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Synthesis and Luminescence Properties of Cr(III) Complexes with Cyclam-Type Ligands Having Pendant Chromophores, *trans*-[Cr(L)Cl_2]Cl[1]

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The synthesis and spectroscopic properties of new cyclam-type ligands 5,7-dimethyl-6-R-1,4,8,11-tetraazacyclotetradecane (L), where R is a pendant chromophore such as an anthracene derivative, are reported. These ligands were prepared according to a nickel(II) template procedure, and the X-ray crystal structures of several Ni(II) intermediates are described. Reaction of the free base ligands L with $CrCl_3$·3THF resulted in facile formation of *trans*-[Cr(L)Cl_2]Cl complexes, and the structures and spectroscopic characterizations of these complexes are also described. Examination of the photophysical properties of *trans*-[Cr(L)Cl_2]Cl solutions at 77 K demonstrated the emission spectra to be dominated by phosphorescence from the ligand field doublet of the chromium(III) center. This also applies to the Cr(III) complex *trans*-[Cr(mac)Cl_2]Cl, where mac is the anthracene derivative 5,7-dimethyl-6-anthracenylcyclam. Excitation into the π–π^* states of the anthracene leads to marked quenching of the fluorescence from this chromophore and sensitized phosphorescence from the metal-centered doublet state.

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] Materials of interest in this regard include 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, the extinction coefficients are small. Therefore, it would be desirable to build systems with ligand-based chromophores having higher extinction coefficients that can serve as internal antennae and sensitizers of metal-centered photoreactions.

We have recently reported the synthesis and characterization of Cr(III) macrocyclic tetraamine complexes *cis*-[CrL′Cl_2]Cl with chromophores appended to the 1,8-nitrogens of a cyclam ligand (L′).[11] However, once formed these Cr(III) complexes proved to be resistant to isomerization. The crystal structures showed the tertiary nitrogens to be positioned along the ligand folding axis, and the absence of ionizable protons at those sites may inhibit the cis−trans isomerization. In this context, it appeared desirable to prepare macrocyclic complexes having the pendant chromophore attached at a ring carbon instead. Described here are preparations of several cyclam-based ligands of the type 5,7-dimethyl-6-R-1,4,8,11-tetraazacyclotetradecane, where R is a C-bound pendant chromophore. These ligands L were prepared via nickel(II) template methods,[12,13] and intermedi-

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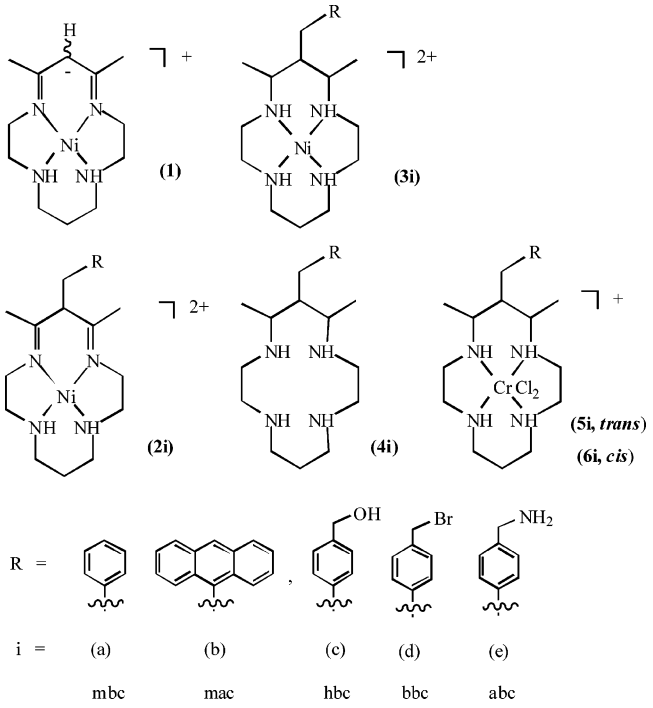
Scheme 1. Compounds Prepared[a]



[a] The numerical labels for the complexes refer to various salts of the cations as indicated in the text. The ligands bbc and abc were prepared by modifying the pendant group after coordination to Cr(III).

ates along this scheme were characterized. The corresponding Cr(III) complexes were formed by the direct reaction with $CrCl_3$, and the more stable[14−16] *trans*-$[Cr(L)Cl_2]Cl$ isomers were the first products isolated. The analogous reaction with cyclam gives largely (>90%) the cis isomer as previously reported.[17] Spectroscopic characterization for all new species is reported as well as several X-ray crystal structures. Scheme 1 illustrates the complexes and ligands prepared and the shorthand notation used to designate them.

Experimental Section

1. Materials, Procedures, and Instrumentation. Syntheses were carried out in the presence of air with the exception of the halide exchange reaction.[18] *N*,*N*′-Bis(2-aminoethyl)-1,3-propanediamine (2,3,2-Tet) was purchased from Acros Organics, and 2,4-pentanedione and *p*-xylene glycol were purchased from TCI Chemicals Co. Sodium borohydride, concentrated HBr (48%), 1-hydroxybenzatriazole, 9-chloromethylanthracene (anthracyl chloride), and $NiCl_2 \cdot 6H_2O$ were purchased from Aldrich and used without further purification. The synthesis precursor *p*-(hydroxymethyl)benzyl bromide was prepared from *p*-xylene glycol in excellent yield following a reported preparation[19] and was characterized by ^{1}H NMR and ESI-TOF mass spectrometry. $CrCl_3 \cdot 3THF$ (THF = tetrahydrofuran) was purchased from the Strem Chemical Co. Dimethylformamide (DMF) was dried over 3 Å molecular sieves before use. Acetonitrile was distilled over CaH_2. All other solvents were used as received.

Elemental analyses (C, H, N) were performed by the UCSB Marine Science Institute Analytical Laboratory.

Electronic spectra were recorded using a Hewlett-Packard model HP8452A diode array spectrophotometer or a Shimadzu model 2401PC 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 7.260 ppm). Infrared spectra (KBr pellets) were recorded using a BioRad model FTS 60 SPC 3200 FTIR spectrometer.

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 EtOH/MeOH glass matrixes (4:1 v/v).

Emission 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. Syntheses of Ni(II) Complexes. [(5,7-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-dienato)nickel(II)] Nitrate ([Ni(dienato)]NO_3, 1) was prepared according to literature methods.[20] Yield: 6.587 g (76.0%). ESI-MS: *m*/*z* 281 (M^+). IR (KBr): 1558 cm^{-1} (C═C), 1537 cm^{-1} (C═N).

[(5,7-Dimethyl-6-benzyl-1,4,8,11-tetraazacyclotetradeca-4,7-dienenickel(II)] Nitrate Bromide ([Ni(benzyl diene)]NO_3,Br, 2a) was prepared in 74.3% yield following a reported synthesis[21] and characterized by ESI-TOF mass spectrometry.

[(5,7-Dimethyl-6-anthracyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene)nickel(II)] Nitrate Iodide ([Ni(anthracyl diene)]I,NO_3, 2b) was synthesized in a manner similar to that reported for **2a**.[21] A solution of **1** (0.434 g, 1.26 mmol) in 25 mL of absolute ethanol was mixed with 1 equiv of 9-iodomethylanthracene (anthracyl iodide, 1.26 mmol) in acetone via cannulation. The anthracyl iodide had been prepared in situ from anthracyl chloride by the Finklestein reaction.[18] The acetone was allowed to boil off, and a condenser was attached. The solution was refluxed for ∼4 h, affording a bright yellow precipitate. The product was recrystallized via slow evaporation of an aqueous solution. Yield: 0.62 g (73.3%). ESI-MS: *m*/*z* 236 (M^{2+}). IR (KBr): 1663 cm^{-1} (C═N). An X-ray crystal structure was obtained.

[(5,7-Dimethyl-6-(*p*-hydroxymethylbenzyl)-1,4,8,11-tetraazacyclotetradeca-4,7-diene)nickel(II)] Nitrate Bromide (2c) was synthesized in a similar manner. A 4.00 g portion of **1** (11.6 mmol) was partially dissolved in ∼80 mL of absolute ethanol with about 1 equiv of *p*-hydroxymethylbenzyl bromide (3.50 g, 17.4 mmol).

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The solution was refluxed for 4 h, during which time a yellow precipitate formed. After the solution was cooled, the precipitate was collected by filtration and washed with cold absolute ethanol followed by ether. Yield: 5.14 g (81.0%). ESI-MS: *m*/*z* 401 ($M^{2+} - H^+$), 201 (M^{2+}). IR (KBr): 1667 cm^{-1} (C═N), 3450 cm^{-1} (−OH).

[(5,7-Dimethyl-6-benzyl-1,4,8,11-tetraazacyclotetradecane)-nickel(II)] Perchlorate ([Ni(mbc)]$(ClO_4)_2$, 3a) was prepared following an original procedure. A 0.500 g portion of **2a** (9.71×10^{-4} mol) was partially dissolved in ∼7 mL of methanol. A large excess of $NaBH_4$ (0.551 g, 14.6 mmol) was added, and the yellow solution became immediately red, followed by the formation of a pink precipitate. The mixture was allowed to stir at room temperature for 2 h. Upon completion, the pink precipitate was collected by filtration and redissolved in hot H_2O. Saturated aqueous $NaClO_4$ was added dropwise, affording a light orange powder. The solution was cooled, and the powder was collected by filtration and washed with ice-cold water and then with ether. Yield: 0.559 g (∼100%). ESI-MS: *m*/*z* 375 ($M^{2+} - H^+$), 475 ($M^{2+} + ClO_4^-$). IR (KBr): 3210 cm^{-1} (N−H). Anal. Calcd for $NiC_{19}H_{34}N_4Cl_2O_8 \cdot H_2O$: C, 38.41; H, 6.10; N, 9.43. Found: C, 38.86; H, 5.71; N, 9.41. An X-ray crystal structure was obtained. *Note: Perchlorate salts may be explosive and should be handled with care!*

[(5,7-Dimethyl-6-anthracyl-1,4,8,11-tetraazacyclotetradecane)-nickel(II)] Perchlorate ([Ni(mac)]$(ClO_4)_2$, 3b) was synthesized in a manner similar to that of **3a**. A 0.500 g portion of **2b** (7.55×10^{-4} mol) was partially dissolved in ∼55 mL of methanol. To this solution was added 15 equiv of $NaBH_4$ (0.429 g, 11.3 mmol), during which time the yellow solution became peach-colored, followed by the formation of a pink precipitate. After being stirred at room temperature for 2 h, the mixture was filtered and the resulting solid redissolved in hot H_2O. Saturated aqueous $NaClO_4$ was added dropwise, the solution was cooled, and the resulting orange powder was collected by filtration and washed with ice-cold water and then ether. Yield: 0.510 g (∼100%). ESI-MS: *m*/*z* 238 (M^{2+}), 575 ($M^{2+} + ClO_4^-$). IR (KBr): (loss of C═N peak at 1663 cm^{-1}), 3215 cm^{-1} (N−H). Anal. Calcd for $NiC_{27}H_{38}N_4Cl_2O_8 \cdot 2H_2O$: C, 45.53; H, 5.94; N, 7.86. Found: C, 45.55; H, 5.35; N, 7.68. An X-ray crystal structure was obtained. *Note: Perchlorate salts may be explosive and should be handled with care!*

[(5,7-Dimethyl-6-(*p*-hydroxymethylbenzyl)-1,4,8,11-tetraazacyclotetradecane)nickel(II)] Perchlorate (Ni(hbc)]$(ClO_4)_2$, 3c) was synthesized in the same manner as **3a**. A portion of **2c** (1.00 g, 1.83 mmol) was partially dissolved in ∼10 mL of CH_3OH, and then 15 equiv of $NaBH_4$ (1.039 g, 27.5 mmol) was added. The yellow solution became immediately red and then formed a pink precipitate. After the solution was stirred at room temperature for 2 h, the pink precipitate was collected by filtration and redissolved in hot H_2O. Saturated aqueous $NaClO_4$ in water was added dropwise, affording a light orange powder. The solution was cooled, and the hygroscopic orange powder was collected by filtration and washed with ice-cold water, followed by ether. Yield: 1.110 g (∼100%). ESI-MS: *m*/*z* 203 (M^{2+}), 505 ($M^{2+} + ClO_4^-$). IR (KBr): 3210 cm^{-1} (N−H), 3450 cm^{-1} (−OH). *Note: Perchlorate salts may be explosive and should be handled with care!*

3. Synthesis of Free Ligands. 5,7-Dimethyl-6-benzyl-1,4,8,11-tetraazacyclotetradecane (mbc, 4a) was prepared from **3a** using a modified procedure based on a previously reported synthesis.[22] [Ni(mbc)]$(ClO_4)_2$ (0.444 g, 7.7×10^{-4} mol) was dissolved in H_2O (125 mL) by warming the solution. A large excess of NaCN (0.755 g, 15.4 mmol) was added, and a banana-colored precipitate formed immediately, presumed to be the cyano adduct. However, upon bringing the solution to reflux, the mixture again became homogeneous. The solution was refluxed for 2 h, during which time the orange color of the starting material had given way to the yellow color of $Ni(CN)_4^{2-}$. Once completed, the solution was cooled to room temperature and 6 M aqueous NaOH s was added dropwise until the pH was greater than 12. The solution was extracted with $CHCl_3$ (6 × 50 mL), and the organic layers were collected and dried with $MgSO_4$. The solution was filtered and the solvent removed under reduced pressure to give a white precipitate. Yield: 0.198 g (80.7%). ESI-MS: *m*/*z* 319 ($M + H^+$). ^1H NMR ($CDCl_3$): δ 0.96 (d, 6H), 1.74 (q, 2H), 1.92 (t, 1H), 2.23 (s, 4H), 2.42 (td, 2H), 2.66 (m, 6H), 2.84 (m, 8H), 7.19 (m, 5H). Anal. Calcd for $C_{19}H_{34}N_4 \cdot 0.5H_2O$: C, 69.67; H, 10.77; N, 17.11. Found: C, 69.24; H, 10.12; N, 16.72.

5,7-Dimethyl-6-anthracyl-1,4,8,11-tetraazacyclotetradecane (mac, 4b) was prepared from **3b** following an original procedure. [Ni(mac)]$(ClO_4)_2$ (0.500 g, 7.39×10^{-4} mol) was dissolved in a solution of H_2O (7 mL) and DMSO (30 mL), and 30 equiv of NaCN (1.087 g, 22.2 mmol) was added slowly. A banana-colored precipitate formed immediately; however, the mixture became homogeneous when heated to reflux. The solution was refluxed for 2 h, during which time it became darker orange. The solution was then cooled to room temperature and placed in a refrigerator overnight. Large white crystals were collected by filtration from the pale yellow solution and dried in vacuo for 2 days. Yield: 0.279 g (90.2%). ESI-MS: *m*/*z* 419 ($M + H^+$). ^1H NMR ($CDCl_3$): δ 0.736 (d, 6H), 1.765 (quint, 2H), 2.366 (m, 9H), 2.366−2.768 (m, 8H), 2.899 (m, 4H), 7.464 (quint, 4H), 7.981 (d, 2H), 8.321 (s, 1H), 8.520 (d, 2H). ^{13}C NMR: δ 19.72 (2C, $-CH_3$), 29.52 (1C, β-C), 38.74 (1C, β-C), 47.33 (2C, α-C), 50.35 (2C, α-C), 51.30 (4C, α-C), 61.91 (1C, CH_2-arom), 124.90 (4C, arom), 125.35 (4C, arom), 126.09 (1C, arom), 126.20 (1C, arom), 129.49 (4C, arom). Anal. Calcd for $C_{27}H_{38}N_4 \cdot 1.5H_2O$: C, 72.77; H, 9.27; N, 12.58. Found: C, 73.57; H, 9.05; N, 12.69.

5,7-Dimethyl-6-(*p*-hydroxymethylbenzyl)-1,4,8,11-tetraazacyclotetradecane, (hbc, 4c) was prepared from **3c** using a procedure modified from an earlier paper.[22] [Ni(hbc)]$(ClO_4)_2$ (1.86 g, 3.06 mmol) was dissolved in H_2O (80 mL), and the solution was warmed to ensure homogeneity. After 30 equiv of NaCN (4.50 g, 91.8 mmol) was added, the solution turned purple and then light yellow, and a precipitate formed and then redissolved upon bringing the solution to reflux. During the 2 h reflux, the orange color of the starting material gave way to the yellow of $Ni(CN)_4^{2-}$. The solution was then cooled to room temperature, and a 6 M NaOH solution was added dropwise until the pH was greater than 12. The solution was extracted with $CHCl_3$ (6 × 50 mL), the organic layers were collected, dried with $MgSO_4$, and filtered, and the solvent was removed under reduced pressure, yielding a viscous oil. The oil was placed under vacuum to yield a white crystalline precipitate, which was *very* hygroscopic. Yield: 0.972 g (91.1%). ESI-MS: *m*/*z* 349 ($M + H^+$). ^1H NMR ($CDCl_3$): δ 0.915 (d, 6H), 1.674 (t, 2H), 1.825 (t, 2H), 2.336−2.876 (m, 15H), 4.597 (s, 2H), 7.20 (d, 4H). ^{13}C NMR: δ 20.28 (2C, $-CH_3$), 29.22 (1C, β-C), 29.39 (1C, β-C), 47.47 (2C, α-C), 50.05 (2C, α-C), 51.03 (2C, α-C), 52.17 (2C, α-C), 61.11 (1C, CH_2-arom), 64.54 (1C, CH_2OH), 127.04 (2C, arom), 129.03 (2C, arom). Anal. Calcd for $C_{20}H_{36}N_4 \cdot CHCl_3$: C, 53.90; H, 7.97; N, 11.97. Found: C, 53.97; H, 7.95; N, 11.35.

4. Synthesis of Chromium(III) Complexes. *trans*-[Dichloro-(5,7-dimethyl-6-benzyl-1,4,8,11-tetraazacyclotetradecane)chromium(III)] Chloride (*trans*-[Cr(mbc)Cl_2]Cl, 5a) was prepared from **4a** by a procedure adapted from that reported by Tobe and

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Ferguson for the synthesis of the cyclam analogues.[17] A solution prepared from the macrocyclic ligand mbc (0.200 g, 6.28×10^{-4} mol) and $CrCl_3 \cdot 3THF$ (0.235 g, 6.27×10^{-4} mol) in ~20 mL of dry DMF was refluxed for ~20 min, during which time the color changed from a deep purple to a gray-brown, and then to green upon cooling. The solvent was removed under reduced pressure, and the residue was redissolved in a *minimum* amount of hot H_2O and placed in a refrigerator overnight to give light green needles. Yield: 0.258 g (86.2%). ESI-MS: *m*/*z* 440 (M^+). UV−vis (H_2O) {λ_{max}, nm (ϵ, M^{-1} cm^{-1})}: 242 (4.17×10^3), 372 (30.1), 420 (26.2) sh, 572 (16.7). An X-ray crystal structure was obtained.

***trans*-[Dichloro(5,7-dimethyl-6-anthracyl-1,4,8,11-tetraazacyclotetradecane)chromium(III)] Chloride (*trans*-[Cr(mac)Cl$_2$]Cl, 5b)** was prepared from **4b** by a procedure modified from that reported by Hay et al.[23] The macrocyclic ligand mac (0.150 g, 3.58×10^{-4} mol) and $CrCl_3 \cdot 3THF$ (0.133 g, 3.57×10^{-4} mol) were dissolved in ~20 mL of dry DMF, and the solution was refluxed for ~30 min, during which time the color changed from a deep purple to a gray-brown. The solution was reduced in volume by ~2/3 by solvent evaporation, and then the mixture was refrigerated overnight, during which time purple granular crystals formed. Yield: 0.198 g (95.6%). ESI-MS: *m*/*z* 540 (M^+). UV−vis (H_2O) {λ_{max}, nm (ϵ, M^{-1} cm^{-1})}: 336 (3.37×10^3), 354 (6.84×10^3), 372 (10.8×10^3), 392 (10.2×10^3), 572 (18.9). An X-ray crystal structure was obtained.

***trans*-[Dichloro(5,7-dimethyl-6-(*p*-hydroxymethylbenzyl)-1,4,8,11-tetraazacyclotetradecane)chromium(III)] Chloride (*trans*-[Cr(hbc)Cl$_2$]Cl, 5c)** was synthesized in the same manner as **5b**. A solution of the macrocyclic ligand hbc (1.23 g, 3.50 mmol) and $CrCl_3 \cdot 3THF$ (1.28 g, 3.41 mmol) in ~30 mL of dry DMF was refluxed for ~20 min, during which time the color changed from a deep purple to a gray-purple and a light purple precipitate began to form. The solution was reduced in volume by ~2/3 by solvent evaporation, and then was refrigerated overnight. A light purple powder formed and was collected by filtration, rinsed with acetone and then ether, and dried under vacuum. Yield: 1.30 g (75.2%). ESI-MS: *m*/*z* 470 (M^+). UV−vis (H_2O) {λ_{max}, nm (ϵ, M^{-1} cm^{-1})}: 242 (4.28×10^3), 374 (46.9), 420 sh (42.6), 568 (25.4). Anal. Calcd for $C_{20}H_{36}N_4 \cdot CH_3OH$: C, 46.79; H, 7.48; N, 10.39. Found: C, 46.56; H, 7.37; N, 10.33.

***cis*-[Dichloro(5,7-dimethyl-6-benzyl-1,4,8,11-tetraazacyclotetradecane)chromium(III)] Chloride (*cis*-[Cr(mbc)Cl$_2$]Cl, 6a)** was prepared following an original procedure. A solution of the macrocyclic ligand mbc (0.054 g, 1.69×10^{-4} mol) and $CrCl_3 \cdot 3THF$ (0.063 g, 1.69×10^{-4} mol) in ~20 mL of dry DMF was heated for 5 min at 100 °C, during which time the color changed from magenta to deep purple. Upon disappearance of the starting material (monitored via UV−vis spectroscopy), the solution was cooled, and the solvent was removed under reduced pressure. The residue was redissolved in a *minimum* amount of methanol and filtered, and the volatiles were removed to give a purple powder. Yield: 0.077 g (95.4%). ESI-MS: *m*/*z* 440 (M^+). UV−vis (H_2O) {λ_{max}, nm}: 242, 404, 542.

***cis*-[Dichloro(5,7-dimethyl-6-anthracyl-1,4,8,11-tetraazacyclotetradecane)chromium(III)] Chloride (*cis*-[Cr(mac)Cl$_2$]Cl, 6b)** was prepared by a procedure analogous to that used for the preparation of **6a**. A solution of the macrocyclic ligand mac (0.060 g, 1.43×10^{-4} mol) and $CrCl_3 \cdot 3THF$ (0.054 g, 1.43×10^{-4} mol) in 20 mL of dry DMF was heated for 5 min at 100 °C, during which the color changed from magenta to a deep purple. The solution was cooled, and the solvent was removed under reduced pressure. The residue was redissolved in a *minimum* amount of methanol and filtered, and the volatiles were removed to give a purple powder. Yield: 0.080 g (96.7%). ESI-MS: *m*/*z* 540 (M^+). UV−vis (H_2O) {λ_{max}, nm}: 336, 354, 370, 392, 540.

***trans*-[Dichloro(5,7-dimethyl-6-(*p*-bromomethylbenzyl)-1,4,8,11-tetraazacyclotetradecane)chromium(III)] Bromide (*trans*-[Cr(bbc)Cl$_2$]Br, 7)** was prepared from **5c** following an original procedure. A 0.100 g portion of *trans*-[Cr(hbc)Cl$_2$]Cl (1.97×10^{-4} mol) was partially dissolved in ~5 mL of concentrated HBr (48%) and the resulting solution stirred for 3 h at room temperature. The resulting gray-purple precipitate was collected by filtration and rinsed with acetone followed by ether. Yield: 0.121 g (~100%). ESI-MS: *m*/*z* 534 (M^+). UV−vis (MeOH) {λ_{max}, nm (ϵ, M^{-1} cm^{-1})}: 240 (6.54×10^3), 382 (54.4), 424 sh (35.9), 562 (21.0).

***trans*-[Dichloro(5,7-dimethyl-6-(*p*-aminomethylbenzyl)-1,4,8,11-tetraazacyclotetradecane)chromium(III)] Bromide Hydrobromide (*trans*-[Cr(abc)Cl$_2$]Br·HBr, 8)** was prepared from **7** following an original procedure. A 0.176 g portion of *trans*-[Cr(bbc)Cl$_2$]Br (2.87×10^{-4} mol) was dissolved in dry acetonitrile (15 mL), and the resulting pink solution was treated with ~15 drops of concentrated NH_4OH and stirred for 12 h at room temperature. The solution was then filtered, and the solvent was removed under reduced pressure. The pink precipitate was recrystallized via ether diffusion into a concentrated methanol solution. Large purple crystals were obtained. Yield: 0.145 g (80.1%). ESI-MS: *m*/*z* 469 (M^+). UV−vis (H_2O) {λ_{max}, nm (ϵ, M^{-1} cm^{-1})}: 242 (3.50×10^3), 372 (37.3), 420 sh (31.0), 570 (17.8). Anal. Calcd for $C_{20}H_{38}N_5 \cdot CH_3OH$: C, 37.96; H, 6.37; N, 10.54. Found: C, 37.59; H, 5.79; N, 9.90. An X-ray crystal structure was obtained.

5. Crystal Growth and Structure Determination. Crystal structures for compounds **2b**, **3a**, **3b**, **5a**, **5b**, and **8** have been determined. Crystals of **2b** were grown via slow evaporation of an aqueous solution to yield large yellow hexagonal crystals. Crystals of **3a** and **3b** were grown via slow vapor diffusion of ether into a concentrated acetone solution to yield orange rectangular crystals. Crystals of **5a**, **5b**, and **8** were grown in a manner similar to that of **3a** and **3b** only using methanol in place of acetone to yield long purple needles.

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 a 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.

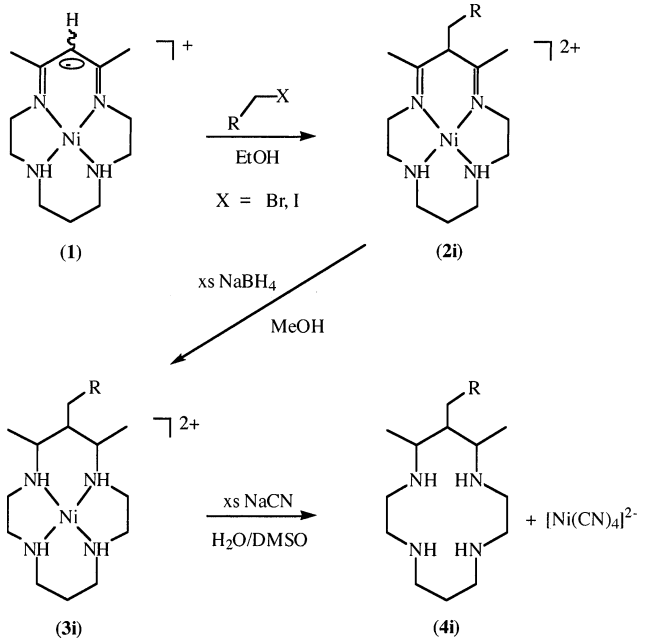
Hydrogen atoms attached to carbon atoms were calculated at ideal positions and refined as riding atoms of the parent carbon atoms. Calculations were performed using SHELXTL running on Silicon Graphics Indy 5000. Final full-matrix refinements were against F^2. Further details are given in the Supporting Information.

Results and Discussion

1. Synthesis and Characterization of Macrocyclic Ni(II) Complexes and Free Ligands. Scheme 2 outlines a synthetic platform for preparing tetraamine macrocyclic complexes with pendant chromophores attached to the carbon backbone using Ni(II)-templated Schiff base condensations.[20,21] Reaction of the R′CH_2X with the dienatonickel(II) complex **1** is more facile if X is Br or I. For example, this was unsuccessful when R′CH_2X was anthracyl chloride, but accomplished in good yields (**2b**, >70%) by the reaction

(23) House, D. A.; Hay, R. W.; Akbar Ali, M. *Inorg. Chim. Acta* **1983**, *72*, 239−245.

Scheme 2. Outline of the Synthetic Route to Pendant-Derivatized Tetraamine Macrocycles **4a**, **4b**, and **4c**



(**1**) (**2i**) (**3i**) (**4i**)

of **1** with anthracyl iodide. The latter was prepared from the chloride in situ using the Finklestein reaction.[18] X-ray crystallographic (**2b**) and IR, MS, and elemental analysis data confirmed the identity of the product. Analogous procedures were used to form the *p*-hydroxymethylbenzyl derivative [Ni(hbc diene)]Br,NO_3 (**2c**) using *p*-hydroxymethylbenzyl bromide.

The reduction of the nickel(II) diimine complexes **2a** and **2b** presented several problems. Although analogous compounds were reported to be reduced by excess $NaBH_4$ in aqueous pyridine/HCl buffer (0.1 M, pH 5.1),[21] we found that only one imine group was reduced. Quantitative reduction was achieved by *partially* dissolving the diimine complex in a small amount of methanol and then adding a ~15−20-fold excess of $NaBH_4$. An immediate color change of the solution from yellow to red was apparent, and a pink precipitate began to form. After 2 h at room temperature the precipitate was collected by filtration. This method was effective for the synthesis of **3a**, **3b**, and **3c**.

Crystal structures were determined for Ni(II) complexes **2b**, **3a**, and **3b**. The coordination geometry in each case was square planar. Selected bond lengths and angles are listed in Table 1. Figure 1 shows the ORTEP diagram for the diimine ligand complex [Ni(anthracyl diene)]$^{2+}$ (**2b**). The N(1)−C(1) and N(2)−C(3) bond lengths are 1.275(4) and 1.278(4) Å, respectively, typical for C═N double bonds,[24] and the N(1)−C(1)−C(11) and N(2)−C(3)−C(12) angles are 123.8(3)° and 123.9(3)°, consistent with sp^2 hybridization at C(1) and C(3). The distance from the center of the anthracene to the Ni(II) metal center is 3.55 Å, suggesting weak attraction between the two centers as was reported for the naphthyl analogue.[24]

Figures 2 and 3 show ORTEP diagrams of the reduced complexes [Ni(mbc)]$^{2+}$ and [Ni(mac)]$^{2+}$. The N(1)−C(1) and N(2)−C(3) bond lengths are 1.487(10) and 1.520(9) Å and 1.504(4) and 1.507(4) Å, respectively, as expected for C−N single bonds. In addition, the N(1)−C(1)−C(11) and N(2)−C(3)−C(12) bond angles are 111.5(8)° and 111.9(7)° for **3a** and 111.6(3)° and 113.2(3)° for **3b**, appropriate for sp^3-hybridized central atoms. For both complexes, the 5- and 7-methyl groups lie in macrocycle equatorial positions while the pendant aromatic chromophore is axial with respect to

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Ni(II) Complexes [Ni(anthracyl diene)]I_2 (**2b**), [Ni(mbc)]$(ClO_4)_2$ (**3a**), and [Ni(mac)]$(ClO_4)_2$ (**3b**)

	2b	3a	3b
Ni(1)−N(1)	1.886(2)	1.960(5)	1.952(3)
Ni(1)−N(2)	1.878(2)	1.942(5)	1.945(3)
Ni(1)−N(3)	1.919(2)	1.937(5)	1.935(3)
Ni(1)−N(4)	1.915(2)	1.939(7)	1.935(3)
N(1)−C(1)	1.275(4)	1.487(10)	1.504(4)
N(2)−C(3)	1.278(4)	1.520(9)	1.507(4)
N(3)−C(6)	1.482(4)	1.484(9)	1.485(4)
N(4)−C(8)	1.486(4)	1.487(12)	1.489(5)
N(1)−C(1)−C(2)	121.4(2)	110.9(8)	112.8(3)
N(1)−C(1)−C(11)	123.8(3)	111.5(8)	111.6(3)
N(2)−C(3)−C(2)	121.0(2)	110.4(6)	109.8(3)
N(2)−C(3)−C(12)	123.9(3)	111.9(7)	113.2(3)
N(1)−Ni(1)−N(3)	174.68(10)	178.9(4)	179.42(13)
N(2)−Ni(1)−N(4)	174.98(11)	177.1(3)	177.12(12)
C(2)−C(13)−C(14)	113.9(2)	118.9(7)	116.9(3)

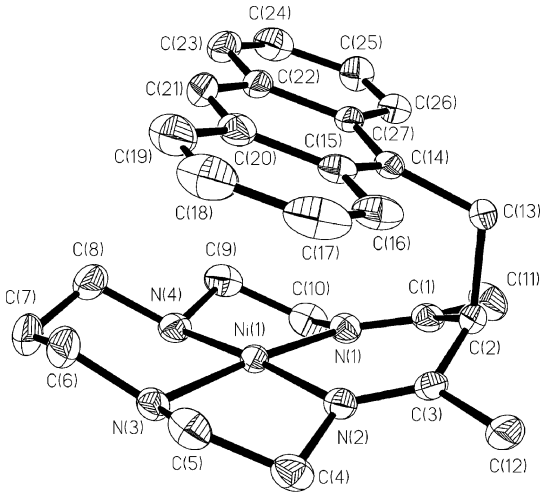


Figure 1. Molecular structure and numbering of atoms for the cation of [Ni(anthracyl diene)]I_2 (**2b**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

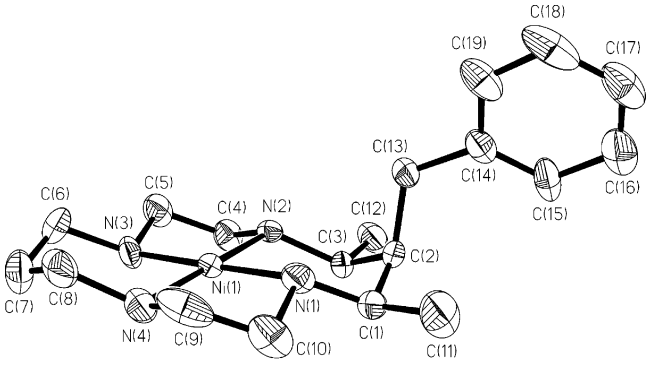


Figure 2. Molecular structure and numbering of atoms for the cation of [Ni(mbc)]$(ClO_4)_2$ (**3a**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

(24) Fabbrizzi, L.; Lichelli, M.; Rospo, C.; Sacchi, D.; Zema, M. *Inorg. Chim. Acta* **2000**, *3002*−*302*, 453−461.

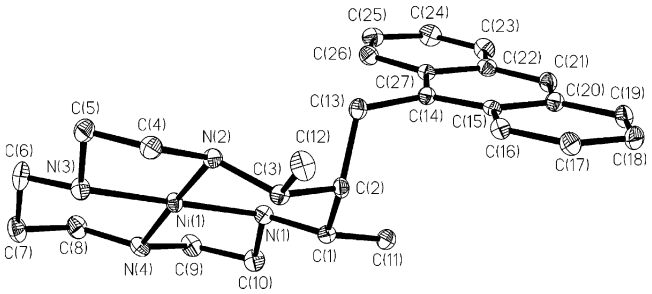


Figure 3. Molecular structure and numbering of atoms for the cation of [Ni(mac)](ClO$_4$)$_2$ (**3b**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

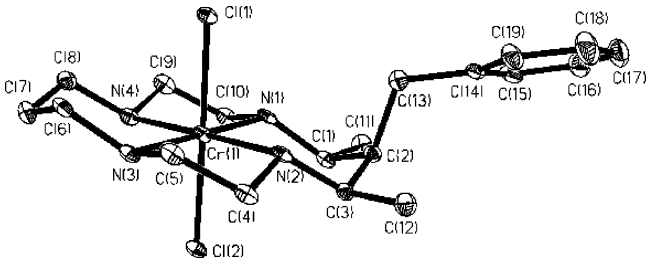
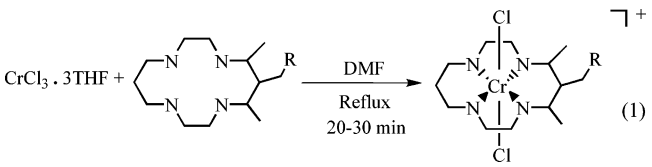


Figure 4. Molecular structure and numbering of atoms for the cation of *trans*-[Cr(mbc)Cl$_2$]Cl (**5a**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

the six-membered ring. This can be explained by attack of BH_4^- at the unsaturated carbon from the less crowded "proximal" side of the diimine functionality complex owing to steric hindrance from the substituent.

Free Ligands. Cyanide removal of the Ni^{2+} from such complexes gave the free macrocyclic ligands.[22] For **3a** and **3c**, reaction in refluxing aqueous solution with a large excess of CN^- (20−30-fold) followed by chloroform extraction recovered mbc and hbc (**4a** and **4c**). With [Ni(mac)](ClO$_4$)$_2$ (**3b**), the same procedure gave an insoluble cyano adduct that did not react further; however, in DMSO/H$_2$O (4.5:1 v/v), the reaction proceeded smoothly. The anthracene-derivatized mac ligand (**4b**) crystallized upon cooling of the solution and was isolated by filtration. ^{1}H and ^{13}C NMR and MS spectral data support the identity of all three ligands.

2. Synthesis and Characterization of Chromium(III) Complexes. Reaction of the cyclam derivatives **4a**, **4b**, and **4c** with CrCl$_3$·3THF in refluxing DMF gave cleanly the *trans* products *trans*-[Cr(mbc)Cl$_2$]Cl (**5a**), *trans*-[Cr(mac)Cl$_2$]Cl (**5b**), and *trans*-[Cr(hbc)Cl$_2$]Cl (**5c**) (eq 1).



(1)

Notably, reaction of unsubstituted cyclam with CrCl$_3$·3THF gives *cis*-[Cr(cyclam)Cl$_2$]Cl as the major product (>90%) with only a small amount of the trans isomer under comparable conditions.[17] It is necessary to reflux solutions of cyclam and CrCl$_3$·3THF in dry DMF for 6 h to effect complete formation of the trans isomer. Samples of *cis*-[Cr(mbc)Cl$_2$]Cl (**6a**) and *cis*-[Cr(mac)Cl$_2$]Cl (**6b**) could be isolated, but only by reducing the reaction time (5−7 min) and temperature (∼100°C) while monitoring the solution optical spectrum. These were obtained as purple powders and purified by fractional recrystallization in MeOH. The assignment of the cis configuration was based on the similarity of the visible spectra to that of [*cis*-Cr(cyclam)Cl$_2$]Cl. However, the low extinction coefficients suggested that the isolated materials might not be pure.

Ready formation of the trans isomer has also been seen for the reaction between *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-A) and CrCl$_3$·3THF.[23] This was interpreted in terms of unfavorable steric interactions between the methyl substituents in the 5 and 12 positions with coordinated chlorides in the cis formation,[23] leading to accelerated isomerization of the initially formed cis complex to the trans analogue. For the present systems substituents in the 5, 6, and 7 positions of the macrocycles may generate similar steric crowding.

Further modification of the Cr(III)-coordinated tetraazo macrocycles was accomplished by utilizing the *p*-hydroxymethylbenzyl derivative **5c** as the starting point. The alcohol functional group was easily converted to the bromo derivative **7** by the reaction of **5c** with concentrated HBr (48%) (3 h at ambient *T*). The heterogeneous mixture was filtered to give *trans*-[Cr(bbc)Cl$_2$]Br in near quantitative yields. Reaction of **7** with aqueous ammonia gave the amino derivative *trans*-[Cr(abc)Cl$_2$]Br·HBr (**8**) for which the X-ray crystal structure was determined (see below). The $-CH_2OH$ and $-CH_2NH_2$ functional groups on the pendant benzyl group were introduced as an entry for the attachment of other chromophores. For example, in preliminary studies,[1] the dye molecule gallocyanine (7-dimethylamino-4-hydroxy-3-oxo-3*H*-phenoxazine-1-carboxylic acid) was attached at the amine group of *trans*-[Cr(abc)Cl$_2$]$^+$ by use of the coupling agent 1-ethyl-3-propyldimethylaminocarbodiimide (EDC) to form an amide bond. The resulting compound was characterized by mass spectroscopy, displayed a strong absorption band at 610 nm ($\epsilon > 10^4$ M^{-1} cm^{-1}), and showed some promise as the forerunner of new dye conjugates; however, purification problems stymied its use in the photophysical studies described below. Another application along this theme is based on the hydroxymethyl derivative **5c**. As described elsewhere,[1,32] this complex can be first converted to the *trans*-dinitrito analogue *trans*-[Cr(hbc)(ONO)$_2$]BF$_4$ by reaction with silver nitrite and then linked at the CH_2OH site to 1-pyrenecarboxylic acid via an ester linkage.

Figures 4−6 are ORTEP diagrams for the Cr(III) cations *trans*-[Cr(mbc)Cl$_2$]$^+$, *trans*-[Cr(mac)Cl$_2$]$^+$, and *trans*-[Cr(abc)Cl$_2$]Br$_2$, respectively. Selected bond lengths and angles are listed in Table 2. The Cl−Cr−Cl bond angles of ∼180° and Cr−Cl bond distances which fall in the range 2.319(2)−2.340(2) Å are similar to those reported for *trans*-[Cr(cyclam)Cl$_2$]Cl.[25] The carbon-substituted macrocycles are coordinated in the trans-III conformation.[14] The methyl groups (C(11) and C(12)) in the ring 5 and 7 positions occupy

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

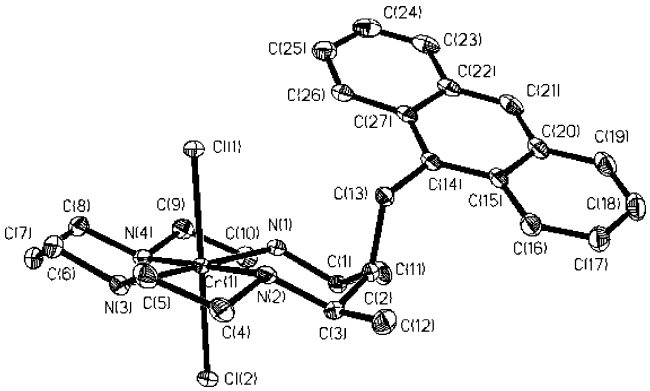


Figure 5. Molecular structure and numbering of atoms for the cation of *trans*-[Cr(mac)Cl_2]Cl (**5b**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

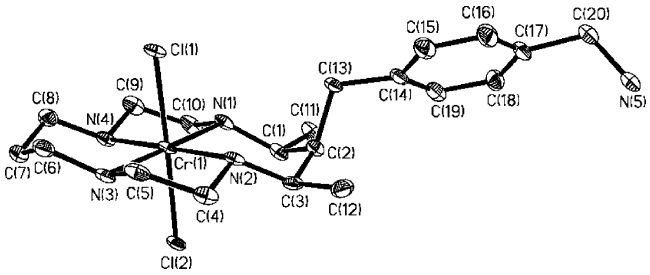


Figure 6. Molecular structure and numbering of atoms for the cation of *trans*- [Cr(abc)Cl_2]Br_2 (**8**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Cr(III) Complexes *trans*-[Cr(mbc)Cl_2]Cl (**5a**), *trans*-[Cr(mac)Cl_2]Cl (**5b**), and *trans*-[Cr(abc)Cl_2]Br_2 (**8**)

	5a	5b	8
Cr(1)−N(1)	2.076(4)	2.0917(16)	2.073(4)
Cr(1)−N(2)	2.074(5)	2.0881(17)	2.074(4)
Cr(1)−N(3)	2.063(4)	2.0553(17)	2.065(4)
Cr(1)−N(4)	2.068(5)	2.0606(17)	2.068(4)
Cr(1)−Cl(1)	2.3189(17)	2.3380(7)	2.3071(13)
Cr(1)−Cl(2)	2.3400(17)	2.3200(7)	2.3448(13)
N(1)−Cr(1)−N(2)	95.00(18)	94.93(6)	94.53(14)
N(1)−Cr(1)−N(3)	179.19(18)	179.40(6)	179.84(15)
N(1)−Cr(1)−N(4)	85.82(18)	85.28(6)	85.99(15)
N(2)−Cr(1)−N(3)	85.72(18)	85.67(6)	85.61(15)
N(2)−Cr(1)−N(4)	178.90(17)	179.80(6)	179.07(14)
N(3)−Cr(1)−N(4)	93.46(18)	94.13(7)	93.87(15)
Cl(1)−Cr(1)−Cl(2)	178.97(6)	179.23(2)	177.97(5)

the equatorial positions, while the aryl methyl substituents occupy the axial position. This "equatorial, axial, equatorial" configuration has been seen previously in analogous complexes.[24]

3. Electronic Absorption and Emission Spectra. The electronic spectra of the modified cyclam complexes *trans*-Cr(L)Cl_2^+ each display a visible range, low-intensity quartet-to-quartet absorption band with a λ_{max} at ∼570 nm (Figure 7 and Supporting Information Figure S1) quite similar to that of *trans*-[Cr(cyclam)Cl_2]$^+$. With the exception of the anthracene derivative **5b**, each of these spectra also showed the expected second quartet absorption band (∼370−420 nm) split as predicted for a d^3 ion in a tetragonally distorted ligand field.[17,26−30] These visible range spectra demonstrate that the substituents have only modest effects on the ligand field strengths of these tetraazo macrocycles when bound in the

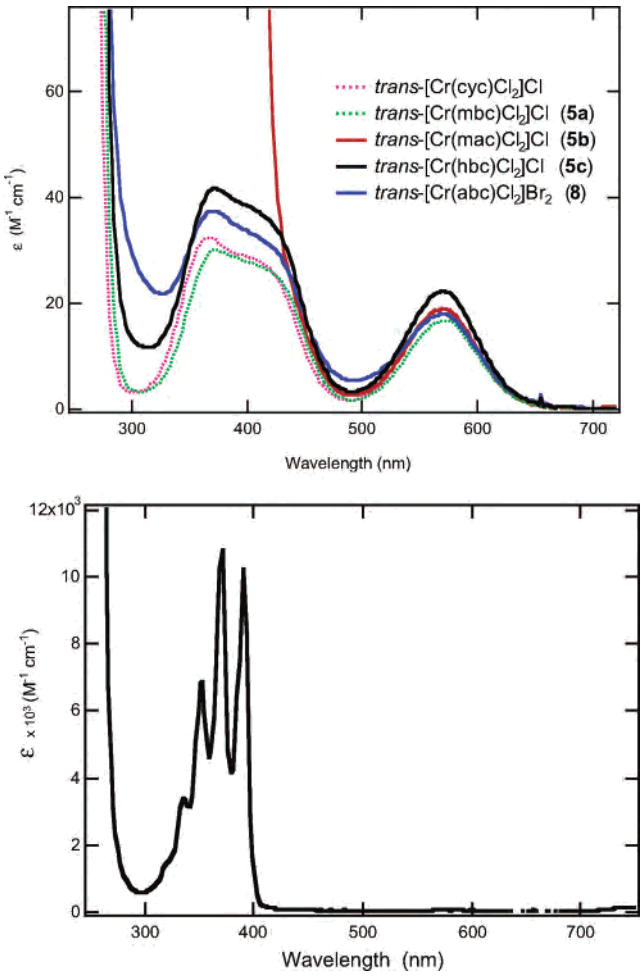


Figure 7. (Top) Optical spectra for **5a**, **5b**, **5c**, **8**, and **10** in aqueous solution (5 mM). The small signal at ∼660 nm is an instrumental artifact (see Supporting Information Figure S1). (Bottom) Spectrum of **5b** recorded in dilute solution (50 μM).

trans position. The spectrum of the anthracene derivative *trans*-Cr(mac)Cl_2^+ differs primarily in that the antenna dominates the near-UV spectrum owing to the strong $\pi-\pi^*$ band that obscures the quartet band in this region (Figure 7b). These spectra and those of several cis analogues are summarized in Table 3. Notably, the spin-forbidden, doublet absorptions predicted for chromium(III) complexes and found at ∼700 nm for related *cis*-dichlorochromium(III) complexes of cyclam derivatives with extinction coefficients of 1−9 M^{-1} cm^{-1} [11] were not obvious in the spectra of the *trans*-dichloro analogues described here. Spectra were recorded for solutions near the solubility limits of the compound (either 5 or 10 mM), and no sharp absorption bands typical of Cr(III) Q_0 to D_0 transitions were seen that could be discerned from the baseline noise (ΔAbs ± 0.001). However, a broad shoulder in the region 650−700 nm ($\epsilon \approx 1$ M^{-1} cm^{-1}) was apparent in this region for each of the compounds described (see Supporting Information Figure S1).

(26) Poon, C. K.; Pun, K. C. *Inorg. Chem.* **1980**, *19*, 568−569.
(27) Meyerstein, D.; Wasgestian, F.; Guldi, D. *Inorg. Chim. Acta* **1992**, *194*, 15−22.
(28) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1992**, *31*, 1108−1110.
(29) Kane-Maguire, N. A. P.; Wallace, K. C.; Miller, D. B. *Inorg. Chem.* **1985**, *24*, 597−605.
(30) Chen, Y.; Perkovic, M. W. *Inorg. Chim. Acta* **2001**, *317*, 127−132.

Table 3. Optical Spectra of *cis*- and *trans*-Dichlorochromium(III) Complexes in Aqueous Media

complex	$\pi-\pi^*$ λ (nm) (ϵ x 10^{-3}, $M^{-1}\,cm^{-1}$)	Q_2 λ (nm) (ϵ, $M^{-1}\,cm^{-1}$)	Q_1 λ (nm) (ϵ, $M^{-1}\,cm^{-1}$)	ref
cis-[Cr(cyclam)Cl_2]Cl		408 (123)	536 (122)	30
		404 (106)	529 (111)	17
cis-[Cr(mbc)Cl_2]Cl (**6a**)	242	406	542	*b*
cis-[Cr(mac)Cl_2]Cl (**6b**)	336, 354, 372, 392	*a*	540	*b*
trans-[Cr(cyclam)Cl_2]Cl		370 (34)	567 (20)	17
		~404 (30) sh		
trans-[Cr(mbc)Cl_2]Cl (**5a**)	242 (4.2)	370 (30)	567 (19)	*b*
		~420 (26) sh		
trans-[Cr(mac)Cl_2]Cl (**5b**)	336 (3.4), 354 (6.8), 372 (10.8), 392 (10.2)	*a*	572 (19)	*b*
trans-[Cr(hbc)Cl_2]Cl (**5c**)	242 (4.3)	372 (47)	567 (25)	*b*
		~420 (43) sh		
trans-[Cr(bbc)Cl_2]Br (**7**)[c]	240 (6.5)	382 (54)	562 (21)	*b*
		~424 (36) sh		
trans-[Cr(abc)Cl_2]Br_2 (**8**)	242 (3.5)	372 (35)	569 (18)	*b*
		~420 (30) sh		

[a] Q_2 band hidden by anthracene absorption. [b] This work. [c] Spectrum taken in methanol.

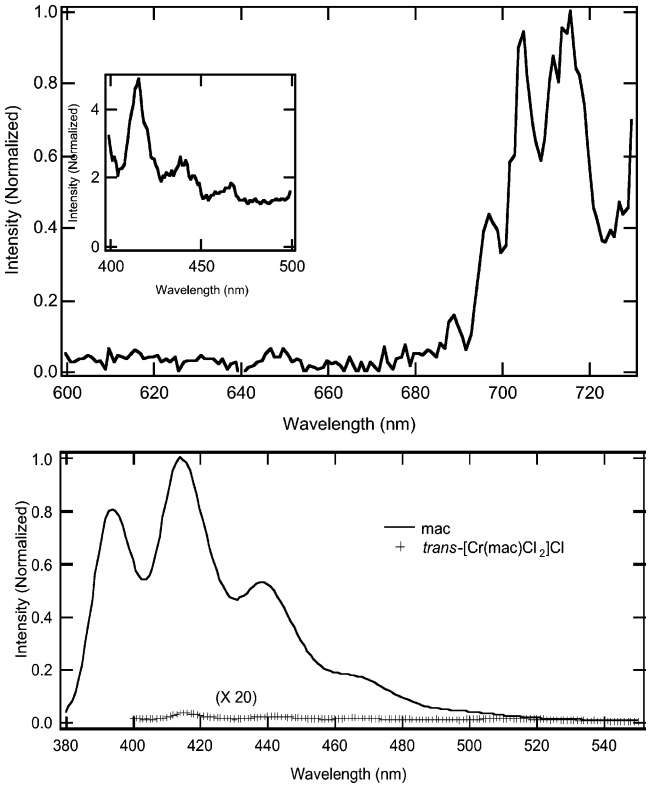


Figure 8. (Top) Emission spectrum for a dilute solution of *trans*-[Cr(mac)Cl_2]Cl (**5b**) (50 μM) in EtOH:MeOH (4:1 v/v) at 77 K (λ_{ex} = 370 nm) showing both the fluorescence from the aromatic chromophore and phosphorescence from the Cr(III) doublet states. (Bottom) Comparison of emission spectra from free mac (50 μM) in aqueous solution vs that from *trans*-[Cr(mac)Cl_2]Cl (50 μM) in 4:1 EtOH/MeOH.

The photoluminescence spectra and lifetimes of **5a** and **5b** were measured at 77 K in 4:1 EtOH/MeOH glasses (5 mM in each case). With 370 nm excitation, each of these compounds displayed weak emission with sharp bands around 700 nm (Figure 8 and Supporting Information Figure S2). The emission spectra and qualitative intensities for both complexes were very close to those we have recorded for the luminescence from *trans*-[Cr(cyclam)Cl_2]Cl (**10**) under identical conditions (Supporting Information Figure S3). In analogy to other Cr(III) compounds, these sharp spectra are attributed to phosphorescence from the lowest energy, doublet ligand field (LF) excited state(s) ($D_o \rightarrow Q_o$).[31] The behavior of **5b** was different; excitation at 370 nm led to weak emission at 416, 442, and 466 nm characteristic of the $\pi-\pi^*$ fluorescence from an anthracene chromophore in addition to the metal-centered doublet phosphorescence (Figure 8). For comparison, emission from the mac free ligand is 500-fold stronger under comparable conditions. This did not diminish in intensity after repeated recrystallization of **5b**, so we attribute it to weak fluorescence from the aromatic appendage of the coordinated mac ligand. Despite this weak $\pi-\pi^*$ emission, it is clear that the singlet state of the anthracene antenna is efficiently quenched (>99%) by the Cr(III) center from which the doublet emission is observed.

The excitation spectra of **5a** and **5b** (λ_{mon} = 704 nm) closely track the absorption spectra in a manner consistent with efficient intramolecular intersystem crossing/internal conversion from the $\pi-\pi^*$ states of the ligand chromophore and from the Cr(III) quartet LF states to the emissive doublet LF state(s). Notably, the bands in the excitation spectra recorded in the 77 K glasses and attributed to the $Q_0 \rightarrow Q_1$ absorptions are blue shifted (to 555 and 558 nm, respectively) from those of the ambient temperature solution absorption spectra. A similar pattern was seen for the excitation spectrum of **10**, where the Q_1 λ_{max} appeared at 552 nm and has been described previously for several *cis*-dichloro(*N*,*N*′-disubstituted cyclam)chromium(III) complexes.[11]

The phosphorescence lifetimes of **5a** and **5b** in (4:1 v/v) EtOH/MeOH glassy solutions at 77 K were determined using 355 nm excitation and monitoring at 704 nm (Table 4). The decay curves were exponential, and the lifetimes determined under these conditions were 88.6 and 27.7 μs, respectively, using 5 mM solutions. For the anthracenyl derivative **5b**, lowering the concentration to 50 μM had no affect on the doublet lifetime; however, the weak anthracene-centered fluorescence was too short-lived (<15 ns) to be measured on our nanosecond laser system. As a reference point, the

(31) (a) Forster, L. S.; Mønsted, O. *J. Phys. Chem.* **1986**, *90*, 5131−5134. (b) Porter, G. B. Chapter 2; Zinato, E. Chapter 4. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; John Wiley and Sons: New York, 1975.
(32) DeRosa, F.; Bu, X.; Ford, P. C. Submitted for publication.

Table 4. Emission Lifetime Data for **10**, **5a**, and **5b**[a]

complex	τ_1 (μs)	ref
trans-[Cr(cyclam)Cl_2]Cl (**10**)	86.9	31
	81.1	*b*
trans-[Cr(mbc)Cl_2]Cl (**5a**)	88.6	*b*
trans-[Cr(mac)Cl_2]Cl (**5b**)	27.7	*b*
	27.5[c]	

[a] Lifetime data were obtained for solutions in EtOH/MeOH (4:1 v/v) glass matrixes (77 K). $\lambda_{ex} = 355$ nm. $\lambda_{mon} = 704$ nm. [b] This work. [c] Solution diluted to 50 μM.

lifetime of **10** was measured as 81.1 μs under these conditions, in reasonable agreement with that (86.9 μs) reported by Forster and Mønsted[31a] under similar circumstances.

Near the conclusion of the present study,[1] Funston et al. reported[33] the template synthesis of several cobalt(III) complexes of cyclam-type ligands with a pendant anthracenyl group, for example, *trans*-[Co(6-anthracenylcyclam)Cl_2]Cl. These workers also reported that the anthracene chromophore fluorescence that is very strong for the free ligand is largely, but not entirely, quenched by coordination to the metal center, and attributed this quenching either to Forster resonance energy transfer to metal-centered states and/or electron-transfer mechanisms involving the cobalt(III) center. As a consequence of irradiating at the wavelengths leading to excitation of the anthracene chromophore, spectral changes attributed to reactions at the cobalt(III) center were observed that were uncharacterized but were consistent with substitutions of the cobalt chloride. Under comparable conditions, photolysis of analogous solutions of *trans*-[Co(cyclam)Cl_2]$^+$ gave no measurable photochemistry; thus, in that case as well, the pendant anthracenyl group apparently serves as an antenna to internally sensitize the excited-state reactions of a metal complex.

(33) Funston, A. M.; Ghiggino, K. P.; Grannas, M. J.; McFadyen, W. D.; Tregloan, P. A. *Dalton Trans.* **2003**, 3704−3712

In summary, in this paper we describe the preparation of several new macrocyclic ligands L with pendant aromatic chromophores R of the type 5,7-dimethyl-6-R-cyclam via a Ni^{2+} template based synthetic scheme. The X-ray structures of several of these Ni(II) intermediates have been determined. The ligands L were then used to prepare chromium(III) complexes with the geometry *trans*-[Cr(L)Cl_2]Cl as determined by X-ray crystallography. Notably, the modified cyclams give the trans Cr(III) coordination geometries much more rapidly than does cyclam itself, and it is likely that this is due to steric interactions from the substituents in the 5, 6, and 7 positions of the macrocycle. The photophysical properties upon $\pi-\pi^*$ excitation of the anthracene antenna tethered to the macrocyclic ligand of *trans*-[Cr(mac)Cl_2]Cl are characterized by nearly complete quenching of the anthracene-centered fluorescence coupled to phosphorescence from Cr(III)-centered ligand field doublet states. Notably, the *trans*-[Cr(L)Cl_2]Cl complexes described here are synthons for various dinitrito complexes *trans*-[Cr(L)$(ONO)_2$]BF_4 that are being studied as possible photochemical precursors for nitric oxide delivery to biological targets.[8,32] The syntheses and photochemical reactions of several examples of the latter compounds are reported elsewhere.[1,32]

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Supporting Information Available: Three figures showing emission data and listings of complete structure refinement details, bond lengths and angles, anisotropic displacement parameters for non-hydrogen atoms, and hydrogen coordinates and isotropic displacement parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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