, α-CH$_2$), 2.60 (td, 4H, α-CH$_2$), 2.84 (d, 2H, N−CH$_2$−N), 2.70−2.90 (m, 4H, α-CH$_2$), 3.12 (d, 4H, α-CH$_2$), 5.41 (dt, 2H, N−CH$_2$−N). ^{13}C NMR: 20.47 (β-CH$_2$), 49.54 (α-CH$_2$), 53.92 (α-CH$_2$), 69.06 (N−CH$_2$−N).

1,8-Dibenzyl-4,11-diazoniatricyclo[9.3.1.1^{4,8}]hexadecane dibromide (2a) was prepared from **1** as previously described.[11] Yield: 0.891 g (71.5%). MS (ESI): 485 (calcd); 485 (found). ^{1}H NMR (D$_2$O): δ −1.85 (d, 2H), 2.30−2.60 (m, 2H, td, 2H), 2.90 (d, 4H), 3.15−3.65 (m, 10H), 4.42 (t, 2H), 4.50 (d, 2H), 4.70 (d, 2H), 5.50 (d, 2H), 7.50 (m, 10H). ^{13}C NMR: 22.11 (β-CH$_2$), 50.10 (α-CH$_2$), 50.28 (α-CH$_2$), 53.88 (α-CH$_2$), 62.25 (α-CH$_2$), 65.63 (α-CH$_2$), 79.34 (N−CH$_2$−N), 128.59, 131.90, 133.51, 135.56 (6 aromatic C).

1,8-Bis(1-naphthylmethyl)-4,11-diazoniatricyclo[9.3.1.1^{4,8}]-hexadecane diiodide (2b) was prepared in a manner similar to that reported for **2a**. A solution of **1** (0.500 g, 2.23 × 10^{-3} mol) in approximately 20 mL of acetonitrile was transferred via cannulation to a flask containing 2 equiv of 1-iodomethylnaphthalene (4.46 × 10^{-3} mol) in acetone. The latter had been prepared in situ from 1-chloromethylnaphthalene by the Finkelstein reaction.[12] Although a precipitate formed almost immediately, the mixture was stirred for 18 h. The precipitate was collected by filtration, then was washed with a small amount of acetonitrile, and dried under vacuum. A pale yellow powder was obtained.[13] Yield: 1.41 g (83.3%). MS (ESI): 633 (calcd), 633 (found).

1,8-Bis(9-anthracylmethyl)-4,11-diazoniatricyclo[9.3.1.1^{4,8}]-hexadecane diiodide (2c) was prepared in the same manner as **2b**. A solution of **1** (0.492 g, 2.19 × 10^{-3} mol) in approximately 30 mL of acetonitrile was mixed via cannulation with 2 equiv of 9-iodomethylanthracene (4.38 × 10^{-3} mol) in acetone. The mixture was stirred for 48 h. The precipitate was filtered, washed with a small amount of acetonitrile, and dried under vacuum. A light yellow powder was obtained. Yield: 1.53 g (81.3%). MS (ESI): 733 (calcd), 733 (found). ^{1}H NMR (1:3/D$_2$O/acetone-*d*$_6$): δ −1.85 (m, 4H, β-CH$_2$), 2.70−2.90 (m, 16H, α-CH$_2$), 4.63 (s, 4H, N−CH$_2$Anth), 4.70 (s, 4H, N−CH$_2$−N), 7.45 (td, 4H, aromatic), 7.53 (td, 4H, aromatic), 8.04 (d, 4H, aromatic), 8.39 (d, 4H, aromatic), 8.53 (s, 2H, aromatic).

1,8-Dimethyl-4,11-diazoniatricyclo[9.3.1.1^{4,8}]hexadecane diiodide (2d) was prepared from **1** according to a literature method.[11] Yield: 1.10 g (97.6%). MS (ESI): 381 (calcd), 381 (found). ^{1}H NMR (D$_2$O): δ 1.86 (d, 2H), 2.40−2.60 (m, 2H, td, 2H), 2.86 (d, 2H), 2.95 (dt, 2H), 3.11 (m, 2H), 3.14 (s, 6H), 3.31−3.40 (m, 4H), 3.46 (d, 2H), 3.59 (dd, 2H), 4.47 (t, 2H), 5.33 (dt, 2H). ^{13}C NMR: 22.51 (β-CH$_2$), 49.62 (N−CH$_3$), 50.23 (α-CH$_2$), 53.17 (2C, α-CH$_2$), 66.12 (α-CH$_2$), 79.34 (N−CH$_2$−N).

1,8-Dibenzyl-1,4,8,11-tetraazacyclotetradecane (3a, dbc) was prepared by the base hydrolysis of **2a**[11] and was isolated as an oil. Yield: 0.288 g (85.9%). MS (ESI): 381 (calcd), 381 (found). ^{1}H NMR (CDCl$_3$): δ 1.82 (quint, 4H), 2.47−3.01 (m, 18H), 3.68 (s, 4H), 7.22−7.29 (m, 10H, aromatic H). ^{13}C NMR: 25.94 (β-CH$_2$), 47.74 (α-CH$_2$), 50.45 (α-CH$_2$), 52.13 (α-CH$_2$), 54.10 (α-CH$_2$), 57.56 (N−CH$_2$−Ph), 127.18, 128.30, 129.78, 137.44 (6 aromatic C).

1,8-Bis(1-naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane (3b, dnc) was prepared by a procedure similar to that used for **3a.** A sample of solid **2b** (0.512 g, 0.670 mmol) was added to 100 mL of aqueous NaOH (3 M) solution. A 25 mL aliquot of dioxane was added to bring **2b** into solution. After stirring for 8 h, the solution was extracted with CHCl$_3$ (5 × 30 mL). The organic phases were collected, dried over MgSO$_4$, and concentrated under reduced pressure to yield a pale yellow residue. The residue was dissolved in CHCl$_3$, transferred to a vial, evaporated, and weighed. Crude yield: 0.179 g (55.3%). This material was recrystallized from acetone to give a white crystalline solid as the final desired product. Yield: 0.154 g (47.7%). MS (ESI): 481 (calcd), 481 (found). ^{1}H NMR (CDCl$_3$): δ −1.82 (quint, 4H), 2.55−2.67 (m, 16H), 4.00

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(12) Finkelstein reaction: Dissolve *x* amount of NaI in acetone and add 1 equiv of alkyl chloride. Purge with nitrogen and stir for approximately 4 h in the dark. Results should yield desired alkyl iodide. March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; p 430.

(13) Due to a mixture of isomers in the starting material, 1-chloromethylnaphthalene (90%) and 2-chloromethylnaphthalene (10%), NMR data could not be fully elucidated for **2b**. However, these isomers fully separate in the subsequent step via acetone.

(s, 4H), 7.37−7.52 (m, 8H, aromatic H), 7.71−7.86 (dd, 4H, aromatic H), 8.40 (d, 2H, aromatic H). UV−vis ($CHCl_3$) {λ_{max} in nm (ϵ in M^{-1} cm^{-1})}: 276 (1.14×10^4), 284 (1.29×10^4), 296 (9.52×10^3). Anal. Calcd for $C_{32}H_{38}N_4{\cdot}H_2O$: C, 77.06; H, 8.08; N, 11.24. Found: C, 77.13; H, 7.95; N, 11.16.

1,8-Bis(9-anthracylmethyl)-1,4,8,11-tetraazacyclotetradecane (3c, dac) was synthesized in a manner similar to that used to prepare **3b**. A sample of **2c** (0.334 g, 0.670 mmol) was dissolved in a mixture prepared from 100 mL of aqueous NaOH (3 M) solution and 25 mL of dioxane. After being stirred vigorously for approximately 8 h, the solution was filtered and washed with cold water and dioxane to yield a pale yellow solid. The material was recrystallized via dissolving in hot DMF and cooled slowly. Yield: 0.217 g (96.6%). MS (ESI): 581 (calcd), 581 (found). ^1H NMR ($CDCl_3$): δ 1.68 (m, 4H), 2.25−2.87 (m, 16H), 4.50 (s, 4H), 7.42−7.54 (m, 10H, aromatic H), 7.71−7.86 (m, 4H, aromatic), 8.40 (s, 4H, aromatic). UV−vis ($CHCl_3$) {λ_{max} in nm (ϵ in M^{-1} cm^{-1})}: 336 (5.09×10^3), 352 (7.73×10^4), 370 (1.50×10^4), 392 (1.46×10^4). Anal. Calcd for $C_{40}H_{44}N_4{\cdot}3H_2O$: C, 75.67; H, 7.94; N, 8.83. Found: C, 75.76; H, 7.44; N, 8.67.

1,8-Dimethyl-1,4,8,11-tetraazacyclotetradecane (3d, dmc) was prepared from **2d** according to the literature[11] and was found to be a noncrystalline solid. Yield: 0.181 g (80.6%). MS (ESI): 229 (calcd), 229 (found). ^1H NMR ($CDCl_3$): δ 1.62 (quint, 4H), 2.07 (s, 6H), 2.27−2.35 (m, 8H), 2.49−2.59 (m, 8H), 2.91 (s, 2H). ^{13}C NMR: 26.29 (β-CH_2), 41.76 (α-CH_2), 47.49 (α-CH_2), 50.13 (α-CH_2), 56.95 (α-CH_2), 58.31 (N−CH_3).

***cis*-[Cr(1,8-dibenzyl-1,4,8,11-tetraazacyclotetradecane)Cl_2]Cl, *cis*-[Cr(dbc)Cl_2]Cl (4a).** This compound was prepared by a procedure adapted from that reported by Tobe and Ferguson.[14] A portion of **3a** (0.125 g, 3.28×10^{-4} mol) was dissolved in approximately 40 mL of dry DMF. $CrCl_3{\cdot}3THF$ (1 equiv, 0.123 g, 3.28×10^{-4} mol) was added to the solution. The mixture was heated to reflux for 15−20 min. Upon refluxing, the solution turned blue. After reflux, the solution was cooled to room temperature, and solvent was removed under reduced pressure. The remaining residue was dissolved in acetone and filtered, and volatiles were then removed via rotary evaporation. The residue was then washed several times with diethyl ether, and the product was dried to yield blue powder. This material was recrystallized via slow evaporation of an acetone solution. Yield: 0.149 g (84.7%). MS (ESI): 502 (calcd), 502 (found). UV−vis (THF) {λ_{max} in nm (ϵ in M^{-1} cm^{-1})}: 242 (4.04×10^4), 420 (150), 592 (220), 702 (9.0). Anal. Calcd for $C_{24}H_{36}N_4Cl_3Cr{\cdot}2H_2O$: C, 50.13; H, 7.01; N, 9.74. Found: C, 50.50; H, 6.42; N, 9.74. The X-ray crystal structure of this compound (see details in a following paragraph) demonstrated the presence of two water molecules.

***cis*-[Cr(1,8-bis(1-naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane)Cl_2]Cl, *cis*-[Cr(dnc)Cl_2]Cl (4b).** A procedure analogous to that used for preparation of **4a** was employed. In this case, **3b** (0.050 g, 1.04×10^{-4} mol) and $CrCl_3{\cdot}3THF$ (0.039 g, 1.04×10^{-4} mol) were dissolved in dry DMF (25 mL). The solution was refluxed for 15−20 min, during which time the solution became blue. Upon cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in acetone and filtered, and volatiles were then removed via rotary evaporation. The residue was then washed several times with diethyl ether, and the product was dried to yield blue powder. This was recrystallized via slow vapor diffusion of ether into an acetone solution. Yield: 0.059 g (88.5%). MS (ESI): 602 (calcd), 602 (found). UV−vis (THF) {λ_{max} in nm (ϵ in M^{-1} cm^{-1})}: 276 (3.28×10^4), 286 (3.53×10^4), 298 (2.59×10^4), 420 (158), 590 (232), 702 (9.6). Anal. Calcd for $C_{32}H_{40}N_4Cl_3Cr{\cdot}H_2O$: C, 58.49; H, 6.44; N, 8.53. Found: C, 58.42; H, 6.44; N, 8.48. The X-ray crystal structure (see details in a following paragraph) demonstrated the presence of one water molecule.

***cis*-[Cr(1,8-bis(9-anthracylmethyl)-1,4,8,11-tetraazacyclotetradecane)Cl_2]Cl, *cis*-[Cr(dac)Cl_2]Cl (4c).** A procedure analogous to that used for the preparation of **4a** was employed. Compound **3c** (0.050 g, 8.61×10^{-5} mol) and $CrCl_3{\cdot}3THF$ (0.039 g, 8.61×10^{-5} mol) were dissolved in approximately 25 mL of dry DMF. The solution was refluxed for 15−20 min, during which time the solution became greenish-blue. Upon cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in THF and filtered, and volatiles were then removed via rotary evaporation. The residue was then washed several times with diethyl ether, and the product was dried, affording a blue-green crystalline powder, which was recrystallized via slow vapor diffusion of ether into a THF solution to yield blue crystals. Yield: 0.051 g (80.2%). MS (ESI): 702 (calcd), 702 (found). UV−vis (THF) {λ_{max} in nm (ϵ in M^{-1} cm^{-1})}: 338 (8.90×10^3), 354 (1.73×10^4), 372 (2.70×10^4), 392 (2.64×10^4), 592 (240), 702 (8.5). Anal. Calcd for $C_{40}H_{44}N_4Cl_3Cr{\cdot}H_2O{\cdot}2THF$: C, 63.96; H, 7.16; N, 6.22. Found: C, 63.81; H, 7.08; N, 6.29. The X-ray crystal structure (see details in a following paragraph) demonstrated the presence of one water and two THF molecules.

***cis*-[Cr(1,8-dimethyl-1,4,8,11-tetraazacyclotetradecane)Cl_2]Cl, *cis*-[Cr(dmc)Cl_2]Cl (4d).** A procedure analogous to one used for the preparation of **4a** was employed. A portion of **3d** (0.051 g, 2.22×10^{-4} mol) was dissolved in approximately 40 mL of dry DMF and 1 equiv of $CrCl_3{\cdot}3THF$ (0.083 g, 2.22×10^{-4} mol). The solution was allowed to reflux for 15−20 min. Upon refluxing, the solution turned dark blue. After reflux, the solution was cooled to room temperature, and the solvent was removed under reduced pressure. The remaining residue was dissolved in acetone, filtered, and the solvent was removed via rotary evaporation. The residue was then washed several times with diethyl ether and the product was dried to yield dark blue powder. *This product is hygroscopic!* This was recrystallized via vapor diffusion of diethyl ether into an acetone solution. Yield: 0.080 g (93.8%). MS (ESI): 350 (calcd), 350 (found). UV−vis (THF) {λ_{max} in nm (ϵ in M^{-1} cm^{-1})}: 418 (107), 584 (148), 702 (4.0). Anal. Calcd for $C_{12}H_{28}N_4Cl_3Cr{\cdot}2H_2O$: C, 34.09; H, 7.63; N, 13.26. Found: C, 34.63; H, 7.36; N, 13.26. The X-ray crystal structure (see in details a following paragraph) demonstrated the presence of only 0.5 H_2O per Cr(III) unit; however, the compound is hygroscopic and may have picked up additional water.

3. Crystal Growth and Structure Determination. Crystal structures for compounds **4a−d** have been determined. Crystals for **4a** and **4b** were grown via slow evaporation of acetone to yield blue rectangle crystals. Crystals of **4c** were grown via slow vapor diffusion of ether into a concentrated THF solution. Crystals of **4d** were grown in a manner similar to that of **4c** only using acetone in place of THF.

Suitable crystals were mounted on thin glass fibers with epoxy resin. Room temperature (293 K) as well as low temperature (180 K) single-crystal studies were carried out on a Bruker Smart 1000 diffractometer equipped with normal-focus 2.4 kW sealed-tube X-ray source (Mo Kα radiation) operating at 50 kV and 40 mA with a two-dimensional CCD detector. The crystals were solved by direct methods followed by difference Fourier methods.

Hydrogen atoms attached to carbon atoms were calculated at ideal positions and refined as riding atoms of the parent carbon

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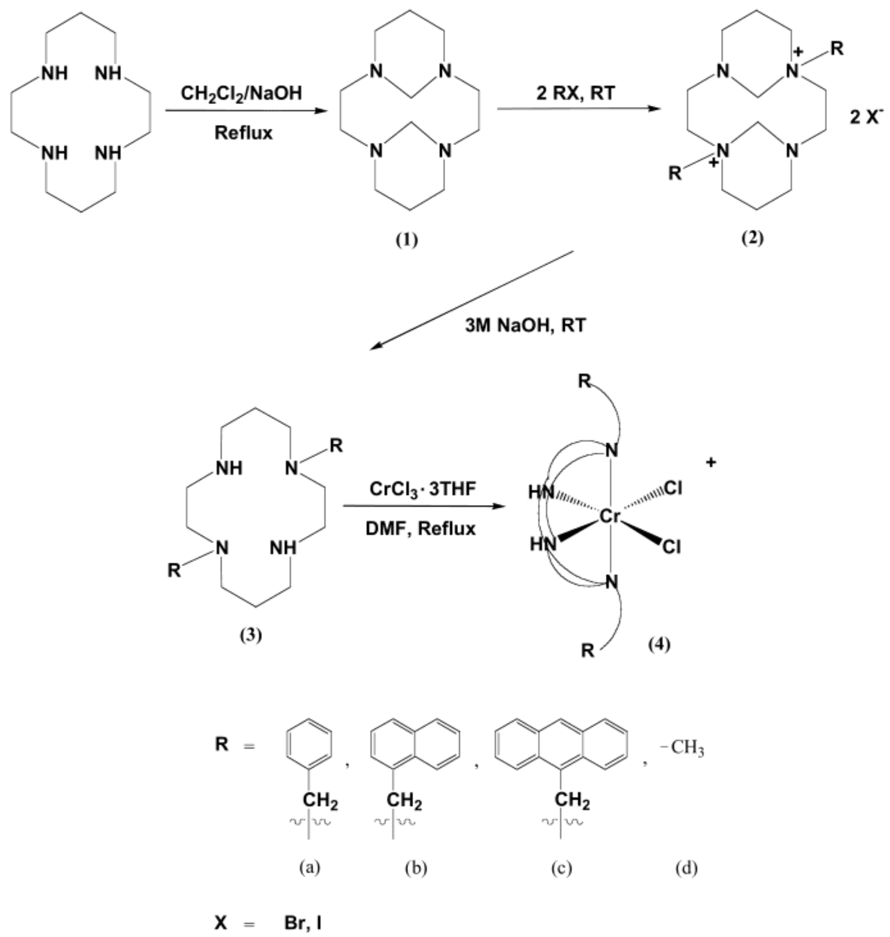
[14] Tobe, J.; Ferguson, M. L. *Inorg. Chim. Acta* **1970**, *4*, 109−112.

Scheme 1



atoms. The calculations were performed using SHELXTL running on Silicon Graphics Indy 5000. Final full-matrix refinements were against F^2.

Results and Discussion

1. Syntheses. The four 1,8-R$_2$cyclam ligands (**3a**−**d**) and the four Cr(III) complexes *cis*-[Cr(R$_2$cyclam)Cl$_2$]Cl (**4a**−**d**) were prepared according to Scheme 1. Certain modifications of the syntheses reported for analogous ligands[11] were imperative to the successful preparations of **3b** and **3c**. Attachment of the 1-naphthylmethyl and 9-anthracylmethyl pendant groups, respectively, was accomplished by the reaction of **1** with the aryl methyl iodides (ArCH$_2$I) prepared from the chloride analogues (ArCH$_2$Cl) in situ using the Finkelstein reaction.[12] Although **2b** could be synthesized using 1-chloromethylnaphthalene directly, the yield was low ($<$50%) and the reaction took much longer (2 weeks) than when the iodide analogue was used. Attempts to prepare **2c** via the reaction of 9-chloromethylanthracene with **1** were unsuccessful.

Reaction of compounds **2a**−**d** with NaOH removed the methylene bridges and converted the tricyclic cations into the respective derivatized cyclam ligands, **3a**−**d**. However, since **2b** and **2c** did not readily dissolve in the basic solution, dioxane was added to increase solubility allowing the reaction to go to completion.

The *cis* Cr(III) complexes **4a**, **4b**, **4c**, and **4d** were each prepared following a procedure analogous to that described by Tobe et al.[14] Refluxing DMF solutions of the ligands with CrCl$_3$•3THF for 20 min was suitable for obtaining high yields of the desired product. All are extremely soluble in THF, all but **4c** are soluble in acetone, but only **4d** is soluble in water.

2. Characterization of Chromium Complexes. Electronic Spectra. The visible range and infrared absorption spectra of **4a**−**d** are consistent with those expected for the *cis* configurations[15] demonstrated by X-ray crystallography (see details in a following paragraph). The visible range absorption spectra in solution (Table 1) each display a broad band at λ_{max} 592 nm for **4a**, **4b**, and **4c** and at 584 nm for **4d** (Figure 1) that can be assigned to the spin-allowed $Q_1 \leftarrow Q_0$ ligand field transition.[16] Although there is little sensitivity to the different pendant groups, it is notable that in all four cases this band is shifted to a significantly longer wavelength from the $Q_1 \leftarrow Q_0$ band of the analogous *cis*-Cr(cyclam)-Cl$_2^+$ ion.[15a,17] There is a smaller shift of the Q_2 bands to lower energy relative to the cyclam complex. The shifts can be attributed to the weaker ligand field strengths of the R$_2$cyclam ligand owing to the longer Cr−N bond lengths for the two tertiary nitrogens (see details in a following

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(15) (a) Poon, C. K. *Inorg. Chim. Acta* **1971**, *5*, 322−324. (b) Swisher, A. G.; Brown, G. A.; Smierciak, R. C.; Blinn, E. L. *Inorg. Chem.* **1981**, *20*, 3947−3951

(16) For an octahedral Cr(III) complex, Q_0 would have the irreducible representation $^4A_{2g}$, Q_1 would be $^4T_{2g}$, Q_2 would be $^4T_{1g}$, and D_0 would be ^2E_g.

(17) Chen, Y.; Perkovic, M. W. *Inorg. Chim. Acta* **2001**, *317*, 127−132.

Table 1. Optical Spectra of *cis*-[Cr(R$_2$-cyclam)Cl$_2$]Cl Salts in Ambient Temperature Tetrahydrofuran[a]

complex	$\pi-\pi^*$ bands λ_{max} (nm) ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1})	Q$_2$ λ_{max} in nm (ϵ in M^{-1} cm^{-1})	Q$_1$ λ_{max} in nm (ϵ in M^{-1} cm^{-1})	D$_0$ λ_{max} (nm) (ϵ in M^{-1} cm^{-1})
cis-[Cr(dbc)Cl$_2$]Cl (**4a**)	242 (40.4)	420 (150)	592 (220)	702 (9.0)
cis-[Cr(dnc)Cl$_2$]Cl (**4b**)	276 (32.8), 286 (35.3), 298 (25.9)	420 (158)	592 (232)	702 (9.6)
cis-[Cr(dac)Cl$_2$]Cl (**4c**)	338 (8.90), 354 (17.3), 372 (27.0), 392 (26.4)	*b*	592 (240)	702 (8.5)
cis-[Cr(dmc)Cl$_2$]Cl (**4d**)		418 (107)	584 (148)	702 (4.0)
cis-[Cr(cyclam)Cl$_2$]Cl[c]		408 (123)	536 (122)	699 (1.0)
		404 (106)	529 (111)	

[a] $\pi-\pi^*$ represents absorption bands of the aromatic chromophores pendant to the macrocyclic ligand. Q$_2$ and Q$_1$ represent spin-allowed quartet–quartet absorption bands, $\{^4T_{1g}, ^4T_{2g}\} \leftarrow ^4A_{2g}$; D$_0$ represents the spin-forbidden quartet–doublet absorption band, $^2E_g \leftarrow ^4A_{2g}$. [b] Q$_2$ band hidden by anthracene absorption. [c] Optical spectrum of *cis*-[Cr(cyclam)Cl$_2$]Cl in H$_2$O according to refs 15a and 17.

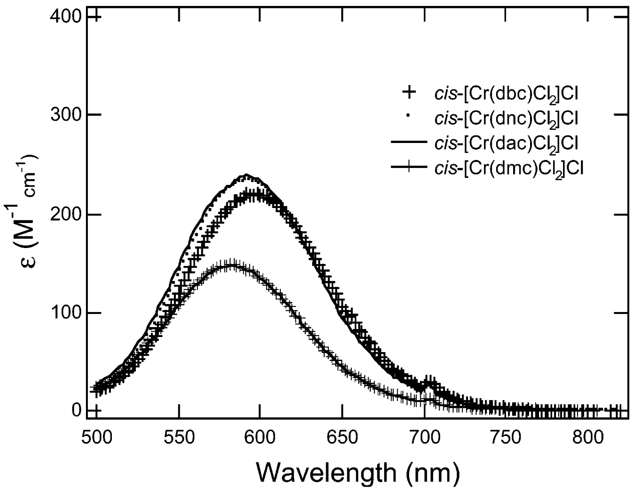

Figure 1. Absorption spectra of the Q$_1 \leftarrow$ Q$_o$ and D$_o \leftarrow$ Q$_o$ transitions for compounds **4a**–**d** in THF (ambient temperature).

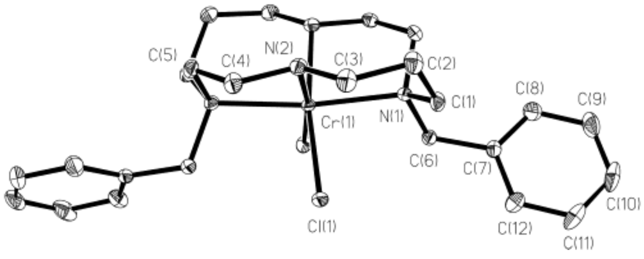

Figure 2. Molecular structure and numbering of atoms for the cation of *cis*-[Cr(dbc)Cl$_2$]Cl (**4a**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

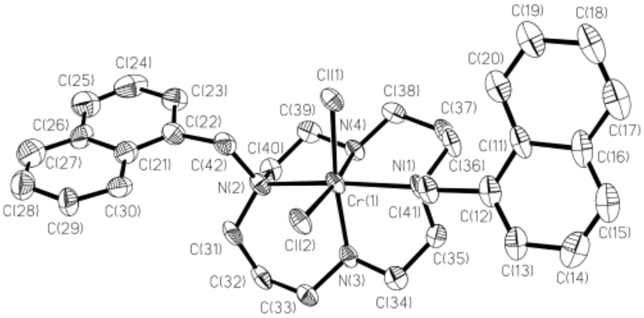

Figure 3. Molecular structure and numbering of atoms for the cation of *cis*-[Cr(dnc)Cl$_2$]Cl (**4b**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

paragraph). In addition, the extinction coefficients for the Q$_1$ and Q$_2$ bands of **4a**–**b** (Table 1) are relatively larger presumably because of the lower symmetries of these complexes. The full optical spectra for complexes **4a**–**d** are shown in Supporting Information Figures S1–4.

Of particular note in the electronic spectra of compounds **4a**–**d** is the appearance of a sharp band at 702 nm that can be assigned as the spin-forbidden quartet to doublet (D$_0 \leftarrow$ Q$_0$) transition (Figure 1). For **4a**, **4b**, and **4c**, the extinction coefficient of this band is approximately 9 M^{-1} cm^{-1}, about an order of magnitude higher than normally seen for D$_0 \leftarrow$ Q$_0$ transitions of hexacoordinate Cr(III) complexes.[18] The dimethyl complex **4d** has an extinction coefficient of 4.0 M^{-1} cm^{-1}, 4-fold larger than that reported for *cis*-[Cr(cyclam)Cl$_2$]Cl (~1 M^{-1} cm^{-1}).[17] These unusually large ϵ values can be attributed to intensity-borrowing from the nearby Q$_1$ band[19] owing to the smaller energy gap between the D$_0$ and Q$_1$ states of **4a**–**d**.

Infrared spectroscopy has been used to differentiate *cis* and *trans* isomers of Cr(III) cyclam complexes, since the *cis* complexes display at least three bands in the range 840–890 cm^{-1} assigned to NH$_2$ rocking modes while the CH$_2$ vibration splits into two bands in the 790–830 cm^{-1} region.[20] Such vibrational modes are found in the IR spectra of **4a**–**d**. For example, *cis*-[Cr(dbc)Cl$_2$]Cl (**4a**) displays NH$_2$ rocking modes at 902, 872, and 839 cm^{-1}, and CH$_2$ vibrations at 817 and 802 cm^{-1}. Complexes **4b**–**d** show similar vibrational spectra.

3. Crystal Structures Determined by X-ray Diffraction Studies. The crystal structures for the cationic *cis* chromium(III) complexes **4a**–**d** are shown as ORTEP diagrams in Figures 2–5, respectively. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. In each case, the macrocycle is coordinated as the *cis* isomer, and the N–Cr–N folding axis includes the two tertiary nitrogens. The *cis* Cl–Cr–Cl angles range from 89.99(8)° to 92.45(5)°. The Cr–N$_{tert}$ (N$_{tert}$ = tertiary nitrogens) bonds are all significantly longer than the Cr–N$_{sec}$ (N$_{sec}$ = secondary nitrogens) bonds in the respective structures. For example, in **4a**–**c** the average Cr–N$_{tert}$ distance is 2.183(4) Å while the Cr–N$_{sec}$ values fall in the range 2.082–2.113 Å. This is consistent with the lower basicity of a tertiary amine relative to that of a secondary amine,[21] as well as the decreased flexibility imposed by the pendent aryl methyl groups.

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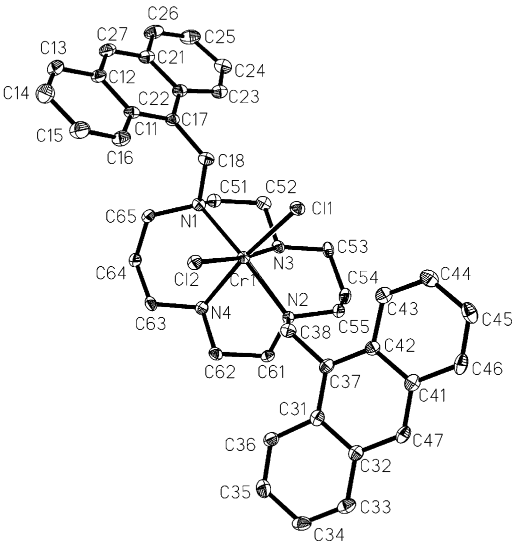

Figure 4. Molecular structure and numbering of atoms for the cation of *cis*-[Cr(dac)Cl_2]Cl (**4c**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

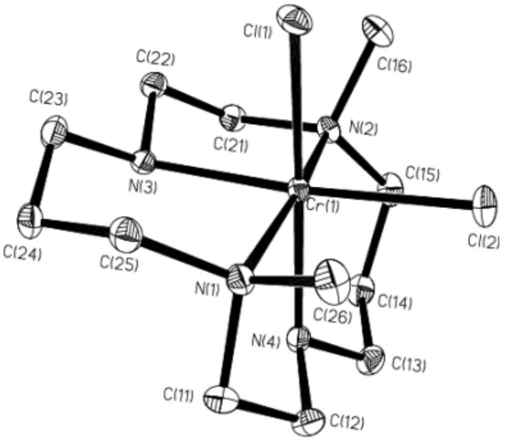

Figure 5. Molecular structure and numbering of atoms for the cation of *cis*-[Cr(dmc)Cl_2]Cl (**4d**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

Crystal structure data for *cis*-[Cr(cyclam)Cl_2]Cl show Cr−N bond lengths comparable to the Cr−N_{sec} values of **4a**−**d** (reported average: 2.099(4) Å).[22]

An important feature of these complexes is that the tertiary nitrogens (N(1)/N(2) for **4b**−**d**, N(1)/N(1#) for **4a**) exclusively occupy the "folding" axes of the coordinated macrocycles. This is quite significant because the nitrogens on this fold need to undergo inversion in order to effect the rearrangement of the N_4-macrocycle to the *trans* configuration, and this mechanism is apparently facilitated by deprotonation of the macrocycle amine at that site (see details in a following paragraph).

Table 2. Selected Bond Lengths [Å] for Complexes **4a**−**d**

***cis*-[Cr(dbc)Cl_2]Cl (4a)**[a]	
Cr(1)−N(1)	2.184(2)
Cr(1)−N(1)#1	2.184(2)
Cr(1)−N(2)	2.082(2)
Cr(1)−N(2)#1	2.082(2)
Cr(1)−Cl(1)	2.3209(9)
Cr(1)−Cl(1)#1	2.3209(9)
***cis*-[Cr(dnc)Cl_2]Cl (4b)**	
Cr(1)−N(1)	2.182(6)
Cr(1)−N(2)	2.186(6)
Cr(1)−N(3)	2.087(6)
Cr(1)−N(4)	2.099(5)
Cr(1)−Cl(1)	2.296(2)
Cr(1)−Cl(2)	2.325(2)
***cis*-[Cr(dac)Cl_2]Cl**	
Cr(1)−N(1)	2.183(4)
Cr(1)−N(2)	2.177(3)
Cr(1)−N(3)	2.109(4)
Cr(1)−N(4)	2.113(4)
Cr(1)−Cl(1)	2.320(2)
Cr(1)−Cl(2)	2.333(2)
***cis*-[Cr(dmc)Cl_2]Cl (4d)**	
Cr(1)−N(1)	2.164(2)
Cr(1)−N(2)	2.170(2)
Cr(1)−N(3)	2.111(2)
Cr(1)−N(4)	2.100(2)
Cr(1)−Cl(1)	2.3277(11)
Cr(1)−Cl(2)	2.3155(9)

[a] #1 refers to symmetry-generated atom.

Table 3. Selected Bond Angles [deg] for Complexes **4a**−**d**

***cis*-[Cr(dbc)Cl_2]Cl (4a)**[a]			
Cl(1)−Cr(1)−Cl(1)#1	92.45(5)	N(1)−Cr(1)−Cl(1)	88.62(6)
N(1)−Cr(1)−N(2)	91.41(8)	N(2)−Cr(1)−Cl(1)	87.58(7)
N(1)#1−Cr(1)−N(2)#1	91.41(8)	N(1)#1−Cr(1)−Cl(1)	97.18(6)
N(1)−Cr(1)−N(1)#1	171.64(10)	N(2)#1−Cr(1)−Cl(1)	171.41(6)
N(2)−Cr(1)−N(1)#1	82.86(8)	N(1)−Cr(1)−Cl(1)#1	97.18(6)
N(2)#1−Cr(1)−N(1)	82.85(8)	N(2)−Cr(1)−Cl(1)#1	171.41(6)
N(2)−Cr(1)−N(2)#1	93.68(13)	N(1)#1−Cr(1)−Cl(1)#1	88.62(6)
		N(2)#1−Cr(1)−Cl(1)#1	87.58(7)
***cis*-[Cr(dnc)Cl_2]Cl (4b)**			
Cl(1)−Cr(1)−Cl(2)	89.99(8)	N(1)−Cr(1)−Cl(1)	88.9(2)
N(1)−Cr(1)−N(2)	168.6(2)	N(2)−Cr(1)−Cl(1)	99.0(2)
N(1)−Cr(1)−N(3)	83.0(2)	N(3)−Cr(1)−Cl(1)	171.6(2)
N(1)−Cr(1)−N(4)	89.6(2)	N(4)−Cr(1)−Cl(1)	89.8(2)
N(2)−Cr(1)−N(3)	89.3(2)	N(1)−Cr(1)−Cl(2)	97.6(2)
N(2)−Cr(1)−N(4)	82.3(2)	N(2)−Cr(1)−Cl(2)	90.6(2)
N(3)−Cr(1)−N(4)	92.5(2)	N(3)−Cr(1)−Cl(2)	88.7(2)
		N(4)−Cr(1)−Cl(2)	172.7(2)
***cis*-[Cr(dac)Cl_2]Cl (4c)**			
Cl(1)−Cr(1)−Cl(2)	91.41(6)	N(1)−Cr(1)−Cl(1)	97.74(10)
N(1)−Cr(1)−N(2)	169.98(13)	N(2)−Cr(1)−Cl(1)	89.35(10)
N(1)−Cr(1)−N(3)	82.83(14)	N(3)−Cr(1)−Cl(1)	89.17(12)
N(1)−Cr(1)−N(4)	89.83(14)	N(4)−Cr(1)−Cl(1)	172.42(11)
N(2)−Cr(1)−N(3)	90.23(14)	N(1)−Cr(1)−Cl(2)	89.70(10)
N(2)−Cr(1)−N(4)	83.17(14)	N(2)−Cr(1)−Cl(2)	97.24(10)
N(3)−Cr(1)−N(4)	92.0(2)	N(3)−Cr(1)−Cl(2)	172.52(11)
		N(4)−Cr(1)−Cl(2)	88.37(12)
***cis*-[Cr(dmc)Cl_2]Cl (4d)**			
Cl(1)−Cr(1)−Cl(2)	91.05(3)	N(1)−Cr(1)−Cl(1)	89.76(6)
N(1)−Cr(1)−N(2)	169.76(8)	N(2)−Cr(1)−Cl(1)	97.45(6)
N(1)−Cr(1)−N(3)	90.77(9)	N(3)−Cr(1)−Cl(1)	88.20(7)
N(1)−Cr(1)−N(4)	82.48(9)	N(4)−Cr(1)−Cl(1)	172.16(7)
N(2)−Cr(1)−N(3)	82.23(9)	N(1)−Cr(1)−Cl(2)	97.42(7)
N(2)−Cr(1)−N(4)	90.39(9)	N(2)−Cr(1)−Cl(2)	89.75(6)
N(3)−Cr(1)−N(4)	92.98(9)	N(3)−Cr(1)−Cl(2)	171.77(7)
		N(4)−Cr(1)−Cl(2)	88.87(7)

[a] #1 refers to symmetry-generated atom.

4. Attempts to Isomerize to the *trans* Configurations. In preparative reactions between various metal ions and cyclam, the *cis* isomer is the kinetically favored product and the first to form. The *trans* isomer is generally more stable,[23−25] and *cis* to *trans* isomerization is usually accomplished by base-catalysis.[26] For example, the reaction of $CrCl_3$ with cyclam in dry DMF first gives *cis*-[Cr(cyclam)-Cl_2]Cl, which can be isomerized by heating in the presence

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(22) Tobe, M. L.; Sosa, M. E.; Bombieri, G.; Forsellini, E.; Parassasi, T. *Acta Crystallogr.* **1986** *C42*, 563−565.

of excess cyclam to the *trans* analogue (eq 1). However, the *cis*-[Cr(1,8-R$_2$cyclam)Cl$_2$]Cl compounds described here could be isolated only as the *cis* isomers and are exceedingly robust. Despite vigorous attempts, isomerization could not be effected.

$$\mathrm{CrCl_3} + \text{cyclam} \rightarrow \textit{cis}\text{-}[\mathrm{Cr(cyclam)Cl_2}]\mathrm{Cl} \xrightarrow{\text{base, }\Delta} \textit{trans}\text{-}[\mathrm{Cr(cyclam)Cl_2}]\mathrm{Cl} \quad (1)$$

For example, refluxing a DMF solution of any of the *cis* complexes **4a**−**d** with varying amounts of excess base for up to 36 h left the complexes unchanged. Reduction by Cr^{II}Cl$_2$ and Zn/Hg amalgam were also employed in separate attempts to generate a Jahn−Teller tetragonally distorted Cr(II) complex followed by oxidation to afford a *trans*-Cr(III) complex. Each method proved unsuccessful in obtaining the desired *trans* isomer for compounds **4a**−**d**.

Another attempt to effect the *cis*-to-*trans* isomerization of a 1,8-R$_2$cyclam complex involved reaction with cyanide ion, which had been reported[27] to effect *cis* to *trans* isomerization of Cr(III) cyclam complexes. *cis*-[Cr(dbc)Cl$_2$]Cl (**4a**) was dissolved in DMSO with excess NaCN and allowed to stir at 65 °C for 70 min, during which time the solution color changed from blue to orange. The solvent was removed under reduced pressure, and the product was recrystallized via slow diffusion of ether into a concentrated methanol solution. Positive ion electrospray ionization mass spectrometry supports the identity of the dicyano product Cr(dbc)(CN)$_2^+$ with a parent peak of 484 *m*/*z*. Infrared data showed only one peak at 2170 cm^{-1}, consistent with a *trans* species; however, a single ν_{CN} band has been seen previously for the *cis*-[Cr(en)$_2$(CN)$_2$]I analogue.[28] The material was then subjected to ligand metathesis analogous to that reported by Meyerstein et al.[29] in which the dicyano complex was refluxed in concentrated HCl. The result was a single isolable product identified as **4a** by UV−vis optical absorption and mass spectrometry. Analogous experiments starting with *cis*-[Cr(cyclam)Cl$_2$]Cl effected the *cis to trans* isomerization;[30] so, we conclude that this did not occur upon reaction of **4a** with cyanide.

The *cis*−*trans* isomerization of cyclam-type metal complexes is base-catalyzed, suggesting that an ionizable proton on a nitrogen macrocycle is essential for this process to occur.[26] The 1,8-R$_2$cyclam ligands do have secondary amines available for deprotonation at the 4 and 11 positions, but these are not at the “hinge” sites that apparently need to undergo inversion in order for isomerization to occur. Instead, **4a**−**d** preferentially formed with the tertiary nitrogens along the hinge of the folded macrocycle, although it’s not clear whether this stereochemistry was defined by steric or electronic factors.

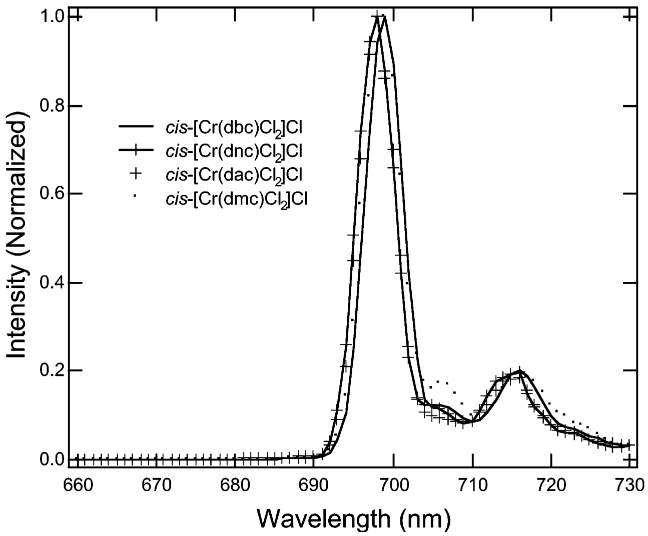

Figure 6. Emission spectra for compounds **4a**−**d** in 2-MeTHF at 77 K. $\lambda_{ex} = 590$ nm.

5. Photophysical Properties. The photoluminescence spectra of **4a**−**d** in low temperature (77 K) glasses each displayed a sharp emission with a λ_{max} of 698 nm, which was assigned as the $D_0 \leftarrow Q_0$ 0−0 transition on the basis of previous literature assignments (Figure 6).[31] (The peaks at 706 and 716 nm are vibronic components of this transition.)[31]

The excitation spectra ($\lambda_{mon} = 720$ nm) (Supporting Information Figures S5−8) closely track the absorption spectra in a manner consistent with efficient intersystem crossing/internal conversion from higher energy states to the emitting doublet ligand field state. This behavior includes both quartet ligand field absorptions and carries over to the $\pi^* \leftarrow \pi$ absorptions of the ligand pendant chromophores, for example, the anthracyl groups of **4c**. The Q$_1$ bands in the excitation spectra are hypsochromically shifted from the ambient temperature solution absorption spectra; however, in low temperature glasses (77 K) **4a**−**d** each displayed a comparable shift in the Q$_1$ absorption bands (to 582, 582, 582, and 578 nm, respectively) as seen qualitatively in a distinct color change from blue to purple upon cooling the solution. The Q$_2$ bands are blue-shifted but only by ∼2 nm in each case.

The efficient intramolecular energy transfer from the pendant chromophores of the dianthracyl complex **4c** is illustrated in Figure 7. The excitation spectrum of a very dilute (4.3×10^{-6} M) 2-MeTHF solution of **4c** ($\lambda_{mon} = 694$ nm) shows peaks at 353, 372, and 393 nm assigned to anthracene π−π^* absorptions. This is also indicated by the strong emission from this solution ($\lambda_{ex} = 370$ nm) although solutions of **4a**, **4b** and **4c** at comparable concentrations showed no significant emission when excited at the same λ_{ex} (Figure 8). While such internal conversion/intersystem crossing from ligand-centered π−π^* excitation has been noted for Cr(III) diimine complexes such as Cr(bpy)$_3^{3+}$ (bpy

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[30] Unpublished results from this laboratory.

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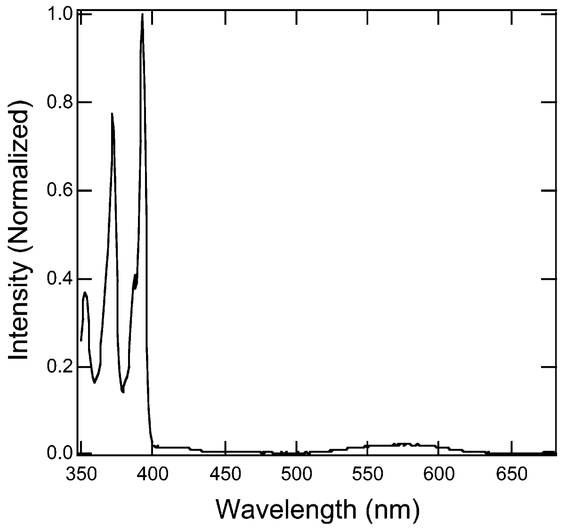

Figure 7. Excitation spectrum of *cis*-[Cr(dac)Cl$_2$]Cl (**4c**) (4.3×10^{-6} M) in 2-MeTHF at 77 K. Emission was monitored at 694 nm.

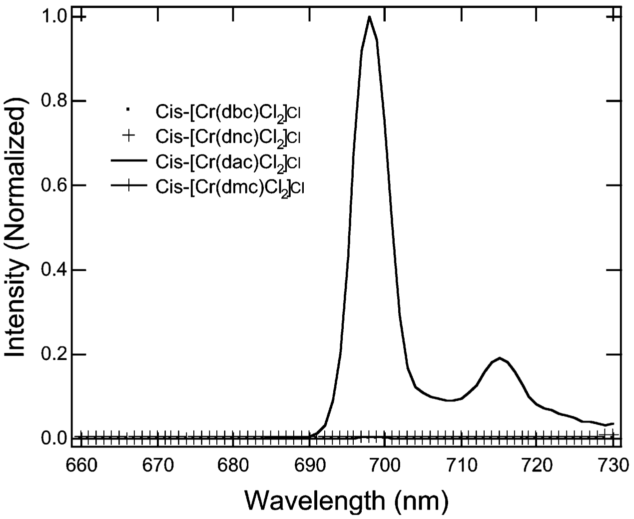

Figure 8. Emission comparison of compounds **4a**−**d** in diluted solutions of 2-MeTHF (4.3×10^{-6} M) at 77 K. The compounds were excited at 370 nm.

is 2,9-bipyridine),[32] the present case represents the first example of intramolecular energy transfer to Cr(III) ligand field states from a pendant chromophore separated from the metal center by an sp^3-hybridized carbon.

Temporal emission behavior was briefly evaluated for **4a**−**d** in 2-MeTHF solutions at 77 K using 532 nm excitation and monitoring at the doublet emission maximum at 694 nm. The lifetimes all fall in the microsecond range. Attempts to analyze these as single exponential decays gave poor fits with the exception of **4d** which gave a τ value of 117 μs. In contrast, the temporal doublet emission of the unsubstituted analogue *cis*-[Cr(cyclam)Cl$_2$]Cl displays a good fit to single exponential decay to give $\tau = 45.3$ μs in agreement with the value 47.6 μs reported by Forster and Mønsted[31] under analogous conditions. Inexplicably, the temporal emissions from **4a**−**d** fit well to biexponential functions giving the lifetimes 9.8 μs (53%) and 73.4 μs (47%), 21.4 μs (35%) and 110 μs (65%), 5.6 μs (69%) and 20.7 μs (31%), and 44 μs (17%) and 132 μs (83%), respectively. (The values in parentheses indicate the amplitudes of components giving the respective lifetimes.) The lifetimes thus determined for a very dilute sample (4.3 μM) of the anthracyl substituted complexes **4c** were comparable (4.9 μs (72%) and 20.1 μs (28%)). There is no obvious rationale for the multiple lifetimes given that photophysical behavior was unchanged by repetitive recrystallization, thereby arguing against impurities being responsible. While photolysis of each complex to (unknown) products during photophysical studies might lead to such results, extended 532 nm irradiation (repetitive laser pulses) of the solutions at 77 K as well as at 293 K did not change the preexponential values nor the lifetimes. We speculate that this behavior might be the result of different conformations in the glassy matrixes due to the positions of the pendant chromophores. The lifetimes between each complex (**4a**−**d**) may be due to a variation in the relative ring strain of the five-membered rings of the ligand.[33]

In summary, new chromium(III) cyclam-type complexes have been synthesized and structurally characterized. The appendages placed in the 1 and 8 position of the macrocycle inhibit *cis* to *trans* isomerization by standard methods such as base catalysis. The preferential coordination of these macrocycles such that the tertiary nitrogens appear along the folding axis of the coordinated ligand appears to be due to a combination of steric and electronic factors and to be responsible for the inertness to isomerization. Photophysical studies show emission only from the lowest energy doublet ligand field excited state in each case and efficient internal conversion/intersystem crossing from higher energy quartet ligand field states as well as intramolecular energy transfer from the π−π* states of the pendant chromophores.

Acknowledgment. These studies were supported by the National Science Foundation (Grant CHE 0095144). This work made use of instrumentation (ESI$^+$/TOF MS) supported under the Army Research Office Award DAAD19-00-1-0026. We are thankful to Engen and Clinton for elemental analysis data.

Supporting Information Available: Figures S1−4 showing full optical absorption spectra of compounds **4a**−**d**. Figures S5−8 showing excitation spectra of compounds **4a**−**d**. Figures S9−12 showing unit cell packing structures for compounds **4a**−**d**. Listings of complete structure refinement details, bond lengths and angles, anisotropic displacement parameters for non-hydrogen atoms, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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