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Synthesis and Complexation of “Back-to-Back” Capped Bis-dioxocyclams

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Pyridine-capped 5,12-dioxocyclams were coupled “back-to-back” directly, with one or two intervening phenyl groups, an ethynyl group, or a diazo group via Suzuki, Sonogashira, or reductive coupling of the 4-nitropyridine monocyclam. These bis-dioxocyclams linked through extended π-conjugated systems were complexed to copper(II) and cobalt(III), producing bis-metal complexes which were characterized spectroscopically and electrochemically. These studies gave little evidence for electronic communication between metal centers across the π-conjugated linkers.

Introduction

Coordinated transition metal centers covalently connected by π-conjugated linkers of various constitution and length, capable of electron or energy transfer, have been extensively investigated for use in areas ranging from the development of “molecular wires” to the modeling of photosynthesis.[1] Transition metal arrays connected via *coordination* linkages with ligands capable of transmitting electronic or magnetic information across the π system of the linking ligands have become important to the study of long-range electron transfer and magnetic interactions.[2] Complexes having the potential to form extended π networks via both covalent and coordination linkages are less common and may share the physical properties of both types of systems, as well as have unique properties. Initial studies directed toward the synthesis of this class of complex are described below.

Recent research in these laboratories has focused on the synthesis and metal complexation studies of dioxocyclams,[3] bis-dioxocyclams,[4] and capped dioxocyclams having additional ligand sites external to the macrocycle,[5] as well as the ability to coordinate additional metals at this site.[6] Application of this methodology to the synthesis of bis-dioxocyclams which are linked back-to-back with conjugated capping groups, as well as their cobalt(III) cyanide complexes, which can form coordinate links to other metals, is described below.

Experimental Section

General Procedures. Acetonitrile was distilled over calcium hydride. Methanol was distilled over calcium hydride and dried over 4 Å molecular sieves. NMR spectra were recorded on Varian JS-300 or JS 400 spectrometers. Infrared spectra were recorded on a Nicolet Magna-IR 760 spectrometer. UV−vis spectra were recorded on an Agilent G 1103 spectrometer. Electrochemical measurements were conducted with an EG and G, Princeton Applied Research, model 75 universal programmer, model 179 digital coulometer, and model 173 potentiostat/galvanostat. The complex was dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile or CH_2Cl_2. The working electrode was glassy carbon, and the counter electrode was a platinum wire. The reference electrode was SCE, and potentials were reported versus

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SCE. Cyclic voltammograms were obtained at a scan rate of 100 mV/s. Data were plotted with the *x* axis equal to 100 mV/cm. Microwave reactions were performed in a GE countertop microwave oven, model number JES1339WC, which had a capacity of 1.3 ft^3 and a watt output of 1100 W. Because the compounds all occlude solvent on crystallization, melting points are broad and elemental analyses are unreliable. Constitution was assessed by high-resolution mass spectroscopy, and purity by high-resolution ^1H and ^{13}C NMR spectroscopy (see Supporting Information).

2,2′,6,6′-Tetrakis(hydroxymethyl)-4,4′-bipyridine 3. 2,2′,6,6′-Tetra(carboxymethyl)-4,4′-bipyridine (**2**)[8] (0.504 g, 1.3 mmol) was placed into a 100 mL round-bottom flask and dissolved in dry absolute EtOH (10 mL). The flask was equipped with a condenser and flushed with Ar. The flask was cooled to 0 °C, and $NaBH_4$ (0.385 g, 11.0 mmol) was added in portions. The blue solution was kept at 0 °C for 1.5 h then warmed to reflux for 24 h under Ar. H_2O (20 mL) was then added to the tan solution and stirred for 6 h at low heat. Solvent was removed under reduced pressure, and the residue was purified using silica gel chromatography eluting with MeOH to afford the white powder (0.307 g, 1.1 mmol). Yield: 85%. ^1H NMR (CD_3OD, 300 MHz) δ 7.79 (s, 4H), 4.77 (s, 8H); ^{13}C NMR (CD_3OD, 75 MHz) δ 163.2, 149.3, 118.0, 65.6; IR (Nujol) ν 2963, 1459 cm^{-1}; HRMS (FAB^+, *m/z*) Calcd for $C_{14}H_{17}N_2O_4$ ($M + H^+$), 277.01188; found, 277.01176; mp = 210 °C dec.

2,2′,6,6′-Tetrakis(bromomethyl)-4,4′-bipyridine 4a. 2,2′,6,6′-Tetrakis(hydroxymethyl)-4,4′-bipyridine (**3**) (0.127 g, 0.46 mmol) and 2 drops of DMF were placed into a 10 mL round-bottom flask equipped with a drying tube, and $SOBr_2$ (6 mL) was added slowly and stirred for 16 h. The reaction solution was transferred to a 250 mL flask, and CH_2Cl_2 (50 mL) was added to the reaction mixture followed by the slow addition of H_2O (50 mL) (***Caution:*** *exothermic!*). Then 40% KOH was added until pH 11 was reached. After partitioning of the two layers, the aqueous solution was extracted with CH_2Cl_2 (50 mL × 2). The combined organic phase was dried over Na_2SO_4 and filtered. Concentration under reduced pressure afforded a white powder (0.135 g, 0.26 mmol). Yield: 56%; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.59 (s, 4H), 4.61(s, 8H) ^{13}C NMR (CD_3OD, 75 MHz) δ 158.3, 147.6, 120.9, 33.24; IR (Nujol) 2955, 1460 cm^{-1}; Elemental analysis: Calcd for $C_{14}H_{13}N_2Br_4$, C 31.85, H 2.29, N 5.31, Br 60.55; found, C 32.04, H 2.18, N 5.12, Br 60.27; mp = 190 °C dec.

2,2′,6,6′-Tetrakis(chloromethyl)-4,4′-bipyridine 4b. 2,2′,6,6′-Tetrakis(hydroxymethyl)-4,4′-bipyridine (**3**) (0.101 g, 0.36 mmol) and 4 drops of DMF were placed into a 10 mL round-bottom flask equipped with a drying tube, and $SOCl_2$ (6 mL) was added slowly and stirred for 16 h. The reaction solution was transferred to a 250 mL flask, and CH_2Cl_2 (50 mL) was added to the reaction mixture followed by the slow addition of H_2O (50 mL) (***Caution:*** *exothermic!*). The solution was brought to pH 8 by slow addition of solid $NaHCO_3$. After partitioning of the two layers, the aqueous solution was extracted with CH_2Cl_2 (50 mL × 2). The combined organic solution was dried over Na_2SO_4 and filtered. Concentration under reduced pressure afforded a white powder (0.090 g, 0.26 mmol). Yield: 71%; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.68 (s, 4H), 4.75(s, 8H) ^{13}C NMR (CD_3OD, 75 MHz) δ 157.9, 147.8, 120.2, 46.4; IR (Nujol) 2965, 1459 cm^{-1}; HRMS (FAB^+, *m/z*) Calcd for $C_{14}H_{13}N_2Cl_4$ ($M + H^+$), 348.9833; found, 348.9832; mp = 154−157 °C.

4,4′-Bipyridine-Capped Bis-dioxocyclam 1a. Dioxocyclam (**5**)[3a] (0.235 g, 0.634 mmol), **4b** (0.110 g, 0.316 mmol), Na_2CO_3 (0.268 g, 2.52 mmol), and NaI (0.047 g, 0.316 mmol) were added to an argon-flushed pressure tube. After dissolution in distilled CH_3CN (100 mL), the reaction was purged with argon. The pressure tube was tightly sealed and placed into a 60−70 °C oil bath with stirring for 4 days. After being cooled to ambient temperature, the reaction mixture was transferred to a 250 mL round-bottom flask and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and H_2O (50 mL) and stirred for 1 h, and the two layers were partitioned. The aqueous layer was extracted with CH_2Cl_2 (100 mL × 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification by flash silica gel chromatography using 0−25% MeOH in EtOAc afforded the solid product (0.230 g, 0.242 mmol). Yield: 77%. X-ray quality crystals were formed from slow evaporation of CH_2Cl_2/hexane; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.06 (s, 1H), 9.05(s, 1H), 7.98 (s, 1H), 7.97 (s, 1H), 7.20 (s, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 7.16 (s, 1H), 4.23 (d, J = 16.8 Hz 2H), 4.14 (d, J = 17.2 Hz 2H), 4.08 (d, J = 17.2 Hz 2H), 4.023 (d, J = 17.2 Hz 1H), 4.016 (d, J = 17.2 Hz 1H), 3.43 (s, 6H), 3.23 (d, J = 14.0 Hz 2H), 3.02−2.90 (m, 10H), 2.60 (d, J = 14.0 Hz 2H), 2.51 (s, 3H), 2.50 (s, 3H), 2.35 (d, J = 14.4 Hz 2H), 1.47 (s, 6H), 1.44 (s, 6H), 1.37 (s, 6H), 1.33 (s, 6H), 1.21 (s, 6H), 1.142 (s, 3H), 1.137 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 172.7, 164.3, 159.8, 147.4, 147.2, 117.1, 117.0, 116.8, 116.6, 82.7, 79.6, 74.6, 72.7, 69.5, 69.4, 67.4, 65.7, 64.7, 56.0, 54.8, 51.9, 50.3, 26.3, 25.6, 23.6, 23.5, 19.2; FT-IR (film) ν 1661 cm^{-1} (C=O); UV−vis ($CHCl_3$) λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 280 (sh) [5980]; MS (FAB^+, *m/z*) for $C_{50}H_{81}N_{10}O_8$ ($M + H^+$) found, 949.15.

4-Bromo-2,6-bis(chloromethyl)pyridine 4c. To dimethyl-4-bromo-2,6-pyridinedicarboxylate[8] (3.3 g, 12 mmol) solution in absolute EtOH (150 mL) was added $NaBH_4$ (1.82 g, 48 mmol) portionwise at 0 °C. After being stirred for 2 h, the reaction mixture was warmed to ambient temperature, stirred overnight, and refluxed for 10 min. After being cooled to room temperature, the solvent was removed under reduced pressure until the mixture became a slurry. H_2O (15 mL) was added, the mixture extracted with CH_2Cl_2 (50 mL × 4), and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum. Without further purification, the obtained white solid (2.3 g) was dissolved in DMF (23 mL) and was cooled to −10 °C. Then, $SOCl_2$ (3.8 mL) was added dropwise. After the mixture was stirred for 1 h at 0 °C, CH_2Cl_2 (50 mL) and EtOAC (100 mL) were added and then H_2O (30 mL) was added slowly to quench the remaining $SOCl_2$ at 0 °C. After the reaction was stirred for 30 min, 10 N NaOH solution was added at 0 °C until pH 8−9 was achieved and the solution was warmed to room temperature. After partitioning of the two layers, the aqueous solution was extracted with EtOAc (50 mL × 4). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification by flash silica gel chromatography using 10% EtOAc in hexane afforded the solid product (2.2 g, 8.73 mmol). Yield: 73%; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.63 (s, 2H), 4.62 (s, 4H).

4-Bromopyridine-Capped Dioxocyclam 7.[5b] Dioxocyclam (**5**)[3a] (0.86 g, 2.3 mmol), **4c** (0.65 g, 2.5 mmol), Na_2CO_3 (0.98 g, 9.24 mmol), and NaI (0.17 g, 1.2 mmol) were placed in an argon-flushed pressure tube. After the mixture was dissolved in distilled CH_3CN (250 mL), the procedure above afforded the desired product (1.21

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g, 2.19 mmol). Yield: 95%. The physical properties of this compound were identical to those previously reported.[5b]

1,4-Bis(1,3,2-dioxaborolanyl)benzene 6a. In freshly distilled THF (100 mL), *p*-dibromobenzene (2.36 g, 10 mmol) and magnesium turnings (0.535 g, 22 mmol) were added and refluxed for 2 days under purging with Ar (white cloudy solution). After cooling to −78 °C, $B(OEt)_3$ (4.25 mL, 25 mmol, neat) was added by syringe. After warming to ambient temperature slowly and stirring for 3 h, the reaction mixture was concentrated under reduced pressure. The obtained white solid was dissolved in ethylene glycol (50 mL) and toluene (100 mL) and then refluxed for 13 h. After the reaction cooled to ambient temperature, the two layers were partitioned. The glycol layer was extracted with toluene (100 mL × 2). The combined toluene extracts were concentrated under vacuum. Recrystallization from CH_2Cl_2/hexane (1:5), washing the precipitate with hexane and drying, under reduced pressure afforded the white solid product (0.436 g, 2.00 mmol). Yield: 20%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (s, 4H), 4.40(s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.3, 117.6, 66.3; FT-IR (solid) ν 2980, 2908, 1519, 1328.

1,4-Bis(4-Pyridyl)benzene-Capped Bis-dioxocyclam 1b. 7 (0.106 g, 0.19 mmol), bis-borate ester (**6a**) (0.020 g, 0.092 mmol), K_2CO_3 (0.054 g, 0.386 mmol), and $Pd(PPh_3)_4$ (0.022 g, 0.019 mmol) were placed in an argon-flushed pressure tube. After being dissolved in distilled MeOH (4 mL), the reaction mixture was degassed by repeating a freeze−pump−thaw sequence three times and was purged with argon. The pressure tube was tightly sealed and placed into a 90−110 °C oil bath with stirring for 4 days. After being cooled to ambient temperature, the resulting brownish reaction mixture was passed through a Celite pad and concentrated under reduced pressure. The mixture was dissolved in CH_2Cl_2 (30 mL) and H_2O (20 mL) and stirred for 1 h, and the two layers were partitioned. The aqueous layer was extracted with CH_2Cl_2 (30 mL × 2). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification by flash silica gel chromatography using 10−25% MeOH in EtOAc afforded the desired product (0.091 g, 0.089 mmol). Yield: 97%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.13 (s, 2H), 8.06(s, 1H), 8.05 (s, 1H), 7.77 (s, 4H), 7.21 (s, 2H), 7.18 (s, 2H), 4.24 (d, J = 16.8 Hz 2H), 4.16 (d, J = 17.2 Hz 2H), 4.09 (d, J = 16.8 Hz 2H), 4.03 (d, J = 17.2 Hz 2H), 3.44 (s, 6H), 3.24 (d, J = 13.6 Hz 2H), 3.01−2.89 (m, 10H), 2.62 (d, J = 14.0 Hz 2H), 2.55 (s, 6H), 2.39 (d, J = 14.0 Hz 2H), 1.48 (s, 6H), 1.45 (s, 6H), 1.40 (s, 6H), 1.34 (s, 6H), 1.21 (s, 6H), 1.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.5, 172.8, 163.9, 159.3, 148.9, 139.3, 127.9, 117.1, 116.9, 82.7, 79.7, 74.7, 72.7, 69.5, 67.5, 65.8, 64.8, 56.0, 54.9, 51.9, 50.3, 26.3, 25.7, 23.7, 23.5, 19.3; FT-IR (film) 1660 ν cm^{-1} (C═O); UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 282 [62400]; HRMS (FAB$^+$, *m/z*) Calcd for $C_{56}H_{85}N_{10}O_8$ (M + H$^+$), 1025.6552; found, 1025.6560; mp = 230−240 °C dec.

4,4′-Bis(1,3,2-dioxaborolanyl)biphenyl 6b. 4,4′-Dibromobiphenyl (1.56 g, 5.00 mmol) was dissolved in distilled THF (70 mL), and the reaction mixture was cooled to −78 °C. *n*-BuLi (1.6 M in hexane, 6.88 mL, 11 mmol) was added by syringe. After the reaction was stirred for 1.5 h at −78 °C, $B(OEt)_3$ (neat, 2.6 mL, 15 mmol) was added by syringe and the reaction mixture was stirred for 1 h at −78 °C and warmed to ambient temperature. After being stirred at room temperature for 2 h, the reaction mixture was concentrated under reduced pressure. The obtained white solid was dissolved in ethylene glycol (50 mL) and toluene (150 mL) and then refluxed for 2 days. After being cooled to ambient temperature, the two layers were partitioned. The glycol layer was extracted with toluene (100 mL × 2). The combined toluene extracts were concentrated under vacuum. Recrystallization from CH_2Cl_2/hexane (1:5), washing the precipitate with hexane, and drying under reduced pressure afforded the white solid product (1.1 g, 3.8 mmol). Yield: 76%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (d, J = 7.8 Hz 4H), 7.68 (d, J = 8.1 Hz 4H), 4.43 (s, 8H).

4,4′-Bis-(4-pyridyl)biphenyl-Capped Bis-dioxocyclam 1c. 7 (0.11 g, 0.19 mmol), **6b** (0.026 g, 0.09 mmol), K_2CO_3 (0.097 g, 0.701 mmol), and $Pd(PPh_3)_4$ (0.022 g, 0.019 mmol) were placed in an argon-flushed pressure tube. Following the procedure above afforded the desired product as a white solid (0.090 g, 0.082 mmol). Yield: 91%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.16 (s, 2H), 8.07 (s, 2H), 7.77 (s, 8H), 7.23 (s, 2H), 7.20 (s, 2H), 4.25 (d, J = 16.8 Hz 2H), 4.17 (d, J = 17.1 Hz 2H), 4.11 (d, J = 16.8 Hz 2H), 4.03 (d, J = 17.1 Hz 2H), 3.45 (s, 6H), 3.24 (d, J = 13.8 Hz 2H), 3.01−2.90 (m, 10H), 2.64 (d, J = 14.1 Hz 2H), 2.56 (s, 6H), 2.40 (d, J = 14.4 Hz 2H), 1.49 (s, 6H), 1.46 (s, 6H), 1.42 (s, 6H), 1.34 (s, 6H), 1.22 (s, 6H), 1.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.5, 172.9, 163.8, 159.2, 149.3, 141.2, 137.8, 128.0, 127.8, 117.1, 116.9, 82.7, 79.7, 74.7, 72.7, 69.6, 67.5, 65.8, 64.8, 56.0, 54.9, 52.0, 50.4, 26.3, 25.7, 23.7, 23.5, 19.3; FT-IR (film) ν 1656 cm^{-1} (C═O); UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 306 [69100]; HRMS (FAB$^+$, *m/z*) Calcd for $C_{62}H_{89}N_{10}O_8$ (M + H$^+$), 1101.6865; found, 1101.6864; mp = 220−225 °C dec.

1,2-Bis(4-pyridyl)ethyne-Capped Bis-dioxocyclam 1d. 7 (0.055 g, 0.100 mmol), 4-ethynylpyridine-capped dioxocyclam (**8**)[7] (0.050) g, 0.100 mmol), CuI (0.002 g, 0.010 mmol), and $PdBr_2(PPh_3)_2$ (0.008 g, 0.010 mmol) were placed in an argon-flushed pressure tube. After being dissolved in distilled MeOH (2 mL) and Et_3N (2 mL), the reaction mixture was degassed by repeating a freeze−pump−thaw sequence three times and was purged with argon. The pressure tube was tightly sealed and placed into 95−100 °C oil bath with stirring for 3 days. After being cooled to ambient temperature, the resulting brownish reaction mixture was passed through a Celite pad and concentrated under reduced pressure. The mixture was dissolved in CH_2Cl_2 (30 mL) and saturated $NaHCO_3$ (20 mL) and stirred for 1 h, and the two layers were partitioned. The aqueous layer was extracted with CH_2Cl_2 (30 mL × 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification by flash silica gel chromatography using 10% MeOH in EtOAc afforded the desired product as a white solid (0.060 g, 0.062 mmol). Yield: 62%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.95 (s, 2H), 7.90 (s, 2H), 7.08 (s, 2H), 7.05 (s, 2H), 4.17 (d, J = 17.2 Hz 2H), 4.08 (d, J = 17.2 Hz 2H), 4.02 (d, J = 17.2 Hz 2H), 3.95 (d, J = 17.2 Hz 2H), 3.42 (s, 6H), 3.21 (d, J = 13.6 Hz 2H), 2.99−2.87 (m, 10H), 2.57 (d, J = 14.0 Hz 2H), 2.56 (s, 6H), 2.32 (d, J = 14.4 Hz 2H), 1.45 (s, 6H), 1.42 (s, 6H), 1.35 (s, 6H), 1.31 (s, 6H), 1.20 (s, 6H), 1.14 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.3, 172.7, 163.6, 159.0, 131.3, 121.3, 120.8, 90.6, 82.7, 79.6, 74.6, 72.8, 69.2, 67.4, 65.5, 64.8, 56.0, 54.8, 52.0, 50.4, 26.3, 25.7, 23.6, 23.5, 19.3; FT-IR (film) ν 1660 cm^{-1} (C═O); UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 280 [27900]; HRMS (FAB$^+$, *m/z*) Calcd for $C_{52}H_{81}N_{10}O_8$ (M + H$^+$), 973.6239; found, 973.6211; mp = 230−240 °C dec.

1,2-Di(pyridine-4-yl)diazine-Capped Bis-Dioxocyclam 1e. 4-Nitropyridine-capped dioxocyclam **9**[5b] (0.180 g, 0.350 mmol) was dissolved in distilled THF (20 mL) in a round-bottomed flask equipped for reflux. After the flask was flushed with Ar, $NaBH_4$ (0.039 g, 1.04 mmol) was added into the reaction. With flowing Ar, the reaction was heated at reflux for a day. EtOH (2 mL) was added to the reaction, and then the refluxing was continued for 3 days (orange-colored solution). After being cooled to ambient temperature, H_2O (50 mL) was added for quenching. After the reaction was stirred for a day, EtOAc (50 mL) was added and the two layers were partitioned. The aqueous layer was extracted with CH_2Cl_2 (30 mL × 2). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification by flash silica gel chromatography 15% MeOH in EtOAc afforded the orange solid product (0.111 g, 0.114 mmol). Yield: 65%. X-ray quality crystals were obtained from EtOAc by slow evaporation; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (s, 2H), 7.95 (s, 1H), 7.94 (s, 1H), 7.38 (s, 2H), 7.37 (s, 2H), 4.31 (d, $J = 17.2$ Hz 2H), 4.18 (d, $J = 17.2$ Hz 2H), 4.12 (d, $J = 15.6$ Hz 2H), 4.08 (d, $J = 16.8$ Hz 2H), 3.42 (s, 6H), 3.22 (d, $J = 13.6$ Hz 2H), 3.00−2.90 (m, 10H), 2.61 (d, $J = 14.4$ Hz 2H), 2.53 (s, 6H), 2.37 (d, $J = 14.4$ Hz 2H), 1.47 (s, 6H), 1.44 (s, 6H), 1.36 (s, 6H), 1.32 (s, 6H), 1.20 (s, 6H), 1.14 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.4, 172.7, 165.5, 160.8, 158.4, 112.5, 111.2, 82.6, 79.6, 74.5, 72.7, 69.5, 67.4, 65.8, 64.7, 55.9, 54.8, 51.9, 50.3, 26.2, 25.6, 23.6, 23.4, 19.2; FT-IR (film) ν 1657 cm^{-1} (C═O); UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 290 [21 100], 460 (sh) [430]; HRMS (FAB$^+$, *m*/*z*) Calcd for $C_{50}H_{81}N_{12}O_8$ (M + H$^+$), 977.6300; found, 977.6328; mp = 230−240 °C dec.

Bis-copper(II) Complex 10a. 1a (0.018 g, 0.200 mmol), K_2CO_3 (0.027 g, 0.200 mmol), and $Cu(BF_4)_2 \cdot xH_2O$ (0.47 g, ≈2 mmol) were placed in a 20 mL pressure tube, and the mixture was suspended in dry distilled MeOH (3 mL). The pressure tube was flushed with Ar, tightly sealed, and heated to 85 °C for 4 days. After being cooled to ambient temperature, the reaction mixture was filtered through a Celite pad and washed with MeOH. The obtained greenish solution was concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 and filtered through a pad of Celite, which was washed with CH_2Cl_2. The solvent was removed under reduced pressure to yield the desired product (0.030 g, 0.016 mmol) as a light-green powder. Yield: 78%. X-ray quality crystals were produced by vapor diffusion using $CHCl_3$ and *n*-pentane. FT-IR (film) ν 1570 cm^{-1}; UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 685 [150]; MS (FAB$^+$, *m*/*z*) $C_{50}H_{77}Cu_2N_{10}O_8$ (M + H$^+$) found, 1071.7; ESR: unsymmetrical two harmonics *G* value: 2.1319(major), 2.0473(minor); mp = 230−240 °C dec.

Bis-copper(II) Complex 10b. 1b (0.093 g, 0.090 mmol), K_2CO_3 (0.125 g, 0.900 mmol), and $Cu(BF_4)_2 \cdot xH_2O$ (0.214 g, ≈0.9 mmol) were placed in a 20 mL pressure tube, and the mixture was suspended in dry distilled MeOH (5 mL). The pressure tube was flushed with Ar, tightly sealed, and heated at 90 °C for 3 days. After being cooled to ambient temperature, the reaction mixture was filtered through a Celite pad and washed with excess MeOH. The obtained greenish solution was concentrated under reduced pressure and purified using silica gel pretreated with 2% Et_3N in MeOH (eluent: from MeOH to 5% Et_3N in MeOH). The obtained green solution was concentrated, dissolved in $CHCl_3$ (3 mL), and filtered through a cotton pad. The filtrate was precipitated by the diffusion of hexane, filtered through a cotton pad again, and the precipitate washed with hexane. Washing out the greenish precipitate from the cotton pad using excess $CHCl_3$ and concentration under vacuum afforded the desired product (0.044 g, 0.038 mmol). Yield: 42%; FT-IR (film) ν 1590 cm^{-1} (C═O); UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 285 (sh) [32 200], 365 (sh) [3640], 676 [190]; MS (electrospray) found for $C_{56}H_{81}Cu_2N_{10}O_8$ (M$^+$ + H), 1149.5; ESR: symmetrical one harmonic *G* value: 2.1273; mp = 230−240 °C dec.

Bis-copper(II) Complex 10c. 1c (0.027 g, 0.025 mmol), K_2CO_3 (0.034 g, 0.250 mmol), and $Cu(BF_4)_2 \cdot xH_2O$ (0.058 g, ≈0.25 mmol) were placed in a 20 mL pressure tube, and the mixture was dissolved in dry distilled MeOH (3 mL). The pressure tube was flushed with Ar, tightly sealed, and heated at 90 °C for 3 days. After being cooled to ambient temperature, the reaction was filtered through a Celite pad and washed with excess MeOH. The obtained greenish solution was concentrated under reduced pressure and purified using silica gel pretreated with eluent (eluent: 2% Et_3N in MeOH). The obtained green eluent was concentrated, and the residue dissolved in CH_2Cl_2 (3 mL), precipitated by the diffusion with hexane, and filtered through a cotton pad. The precipitate was washed with excess EtOAc and hexane. Dissolving the greenish precipitate from the cotton pad using excess $CHCl_3$ and concentration in a vacuum afforded the desired product (0.020 g, 0.016 mmol). Yield: 67%; FT-IR (film) ν 1586 cm^{-1} (C═O); UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 308 [62 900], 375 [8187], 668 [232]; MS (electro spray) Calcd for $C_{62}H_{84}Cu_2N_{10}O_8$ (M$^+$), 1224.507; found, 1223.47 (−H), 1225.27 (+H); ESR: symmetrical one harmonic *G* value: 2.0173; mp = 230−240 °C dec.

Bis-copper(II) Complex 10e. 1e (0.052 g, 0.053 mmol), K_2CO_3 (0.138 g, 1.00 mmol), and $Cu(BF_4)_2 \cdot xH_2O$ (0.237 g, ≈1 mmol) were placed in a 20 mL pressure tube, and the mixture was suspended in dry distilled MeOH (4 mL). The pressure tube was flushed with Ar, tightly sealed, and heated at 90 °C for 4 days. After being cooled to ambient temperature, the reaction mixture was filtered through a Celite pad and washed with excess MeOH. The resulting brown solution was concentrated under reduced pressure and purified using silica gel pretreated with eluent (eluent: 2% Et_3N in MeOH). The brown eluent was concentrated, and the residue dissolved in CH_2Cl_2 (3 mL), precipitated by the diffusion of hexane, filtered through a cotton pad, and washed with excess EtOAc and hexane. Dissolving the brownish precipitate from the cotton pad using excess $CHCl_3$ and concentration in a vacuum afforded the desired product (0.044 g, 0.040 mmol). Yield: 75%; FT-IR (film) ν 1586 cm^{-1} (C═O); UV−vis: λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 277 [20 600], 375 [4970], 660 [130]; MS (electrospray) Calcd for $C_{50}H_{79}Cu_2N_{12}O_8$ (M$^+$ + H), 1100.45; found, 1101.20; ESR: symmetrical one harmonic *G* value: 2.0182; mp = 230−240 °C dec.

Procedure for the Preparation of a Commercial Microwave Oven for Reaction Use. To prepare a commercial microwave oven for reaction conditions, the focus point of the microwave radiation must be determined. The rotation wheel was removed from under the glass plate of the microwave. The plate was then covered evenly with (1/4 in.) 4 Å mol sieves. The microwave was then operated at high power until one area of the sieves started to glow. This spot was marked on the glass plate. This determined the focus point on the horizontal plane. For the vertical plane, a pressure tube was rotated 360° on the marked spot until maximum microwave radiation was found. This was determined by preparation of a cobalt(III) complex. When not in the focus point, the tube would become warm but the solution would remain pink. When in the focus point, the pressure tube would become warm and the solution would turn purple. The direction the tube should point was then marked on the glass plate. This setup procedure is necessary only once to find the focus point. All reactions were performed behind a blast shield starting at a power level of 10% and a time of 30 s. The power level and time were increased until appropriate conditions were determined, and all reactions were cooled to room temperature between microwave sets. The power level and time were never increased above 20% and 3 min, respectively. To prevent explosions or bumping, all reactions were shaken prior to a microwave set. This is especially important if the reaction forms a precipitate. The precipitate must be suspended in solution prior to each microwave set. When all of these precautions were followed, our laboratories safely performed several thousand cycles with no adverse side affects such as explosions.

Bis-cobalt(III) Complex 11a. 1a (0.215 g, 0.227 mmol), $Co(CH_3CO_2)_2 \cdot 4H_2O$ (1.13 g, 4.53 mmol), and $(i\text{-Pr})_2NEt$ (0.586 g, 4.53 mmol) were placed in a 20 mL pressure tube, and the mixture was dissolved in distilled MeOH (5 mL). The pressure tube was tightly sealed, placed in the microwave oven, and subjected to microwave irradiation for a sequence of 10 2-min sessions at 20% power. The resulting mixture was filtered through a Celite pad and washed with excess MeOH. Air was bubbled through the obtained red solution overnight, followed by concentration under reduced pressure. Purification by column chromatography on neutral alumina, eluting traces of the monocobalt complex with 3% MeOH in EtOAc followed by elution with 5% MeOH in EtOAc, gave the desired bis-cobalt complex as the acetate. Dissolution in MeOH (6 mL) containing NaCN (0.220 g, 4.53 mmol) and stirring the reaction for 2 days produced the bis-cyano complex, which was purified using neutral alumina column chromatography (eluent: 5% MeOH in CH_2Cl_2). The resulting orange solution was concentrated, and the residue was dissolved in CH_2Cl_2 (4 mL), precipitated by the diffusion of hexane (5 mL), filtered through a cotton pad, and washed with excess EtOAc. Dissolving the orange precipitate from the cotton pad using excess MeOH and concentration in a vacuum afforded the desired product (0.116 g, 0.104 mmol). Yield: 46%; X-ray quality crystals were formed from CH_2Cl_2. ^1H NMR (CD_3OD, 400 MHz) δ 7.94 (s, 4H), 5.80 (d, $J = 18.8$ Hz 2H), 5.10 (d, $J = 20$ Hz 2H), 4.93 (d, $J = 20$ Hz 2H), 4.77 (d, $J = 18.8$ Hz 2H), 3.81 (d, $J = 13.2$ Hz 2H), 3.64 (d, $J = 12.8$ Hz 2H), 3.53 (d, $J = 12$ Hz 2H), 3.50 (d, $J = 14$ Hz 2H), 3.37 (s 6H), 3.34 (d, $J = 16.8$ Hz 2H), 3.10 (s, 3H), 3.097 (s, 3H), 3.09 (d, $J = 13.2$ Hz 2H), 3.01 (d, $J = 12.4$ Hz 2H), 2.91 (d, $J = 12.4$ Hz 2H), 1.67 (s, 6H), 1.63 (s, 6H), 1.48 (s, 6H), 1.43 (s, 6H), 1.41 (s, 6H), 1.37 (s, 6H);^1H NMR ($CDCl_3$, 400 MHz) δ 7.53 (s, 1H), 7.48 (s, 1H), 7.41 (s, 1H), 7.35 (s, 1H), 6.12 (d, $J = 20.8$ Hz 1H), 6.06 (d, $J = 21.2$ Hz 1H), 5.11 (d, $J = 18.4$ Hz 2H), 4.78 (d, $J = 17.6$ Hz 1H), 4.76 (d, $J = 18.4$ Hz 1H), 4.49 (d, $J = 18.0$ Hz 1H), 4.47 (d, $J = 18.8$ Hz 1H), 3.99 (d, $J = 12.4$ Hz 2H), 3.82−3.68 (m, 6H), 3.48 (s, 6H), 3.30 (s, 3H), 3.26 (s, 3H), 3.12 (d, $J = 13.6$ Hz 2H), 2.94 (d, $J = 12.8$ Hz 2H), 2.73 (d, $J = 11.6$ Hz 2H), 2.62 (d, $J = 12.4$ Hz 2H), 1.73−1.41 (m, 36H); ^{13}C NMR (CD_3OD, 100 MHz) δ 174.8, 174.6, 164.8, 162.5, 149.59, 149.55, 133.2, 118.92, 118.86, 82.9, 81.9, 81.4, 80.1, 70.0, 69.6, 69.5, 69.1, 65.0, 64.3, 52.8, 51.1, 29.6, 28.8, 28.6, 28.4, 27.7, 22.9; FT-IR (film) ν 2126 (CN), 1566 (C═O) cm^{-1}; UV−vis ($CHCl_3$) λ (nm) [ϵ (M^{-1} cm^{-1})] 280 [17 000], 460 [1200]; HRMS (FAB$^+$, m/z) Calcd for $C_{52}H_{77}N_{12}O_8Co_2$ (M + H$^+$), 1115.4651; found, 1115.4661; mp = 230−240 °C dec.

Bis-cobalt(III) Cyanide Complex 11b. 1b (0.087 g, 0.085 mmol), $Co(CH_3CO_2)_2 \cdot 4H_2O$ (0.423 g, 1.70 mmol), and (i-Pr)$_2$NEt (0.220 g, 1.70 mmol) were used for the reaction. The above procedure afforded the desired product (0.044 g, 0.037 mmol). Yield: 43%; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76 (s, 4H), 7.47(s, 2H), 7.46 (s, 2H), 6.09 (d, $J = 18.4$ Hz 1H), 6.07 (d, $J = 18.0$ Hz 1H), 5.06 (d, $J = 18.8$ Hz 2H), 4.72 (d, $J = 18.8$ Hz 2H), 4.44 (d, $J = 18.0$ Hz 2H), 4.00 (d, $J = 13.2$ Hz 2H), 3.79 (d, $J = 11.6$ Hz 2H), 3.77 (d, $J = 11.6$ Hz 2H), 3.68 (d, $J = 12.4$ Hz 2H), 3.48 (s, 6H), 3.29 (s, 3H), 3.28 (s, 3H), 3.11 (d, $J = 13.6$ Hz 2H), 2.93 (d, $J = 13.2$ Hz 2H), 2.72 (d, $J = 12.0$ Hz 2H), 2.60 (d, $J = 12.4$ Hz 2H), 1.70−1.45 (m, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.9, 172.6, 162.5, 159.9, 151.5, 138.3, 129.7, 128.8, 117.0, 116.6, 82.7, 82.0, 79.6, 78.5, 69.3, 68.4, 67.8, 63.7, 62.9, 52.7, 51.6, 30.6, 28.8, 28.6, 28.5, 27.6, 27.1, 23.3; FT-IR (film) ν 2121, 1563 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 300 [31 900], 460 [590]; HRMS (FAB$^+$, m/z) Calcd for $C_{58}H_{81}N_{12}O_8Co_2$ (M + H$^+$), 1191.4964; found, 1191.4986; mp = 230−240 °C dec.

Bis-cobalt(III) Cyanide Complex 11c. 1c (0.090 g, 0.082 mmol), $Co(CH_3CO_2)_2 \cdot 4H_2O$ (0.408 g, 1.64 mmol), and (i-Pr)$_2$NEt (0.212 g, 1.64 mmol) were used for the reaction. The above procedure afforded the desired product (0.043 g, 0.034 mmol). Yield: 41%; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, $J = 8.4$ Hz 4H), 7.71 (d, $J = 8.4$ Hz 4H), 7.46 (s, 4H), 6.10 (d, $J = 18.4$ Hz 2H), 5.07 (d, $J = 18.8$ Hz 2H), 4.70 (d, $J = 18.8$ Hz 2H), 4.44 (d, $J = 18.4$ Hz 2H), 4.04 (d, $J = 13.6$ Hz 2H), 3.83 (d, $J = 12.0$ Hz 2H), 3.81 (d, $J = 13.6$ Hz 2H), 3.71 (d, $J = 12.4$ Hz 2H), 3.52 (s, 6H), 3.32 (s, 6H), 3.12 (d, $J = 14.0$ Hz 2H), 2.94 (d, $J = 13.2$ Hz 2H), 2.72 (d, $J = 12.0$ Hz 2H), 2.60 (d, $J = 12.4$ Hz 2H), 1.73 (s, 6H), 1.68 (s, 6H), 1.60 (s, 6H), 1.52 (s, 6H), 1.50 (s, 6H), 1.48 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.7, 172.6, 162.2, 159.6, 152.2, 142.2, 135.6, 130.1, 128.6, 128.2, 116.8, 116.4, 82.7, 82.1, 79.6, 78.5, 69.4, 69.3, 68.4, 67.8, 63.7, 62.8, 52.7, 51.6, 30.7, 28.8, 28.5, 27.7, 27.1, 23.3; FT-IR (film) ν 2126, 1571 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (nm) [ϵ (M^{-1} cm^{-1})] 323 [48 400], 457 [630]; HRMS (FAB$^+$, m/z) Calcd for $C_{64}H_{84}N_{12}O_8Co_2$ (M$^+$), 1266.5199; found, 1266.5159; mp = 230−240 °C dec.

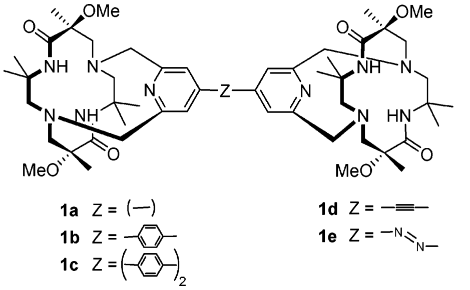
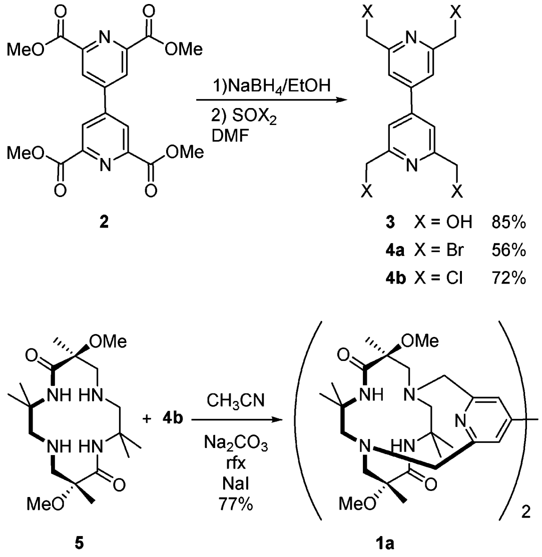


Figure 1.

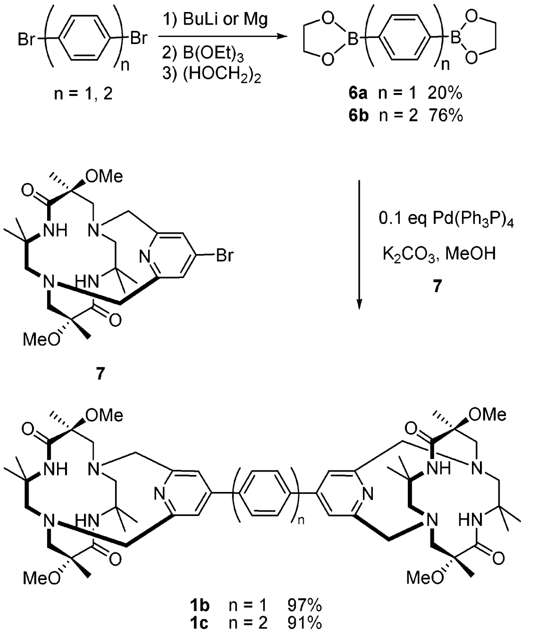
Scheme 1



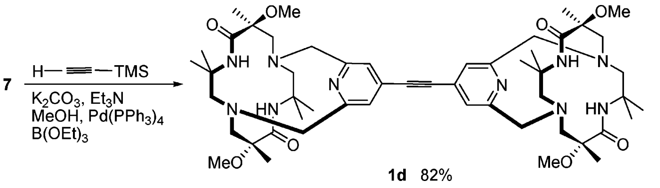
Results and Discussion

Ligand Synthesis. The targeted class of ligands was pyridine-capped bis-dioxocyclams[7] connected through the 4-position of the pyridine group by conjugated groups (Figure 1). The parent bipyridine complex **1a** was synthesized as in Scheme 1. Starting with bipyridine tetraester **2** (synthesized in overall 35% yield in three steps from 2,6-dimethylpyridine),[8] reduction of the ester followed by treatment with thionyl chloride or thionyl bromide produced the desired bipyridine capping agents **4a** and **4b** in fair to good yield. Reaction of the bromo capper, **4a**, with bis-dioxocylam **5** resulted in decomposition of **4a** and recovery of **5**, while use of chloro compound **4b** resulted in no reaction. Suc-

Scheme 2



Scheme 3



cessful capping was achieved under Finkelstein conditions utilizing 1 mol of NaI/mol **4b** (Scheme 1). Higher amounts of NaI resulted in lower yields, presumably due to decomposition of the in-situ-formed benzylic iodide.

Extended back-to-back capped bis-dioxocyclams **1b** and **1c** were efficiently synthesized by Suzuki coupling of 4-bromopyridine-capped cyclam **7**[5b] with the appropriate aryl bis-boronic ester (Scheme 2).[9]

The acetylide-linked bis-dioxocyclam **1d** was synthesized by Sonogashira[10] coupling of 4-ethynylpyridine-capped dioxocyclam[5b] with **7** in fair yield (Scheme 3). Azo-linked bis-dioxocyclam **1e** was made by reductive coupling[11] of 4-nitropyridine-capped dioxocyclam **9** (Scheme 4). It should be noted that, although uncapped dioxocyclam **5** is achiral, two new chiral centers at nitrogen are created by capping, since nitrogen inversion is prevented by the rigidity of the system.[5a] Capped dioxocyclams such as **7** are thus produced as a racemic mixture of enantiomers. Synthesis of bis-dioxocyclams from achiral **5** or racemic capped mono-dioxocyclams *must* produce two diastereoisomeric products, a racemic pair of enatiomers, and a “meso” compound.[5a] Only one diastereoisomer is shown for clarity. With these materials in hand, introduction of metals into these ligand systems was addressed.

Complexation Studies

As anticipated from previous complexation studies[5,6] with capped dioxocyclams, ligands **1a**−**c** and **1e** readily took up copper(II) when treated with copper(II) tetrafluoroborate (Scheme 5). (Complexation of **1d** to copper was not attempted). In contrast, cobalt(III) was more difficult to introduce into these macrocycles and required microwave irradiation in the presence of Hünig’s base (Scheme 6).[11] The products were mixtures of cobalt(III) acetates, methoxides, and hydroxides, (by electrospray mass spectroscopy) and were converted to the corresponding cyanide complexes by treatment with sodium cyanide in methanol. Macrocycles **1a**−**c** produced cobalt(III) cyanide complexes in modest yield, while **1d** and **1e** produced complex, inseparable mixtures.

Properties

The spectroscopic and electrochemical properties of the free ligands and their copper(II) and cobalt(III) complexes are summarized in Table 1. As observed previously,[3−6] the CO stretching frequencies of the amide carbonyl groups were sensitive to complexation, appearing at ≈1660 cm^{-1} in the free ligand and shifting to 1560−1590 cm^{-1} in the metal complexes. In marked contrast, the ^{13}C chemical shift of these carbonyl groups remained virtually the same upon complexation to cobalt(III), ($\delta \approx 173$ ppm). The C≡N stretching frequency in the cobalt(III) cyanide complexes **11a**−**11c** ranged from 2121 to 2126 cm^{-1}, consonant with that observed for the corresponding cobalt(III) cyanide complexes of capped monocyclams.[11] The ^{13}C chemical shift of the cyanide group similarly appeared at between δ 130 and 140 ppm. Surprisingly, although *all* of these bis-dioxocyclam ligands and complexes had to be mixtures of diastereoisomers, their ^{13}C spectra showed a *simple* set of peaks consistent with the presence of a single diastereoisomer. The ^{1}H NMR spectra in CDCl$_3$ were more informative on the issue of diastereoisomers, even though *all* of the peaks on the dioxocyclam ring again indicated the presence of a single diastereoisomer. However, the signals from the pyridine linkers proved diagnostic. For the free, uncomplexed 4-bromopyridine-capped *mono* dioxocyclam **7**, the two protons on the pyridine ring appeared as two singlets at $\delta \approx 7.1$ ppm, and the methylene groups connecting the pyridine to the dioxocyclam appeared as a cluster of doublets ($J \cong 17$ Hz) centered at $\delta \approx 4.0$ ppm. In the corresponding cobalt(III) cyanide complex, the pyridine singlets moved to $\delta \approx$ 7.5 ppm, while the methylene doublets separated and appeared at 4.4, 4.6, 4.9, and 5.8. For the bipyridine-bridged bis-dioxocyclam **1a**, the most upfield methylene signal appeared as two overlapping one-proton doublets, while the pyridine proton signals were *four* singlets clustered around δ 7.3 ppm. The ^{1}H-NMR spectrum of the cobalt(III) cyanide complex **11a** similarly had *four* singlets centered around δ 7.4 ppm for the pyridine signals, and three of the four methylene signals were doubled. Interestingly, in CD$_3$OD, these differences disappeared, and the ^{1}H-NMR spectrum of **11a** displayed four clean doublets for the methylene protons and a *singlet* for the four pyridine protons! As the

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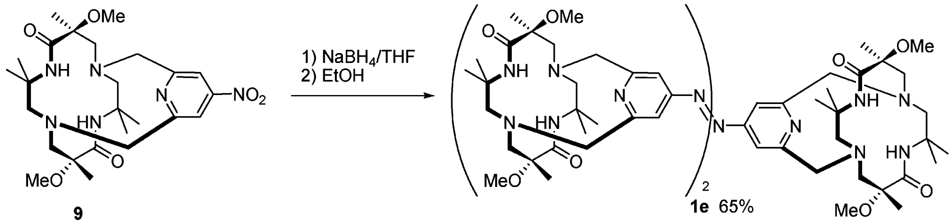
[9] Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 3717.

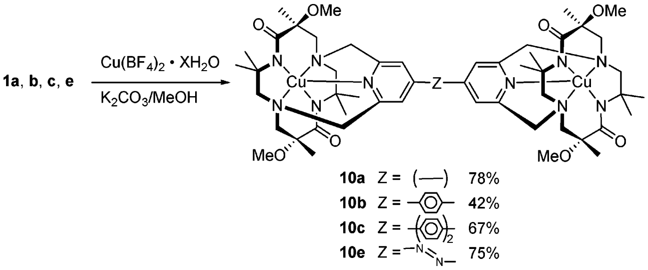
[10] Evans, R. F.; Brown, H. C. *J. Org. Chem.* **1962**, *27*, 1665.

[11] Reiff, A.; Garcia-Frutos, E.; Gil, J. M.; Hegedus, L. S. submitted for publication.

Scheme 4



Scheme 5



Scheme 6

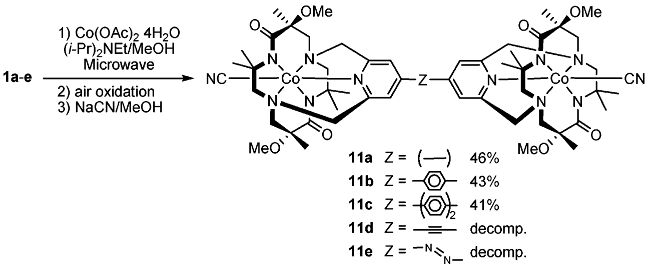


Table 1. Spectroscopic and Electrochemical Data for Compounds **1**, **10**, and **11**

compound	ν, cm^{-1} (CO, CN)	γ_{max}, nm; ϵ	^{13}C δ, ppm (CO, CN)	CV, V/SCE
la	1611	280; 5980	173.4, 172.7	$E_{1/2} = -1.9$; $\Delta E = 160$ mV
1b	1660	282; 62 400	173.5, 172.9	
lc	1656	306; 69 100	173.5, 172.8	
1d	1660	280; 27 900	173.3, 172.7	
1e	1657	290; 21 100 460; 430	173.4, 171.7	
10a	1570	685; 150		$E_{1/2} = -1.4$; $\Delta E = 100$ mV (2e$^-$) $E_{PC} = -2.0$
10b	1590	285; 32 225 365; sh		$E_{1/2} = -1.35$; $\Delta E = 70$ mV (2e$^-$) $E_{PC} = -1.8, -2.0$
10c	1586	308; 62 900 668; 240		
10e	1586	375; sh 660; br. tail		
11a	1566, 2126, CN	280; 17 000 460; 1200	174.8, 174.6 133.2, CN	$E_{PC} = -1.2$(2e$^-$); $\Delta E = 60$ mV $E_{1/2} = -1.3, -1.9$; $\Delta E = 130$ mV
11b	1563 2121, CN	300; 31 900 460; 590	173.9, 172.6 138.3, CN	$E_{PC} = -1.3$(2e$^-$) $E_{1/2} = -1.5, -1.6$; $\Delta E = 120$ mV $\Delta E = 110$ mV
11c	1571 2126, CN	323; 48 400 457; 630	173.7, 172.6 130.1, CN	$E_{PC} = -1.4$ $E_{1/2} = -1.7$

separation between dioxocyclam rings was increased by the interspersion of one (**1b**, **11b**) and two (**1c**, **11c**) phenyl groups, these differences disappeared. The ^{1}H-NMR spectrum of **1b** was indistinguishable from that of a 4-substituted pyridine-capped mono-dioxocyclam, while that of the corresponding cobalt(III) cyanide complex, **11b**, displayed doubling of only the lowest methylene signal to indicate the presence of diastereoisomers. Finally, the ^{1}H-NMR spectra of **1c** and **11c** showed no indication of the presence of diastereoisomers, presumably because of the increased distance between the two cyclam rings.

The UV−vis spectra of the copper complexes **10a**, **b**, **c** all showed well-resolved, although broad, absorption maxima. Interestingly, the bipy-bridged complex **10a** absorbed exactly where the 4-pyridylpyridine-capped *mono*-dioxocyclam copper(II) complex[11] did, at 685 nm ($\epsilon \approx 150$). With the interspersion of additional phenyl groups between the two pyridine units (**10b**, **10c**), the absorption moved to shorter wavelengths, (676 and 668 nm, respectively) approaching that of the pyridine-capped *mono*-dioxocyclam copper(II) complex (658 nm).[5a] (The long-wavelength absorption for **10e** was masked by strong tailing of the azo visible absorption at ≈500 nm). In contrast, the spectra for cobalt(III) complexes **11a**−**c**, had no distinct maxima but rather presented broad shoulders tailing from intense, shorter-wavelength absorptions, all in the region of ≈460 nm. For comparison, a range of substituted pyridine-capped *mono*-dioxocyclam cobalt(III) cyanide complexes (Py, Pz, 4-Py-Py, 4Me$_2$NPhPy, 4-BrPy, 4MeOPy)[11] all had distinct maxima between 454 and 463 nm, indicating insensitivity to the nature of the capping agent. This stands in contrast to the corresponding copper(II) complexes.

Electrochemistry

Guilard[7a] has reported an $E_{1/2} = -1.14$ V/SCE reduction of Cu(II) to Cu(I) in the unsubstituted pyridine-capped 5,-12-dioxo-*mono*cyclam copper(II) complex. The uncomplexed bipyridyl-capped bis-dioxocyclam **1a** underwent a quasi-reversible reduction at $E_{1/2} = -1.9$ V/SCE ($\Delta E = 160$ mV), presumably due to reduction of the bipyridine group. In contrast, the corresponding Cu(II) complex **10a** underwent a quasi-reversible two-electron reduction at $E_{1/2} = -1.4$ V/SCE ($\Delta E = 100$ mV) (Cu^{II} → Cu^{I} based on ref 7a) and an irreversible reduction at $E_p = -2.0$ V/SCE. The phenyl-extended analogue **10b** underwent a reversible two-electron reduction at $E_{1/2} = -1.5$ V/SCE ($\Delta E = 70$ mV) and two irreversible reductions at $E_p = -1.8$ and -2.0 V/SCE. The fact that there is no detectable (by cyclic voltammetry) difference in the reduction potentials of the two metal centers implies little, if any, electronic communication between the two metals.

The electrochemistry of the corresponding cobalt(III) cyanide complexes **11a**−**11c** was markedly different. The pyridine-capped 5,12-dioxo-*mono*-cyclam cobalt(III) cyanide complex underwent irreversible reduction at $E_p = -1.36$ V/SCE.[11,12] The bipyridyl-capped bis-dioxocyclam cobalt(III) cyanide complex **11a** underwent an irreversible two-electron reduction at $E_p = -1.2$ V/SCE ($Co^{(III)} \rightarrow Co^{(II)}$), a reversible one-electron reduction at $E_{1/2} = -1.3$ V (ΔE 60 mV) and a quasi-reversible reduction at -1.9 V/SCE (ΔE 130 mV). The phenyl-extended analogue **11b** underwent an irreversible two-electron ($Co^{(III)} \rightarrow Co^{(II)}$) reduction at $E_p = -1.3$V/SCE and two quasi-reversible reductions at $E_{1/2} = -1.5$ V (ΔE 110 mV) and -1.6 V ($\Delta E = 120$ mV)/SCE. The biphenyl-extended analogue **11c** underwent an irreversible two-electron reduction at $E_p = -1.4$ V, and a quasi-reversible *two*-electron reduction at $E_{1/2} = -1.6$ V/SCE (ΔE 130 mV).

The fact that there is no detectable (by cyclic voltammetry)[13] difference in the reduction potentials of the two cobalts again implies little, if any, electronic communication between the two metal centers. The two quasi-*reversible* reductions observed are likely due to the bypyridyl linker, since similar reversible reductions were observed with the 4-(pyridyl)-pyridine-capped *mono*-cyclam cobalt cyanide complex.[11] As the two pyridine groups are separated by one or two phenyl groups, the degree of communication between the two pyridine groups decreases to zero and both reduce at the same potential.

Structural Studies

Although X-ray crystal structures of the bipyridine-linked free ligand **1a**, the bis-copper(II) complex **10a**, and the bis-cobalt(III) cyanide complex **11a** were obtained, none of the data were of publishable quality, having final *R* indices of 0.1131 and 0.2979 for the free ligand **1a** and of 0.1501 and 0.3819 for copper complex **10a**. Five data sets on different crystals of cobalt complex **11a** from different solvents were acquired, but *none* of them were of sufficient quality to assign accurate bond lengths because of twinning and/or highly disordered solvents of crystallization. Thus, although accurate bond lengths and bond angles cannot be reported, the gross structure of these compounds has been confirmed.

Summary

A series of bis-dioxocyclams linked back-to-back by conjugated 4-substituted pyridine capping groups via the secondary amine nitrogens were synthesized and fully characterized. Copper(II) and cobalt(III) cyanide complexes of these ligands were prepared and characterized by spectroscopic and electrochemical methods. The copper(II) complex of the bipyridyl-linked systems **10a** and **10b** underwent reversible two-electron reductions ($Cu^{II} \rightarrow Cu^{I}$) at $E_{1/2} = -1.4$ to -1.5 V/SCE. In contrast, the cobalt cyanide complexes **10a**−**10c** underwent irreversible two-electron reductions ($Co^{(III)} \rightarrow Co^{(II)}$) at -1.2 to 1.4 V/SCE and showed no indication of electronic communication between the metals. X-ray crystal structures for **1a**, **10a**, and **11a** (five data sets) were acquired, but none were of publishable quality.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **1a**, **1b**, **1c**, **1e**, **11a**, **11b**, and **11c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The reversibility of the $Co^{III/II}$ couple for macrocyclic tetraamine ligands was shown to be dependent on the electrode and ring size. See: (a) Bernhardt, P. V.; Macpherson, P.; Martinez, M. *Inorg. Chem.* **2000**, *39*, 5203. The non-Nernstian behavior of the $Co^{III/II}$ cyclam couple has been attributed to slow axial ligand exchange in conjunction with electron transfer. See: (b) Simon, E.; L'Haridon, P.; Pichon, R.; L'Her, M. *Inorg. Chim. Acta* **1998**, *282*, 173.

(13) If the splitting between the two reductions waves is small, it may not be detected by cyclic voltammetric measurements. See: Geiss, A.; Kolm, J. J.; Janiak, D.; Vahrenkamp, H. *Inorg. Chem.* **2000**, *39*, 4037.