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Synthesis, Complexation, and Coordination Oligomerization of 1,8-Pyrazine-Capped 5,12-Dioxocyclams

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(Methyl)(methoxy)-5,12-dioxocyclam **1** was alkylated on the secondary amines (capped) with 2,6-bis(bromomethyl)-pyrazine. The resulting macrocycle was complexed to copper(II) to produce a five-coordinate complex **5a** which was fully characterized by a range of spectroscopic methods (IR, UV–vis, ESR) as well as by X-ray crystallography. The structure of this complex is similar to the previously reported pyridine complex, with the five-coordinate copper having distorted square pyramidal geometry and a Cu–Pz bond length of 2.125 Å. Attempts to prepare this same complex under microwave irradiation instead produced a trinuclear complex **6a** having an octahedral copper(II) center complexed to two pyrazine–cyclam copper units through the amide carbonyl oxygen and the methoxyl group oxygen of the cyclam unit. The X-ray crystal structure of the trinuclear complex showed extensive distortion in the cyclam rings. The remote nitrogen of pyrazine–cyclam complex **5a** was capable of coordinating an additional metal. Treatment with $RuCl_2(DMSO)_4$ or $Rh_2(OAc)_4$, respectively, produced trimetallic Cu–Ru–Cu complex **7** or tetrametallic Cu–Rh–Rh–Cu complex **8**. The latter was fully characterized, including an X-ray crystal structure, and had two pyrazine–cyclam complexes bridged by a $Rh_2(OAc)_4$ unit through the remote pyrazine nitrogens. There was little distortion in the pyrazine–cyclam copper units as compared to complex **5a**: the four metals were collinear, and the two cyclam units were eclipsed. All of the copper complexes were subjected to cyclic voltametry measurements, and no reversible redox changes were observed. Magnetic measurements of **6a** and **8** showed the copper atoms to be weakly antiferromagnetically coupled.

Introduction

Coordination polymers are multimetallic assemblies resulting either from the complexation of coordinating groups from a monomeric coordination complex to other metal centers, or, more commonly, by the reaction of polydentate ligands with metal complexes having multiple available coordination sites. The resulting arrays are connected by metal−ligand bonds rather than by the covalent bonds utilized in organic polymers. Over the past decade, coordination polymers have undergone development in a number of different directions. Major advances in the utilization of coordination polymerization for the self-assembly of supramolecular nanostructures have been made.[1−3] Many have host−guest properties and can act as synthetic receptors[4] or coordination complex analogues of zeolites.[5] When the ligands bridging the metal centers can transmit electronic information, the resulting coordination polymers may have unusual optical, magnetic,

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or electronic properties, as well as the potential to recruit several metal centers to interact with a single substrate in a catalytic process. This class of bridging ligands includes pyrazines,[5] triazines and tetrazines,[6] cyano[7] and isocyano[8] groups, and polyacetylene-linked bi- and terpyridines.[9]

Dioxocyclams[10] are 14-membered tetraazomacrocycles having two secondary amine nitrogens and two amide nitrogens as part of the macrocycle periphery. They are intermediate between cyclic polyamines and cyclic peptides in their metal-complexation properties and are more selective than their tetramine relatives, the cyclams.[11] The secondary amines in dioxocyclams are reactive nucleophiles and can be alkylated or acylated by appropriate electrophiles.[12] The use of bis-electrophiles results either in linking two macrocycles through the amine nitrogens, or capping one face of the macrocycle across the same positions.[13]

Recently, an efficient synthesis of dioxocyclams has been reported from these labs,[14] along with capping studies with 2,6-bis(bromomethyl)pyridine.[15] By using pyrazine in place of pyridine, capped cyclams capable of coordinating metals both inside the capped macrocycle and outside the cavity through the pyrazine 4-nitrogen should be accessible. Since pyrazine can act as an electron π-mediator (an electronic coupling element between metals[16]), this would permit the synthesis of coordination oligomers containing multiple communicating metal centers having potentially useful electronic, optical, or catalytic properties. Results of synthetic studies addressing this issue are given here.

Experimental Section

Acetonitrile was distilled over calcium hydride. Methanol was dried over molecular sieves. Carbon tetrachloride was used as received. NMR spectra were recorded on a Varian JS-300. Infrared spectra were recorded on a Nicolet Magna-IR 760 spectrometer. UV−vis spectra were recorded on an Agilent G1103A spectrometer. EPR spectra were recorded on a Bruker EMX EPR spectrometer. The light used for photolysis reactions was from a 500 W quartz-halogen shop light lamp by Regent Lighting Corporation, model PQ72. The microwave used was a Sharp model R-2208W. 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. The working electrode was either glassy carbon or platinum. The counter electrode was a platinum wire. The reference electrode was a silver wire. Potentials were calculated versus 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. X-ray crystallographic studies were performed on a Bruker Smart CCD diffractometer, and the intensity of the data set was integrated using Bruker SAINT software. The structures were solved using Bruker SHELXTL version 5.03 software. For magnetic measurements, powdered samples (5−20 mg) were held within gelatin capsules and suspended by a Teflon rod in a Quantum Design MPMS SQUID magnetometer. Samples were cooled to liquid He temperature, and a field of 1.0 T was applied. Magnetization curves indicated that this was a reasonable field for these studies. Susceptibility data were collected at 0.5 K intervals from 2 to 10 K, 1 K intervals from 10 to 40 K, and 5 K intervals to 300 K. Data were corrected for the core diamagnetism of the elements in the ligands as well as crystalline solvent molecules.

Synthesis of 2,6-Bis(bromomethyl)pyrazine (2). A suspension of 2,6-dimethylpyrazine (0.804 g, 7.43 mmol), *N*-bromosuccinimide (3.30 g, 18.6 mmol), and benzoyl peroxide (36 mg, 0.15 mmol) in 40 mL of carbon tetrachloride was stirred under irradiation from two 500 W lamps for 2 h. The solution turned orange, then back to clear, and black solid formed on the surface of the flask. The suspension was filtered through filter paper, and the solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel (25% ethyl acetate/hexanes) to give 0.342 g (17%) of 2,6-bis(bromomethyl)pyrazine as a clear oil. The liquid is very unstable in the pure form and is used immediately. It can be stored in solution at −20 °C without appreciable decomposition for at least several weeks. $R_f = 0.20$. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.64 (s, 2H), 4.55 (s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 151.9, 143.9, 30.1.

Synthesis of Pyrazine-Capped Centrosymmetric Dioxocyclam (4a). A solution of 2,6-bis(bromomethyl)pyrazine (31 mg, 0.12 mmol), sodium carbonate (49 mg, 0.46 mmol), and centrosymmetric dioxocyclam **3a** (43 mg, 0.12 mmol) in 3 mL of acetonitrile was stirred under argon at reflux for 4 days. The solution was filtered through Celite, and the solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel (9% methanol/chloroform), followed by recrystallization from methylene chloride/hexanes, to give 37 mg (71%) of pyrazine-capped centrosymmetric dioxocyclam **4a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.95 (s, 1H), 8.33 (d, $J = 3$ Hz, 2H), 7.34 (s, 1H), 4.12 (m, 4H), 3.45 (s, 3H), 3.23 (d, $J = 14$ Hz, 2H), 3.01 (m, 5H), 2.66 (d, $J = 15$ Hz, 1H), 2.52 (s, 3H), 2.31 (d, $J = 14$ Hz, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.22 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 173.2, 172.6, 158.4, 153.5, 142.0,

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140.6, 82.8, 79.8, 74.9, 72.6, 67.6, 67.1, 65.0, 62.9, 56.2, 54.9, 52.1, 50.5, 26.5, 25.8, 23.6, 19.4. IR (film) ν: 1660 cm^{-1} (CO). Anal. Calcd for $C_{24}H_{40}N_6O_4$: C, 60.48; H, 8.46; N, 17.30. Found: C, 60.60; H, 8.34; N, 17.55.

Synthesis of Copper Complex 5a. A solution of cyclam **4a** (36 mg, 0.08 mmol), copper(II) tetrafluoroborate hexahydrate (137 mg, 0.398 mmol), and potassium carbonate (55 mg, 0.39 mmol) in 5 mL of methanol was stirred at reflux for 1 day. The suspension was filtered through Celite, and the solvent was removed in vacuo by rotary evaporation. The residue was recrystallized from methylene chloride/hexane to give 29 mg (68% yield) of green solid. Mp 210−211 °C. IR (film) ν: 1587 cm^{-1} (CO). UV−vis (methanol) 407 (ϵ = 264), 684 (ϵ = 115) nm. Crystal structure solved.

Synthesis of Pyrazine-Capped C_2 Symmetric Dioxocyclam 4b. A solution of 2,6-bis(bromomethy)pyrazine (467 mg, 1.74 mmol), sodium carbonate (615 mg, 5.80 mmol), and C_2 symmetric dioxocyclam **3b** (540 mg, 1.45 mmol) in 25 mL of acetonitrile was stirred at reflux for 4 days. The solution was filtered through Celite, and the solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel (3% methanol/chloroform) to give 42 mg (6%) of pyrazine-capped C_2 symmetric dioxocyclam capped from the methoxy side (**4c**), 192 mg (28%) of pyrazine-capped C_2 symmetric dioxocyclam capped from the methyl side (**4b**), and 258 mg of starting cyclam, making the total yield 65% based on recovered starting material. Data for major product (Me side) follow. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.07 (s, 2H), 7.95 (s, 2H), 3.94 (dd, J = 16.5, 40.0 Hz, 4H), 3.31 (s, 6H), 3.16 (d, J = 15.0 Hz, 2H), 2.92 (d, J = 14.7 Hz, 2H), 2.80 (d, J = 13.8 Hz, 2H), 2.67 (d, J = 13.5 Hz, 2H), 1.22 (s, 12H), 1.11 (s, 6H). ^{13}C NMR (300 MHz, CDCl$_3$) δ: 172.5, 149.9, 140.1, 83.3, 70.4, 66.6, 63.9, 54.0, 51.4, 29.0, 25.1, 20.2. IR (film) ν: 1653 cm^{-1} (CO). Anal. Calcd for $C_{24}H_{40}N_6O_4$: C, 60.48; H, 8.46; N, 17.63. Found: C, 60.13; H, 8.06; N, 17.30.

Synthesis of Copper Complex 5b. A solution of **4b** (28.0 mg, 0.059 mmol), copper(II) tetrafluoroborate hexahydrate (101 mg, 0.294 mmol), and potassium carbonate (40.6 mg, 0.294 mmol) in 10 mL of methanol was stirred at reflux for 2 days. The suspension was filtered through Celite, and the solvent was removed in vacuo by rotary evaporation. The residue was recrystallized with methylene chloride and filtered through a plug of alumina, leaving 22.0 mg (70% yield) of green solid. IR (film) ν: 1587 cm^{-1} (CO). UV−vis (methanol) 756 (ϵ = 119) nm. HRMS (FAB+) Calcd for $C_{24}H_{38}CuN_6O_4$: 537.2251. Found: 537.2260.

Synthesis of Tris-Copper Complex 6a. A solution of **4a** (50.2 mg, 0.105 mmol), copper(II) tetrafluoroborate hexahydrate (182 mg, 0.526 mmol), and potassium carbonate (72.8 mg, 0.526 mmol) in 5 mL of methanol was placed in a Pyrex pressure tube. The solution was heated in a microwave (Sharp model R-220BW, power setting 1) for 60 s, and the solution turned bluish-purple. The suspension was filtered through Celite, and the solvent was concentrated in vacuo by rotary evaporation to 10 mL. The solution was allowed to stand for 3 days, and blue crystals grew from solution. The solid was collected on a filter and washed with methanol (3 × 10 mL). The solid was dried under high vacuum, to give 62.3 mg (86%) of blue crystals. Mp (decomp) 228 °C. IR (Nujol) ν: 1726, 1576 cm^{-1} (CO). UV−vis (methanol) 558 (ϵ = 637) nm. Crystal structure solved.

Synthesis of Ruthenium-Bridged Copper Complex 7. A solution of copper complex **5a** (25 mg, 0.046) and dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) (11 mg, 0.023 mmol) in 11 mL of methanol was stirred for 16 h. The color of the solution turned from green to brown. Evaporation of the solvent gave a brown solid. IR (film): 1575 cm^{-1} (CO). UV−vis (methanol) 504 (ϵ = 668), 632 (ϵ = 239) nm. MS (FAB+) Calcd for $C_{52}H_{88}Cl_2Cu_2N_{12}O_{10}RuS_2$: 1404.5. Found: 1405.2 (max peak).

Synthesis of Rhodium-Bridged Copper Complex 8. A solution of copper complex **5a** (22 mg, 0.041 mmol) and rhodium(II) acetate (9 mg, 0.02 mmol) in 11 mL of methanol was stirred for 20 min. The color of the solution turned from green to brown. Evaporation of the solvent gave a brown solid. Recrystallization by slow evaporation of CH$_2$Cl$_2$/EtOAc gave dichroic green−brown crystals. IR (film): 1575 cm^{-1} (CO). UV−vis (methanol) 436 (ϵ = 739), 534 (ϵ = 340), 658 (ϵ = 222) nm. MS (FAB+) Calcd for $C_{56}H_{88}Cu_2N_{12}O_{16}Rh_2$: 1518.3. Found: 1518.7. Crystal structure solved.

Results and Discussion

Synthesis and Complexation of Pyrazine-Capped Dioxocylam (4). Pyrazine-capped dioxocyclam **4** was synthesized following the procedure previously developed for the pyridine-capped analogue (eq 1).[15] Although 2,6-bis(bromomethyl)pyridine is commercially available and quite stable, 2,6-bis(bromomethyl)pyrazine (**2**) must be synthesized. While pyrazine **2** is a literature compound,[17] neither the details of its synthesis nor its characterization have been published. The most direct approach involves radical benzylic bromination. Treatment of 2,6-dimethylpyrazine with a slight excess of *N*-bromosuccinimide under incandescent light with benzoyl peroxide as the initiator produced the dibrominated pyrazine **2** in 17% isolated yield. As is typical for reactions of this type,[5e] reaction efficiency is compromised by overbromination. Further, **2** is relatively unstable to the reaction conditions and even decomposes when pure on standing. It is substantially more stable in solution and can be stored for weeks in solution at −20 °C. By limiting reaction times to 2−2.5 h, usable amounts of **2** are readily available. The only characterizable byproduct was the monobrominated compound which could be recycled. Treatment of centrosymmetric dioxocyclam **3a** with **2** under standard[15] capping conditions (acetonitrile, reflux 4 days, Na$_2$CO$_3$) produced pyrazine-capped dioxocyclam **4a** in good yield. Since the tertiary amines cannot invert because of the rigid bridge, they are chiral, and a racemic mixture of **4a** was obtained. Treatment with copper(II) tetrafluoroborate in methanol at reflux gave the desired pyrazine-capped dioxocyclam copper(II) complex **5a** in good yield, as a bright green crystalline solid (eq 1). Recrystallization by slow evaporation from hexane/methylene chloride gave bright green crystals. The X-ray crystal structure and stereoview of **5a** are shown in Figure 1, and selected bond lengths and angles are displayed in Table 1.

The structural parameters resemble those of the closely related *pyridine*-capped copper dioxocyclam complex previously reported.[15] The copper is clearly five-coordinate, with distorted square pyramidal (rather than trigonal bipyramidal) geometry (“equatorial” N−Cu−N angles of 154.8°, 107.9°, and 97.4° vs 180°, 90°, 90° for square pyramidal or 120°, 120°, 120° for trigonal bipyramidal). The pyrazine N5−

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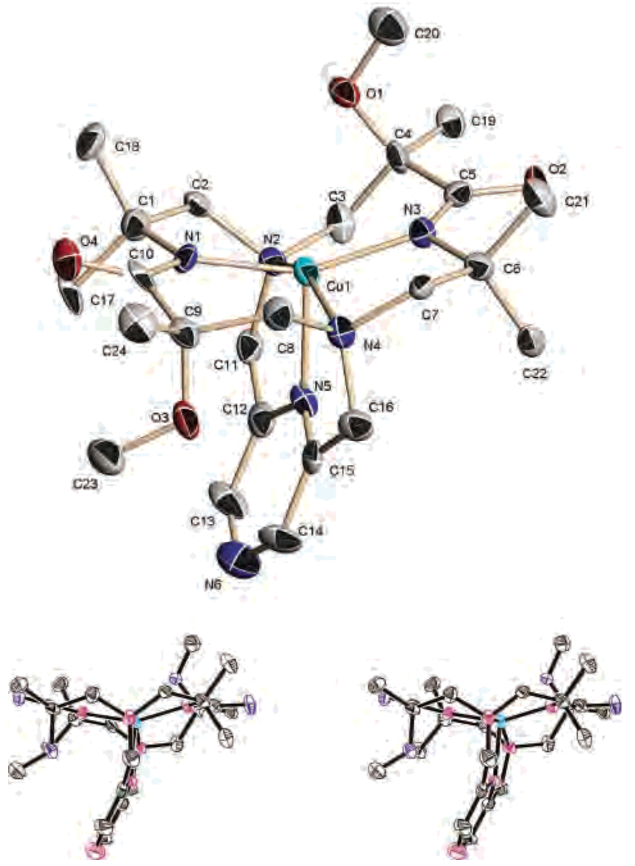
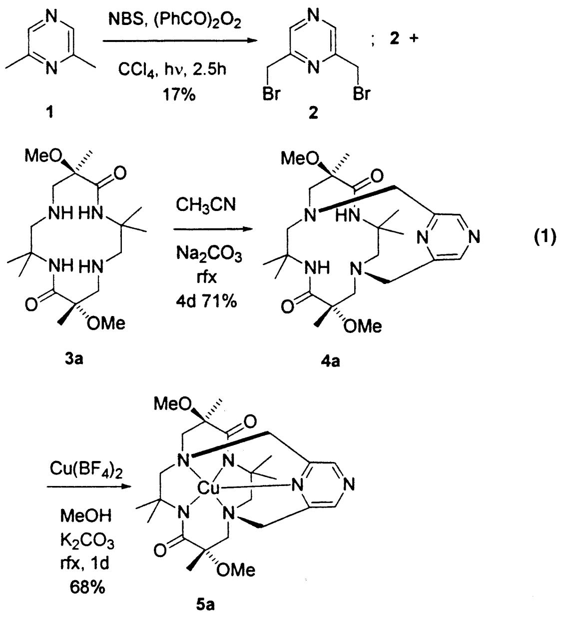


Figure 1. ORTEP diagram and stereoview of **5a**.

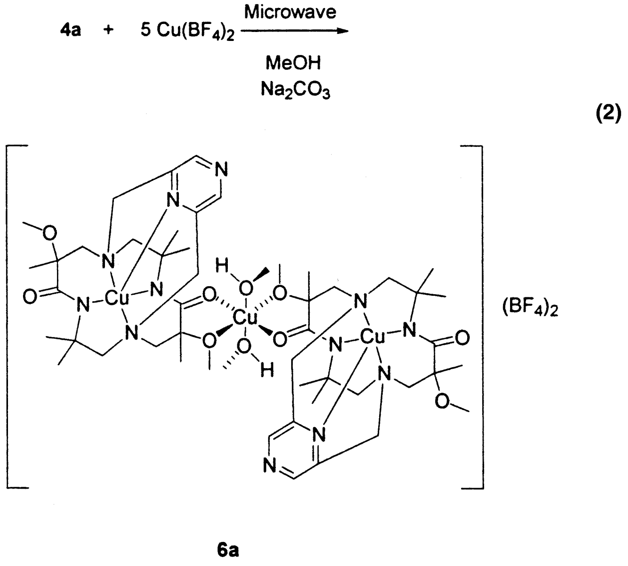
Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **5a** with Estimated Standard Deviations in Parentheses

(amide) N(1)−Cu(1)	1.936(11)	N(1)−Cu(1)−N(2)	97.9(5)
(amine) N(2)−Cu(1)	2.081(12)	N(3)−Cu(1)−N(2)	86.4(5)
(amide) N(3)−Cu(1)	1.975(11)	N(3)−Cu(1)−N(4)	99.4(5)
(amine) N(4)−Cu(1)	2.108(11)	N(1)−Cu(1)−N(4)	86.0(5)
(Pz) N(5)−Cu(1)	2.125(12)	N(1)−Cu(1)−N(3)	154.8(5)
C(1)−O(1)	1.25(2)	N(2)−Cu(1)−N(4)	158.9(4)
C(6)−O(2)	1.227(18)	N(1)−Cu(1)−N(5)	97.4(5)
C(1)−N(1)	1.33(2)	N(2)−Cu(1)−N(5)	79.9(5)
C(6)−N(3)	1.343(18)	N(3)−Cu(1)−N(5)	107.9(5)
		N(4)−Cu(1)−N(5)	78.5(5)

copper bond length of 2.125 Å is identical to that of the pyridine N5− copper bond length in the corresponding pyridine-capped complex,[15] and similar to that found in pyrazine-bridged copper(II) complexes[17] (2.0−2.1 Å).[18]



In an attempt to decrease the reaction time required for complexation, ligand **4a** was irradiated for 2 min in a consumer microwave oven in the presence of a 5-fold excess of copper(II) tetrafluoroborate and sodium carbonate, in methanol in a pressure tube (eq 2). The resulting dark blue solution was filtered through a pad of Celite and allowed to stand for 2 days. Dark blue crystals of complex **6a** were deposited, leaving a colorless solution. These crystals would not redissolve in methanol, even on extended heating, but readily dissolved to give a purple solution when a few drops of water or acetonitrile were added to the methanol suspension. The physical properties of this material suggested it might be an oligomer of **5a**, formed by the coordination of the remote pyrazine N of one molecule to the copper of another. However, the X-ray crystal structure of **6a**, displayed in Figure 2 with bond lengths and angles in Table 2, showed otherwise.



The complex consists of two units of pyrazine-capped dioxocyclam copper complex **5a** bridged by a third copper through one of the amide carbonyl groups and a methoxy group of the cyclam. The coordination sphere of the central copper is completed by two axial methanols. Since racemic **5a** was used, diastereoisomers of **6a** should be formed in equal amounts. The crystal structure is that of the centrosymmetric diastereoisomer.[29]

Complex **6a** has a number of unusual features. It only forms under microwave irradiation. Prolonged heating (methanol at reflux 24 h) of the starting materials only produces

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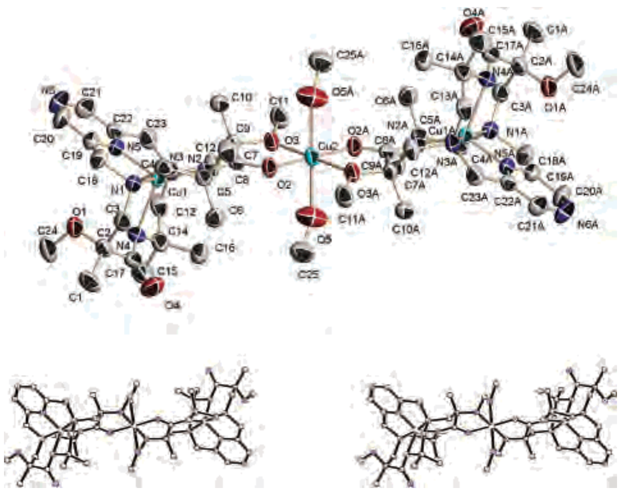


Figure 2. ORTEP diagram and stereoview of **6a** (BF_4^- counterions omitted for clarity),

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **6a** with Estimated Standard Deviations in Parentheses

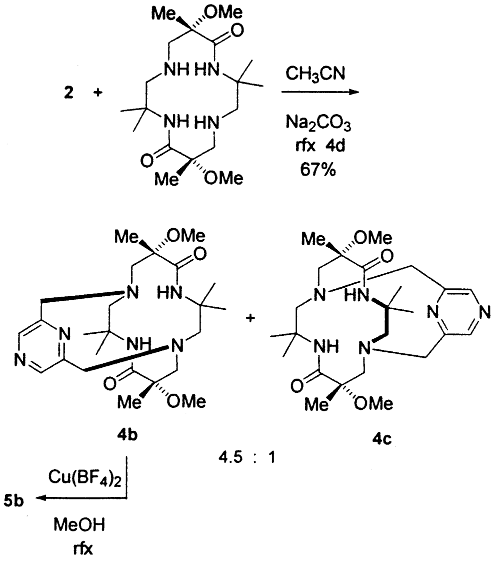
(amine) N(1)−Cu(1)	2.051(3)	O(3)−Cu(2)	2.040(2)
(amide) N(2)−Cu(1)	1.925(3)	O(5)−Cu(2)	2.322(4)
(amine) N(3)−Cu(1)	2.043(3)	N(1)−Cu(1)−N(2)	90.20(11)
(amide) N(4)−Cu(1)	2.309(3)	N(2)−Cu(1)−N(3)	101.96(11)
(Pz) N(5)−Cu(1)	1.905(3)	N(3)−Cu(1)−N(4)	82.30(11)
(bound CO) C(8)−O(2)	1.279(4)	N(1)−Cu(1)−N(4)	93.76(11)
(free CO) C(17)−O(4)	1.209(5)	N(1)−Cu(1)−N(3)	167.28(11)
(bound CN) C(8)−N(2)	1.300(4)	N(1)−Cu(1)−N(4)	125.50(11)
(free CN) C(17)−N(4)	1.394(5)	N(1)−Cu(1)−N(5)	85.07(12)
(bound OMe) C(9)−O(3)	1.470(4)	N(2)−Cu(1)−N(5)	134.53(12)
(free OMe) C(2)−O(1)	1.431(4)	N(3)−Cu(1)−N(5)	83.72(12)
O(2)−Cu(2)	1.895(2)	N(4)−Cu(1)−N(5)	99.95(12)

complex **5a**. Although pyrazine is an excellent ligand for copper(II) and many pyrazine-bridged copper(II) complexes are known,[18,19] the third copper in complex **6a** incorporates into the amide carbonyl/methoxy site rather than the available pyrazine site. Complex **6a** has additional amide carbonyl/methoxy sites on each cyclam ring, yet these did *not* complex additional copper to give oligomers despite the presence of excess copper tetrafluoroborate. Only one such site on each cyclam was coordinated.

The bridging copper causes large distortions in the pyrazine-capped cyclam portion of the molecule, relative to complex **5a**. As might be expected, complexation of one of the amide groups has a profound effect on the copper−amide nitrogen bond lengths, slightly shortening that to the coordinated amide (1.925 vs 1.936 Å in **5a**) and dramatically lengthening that to the free amide to 2.309 Å: a 0.4 Å increase! The coordinated amide carbonyl CO bond is lengthened (1.279 Å vs 1.230 Å in **5a**), and the free CO bond is shortened (1.209 Å). Similarly, the coordinated amide carbonyl C−N bond is shortened (1.300 Å vs 1.33 Å in **5a**), and the free C−N bond is lengthened (1.394 Å). The pyrazine−copper bond length in **6a** is shortened substantially (1.905 vs 2.125 Å in **5a**), and the pyrazine ring is bent away from the bridging amide nitrogen ([N(2)−Cu−N(5)] $\leq$ 134.5° vs 107.9 Å in **5a**). In addition, the cyclam ring is remarkably distorted from the relative planarity observed for complex **5a** [(N(1)−Cu−N(3); N(2)−Cu−N(4) $\approx$ 160° for **5a** vs 167° and 125° for **6a**]. The geometry about the cyclam−copper is a distorted trigonal bipyramid, with equatorial bond angles of 125.5°, 134.5°, and 99.5° (vs 120° for trigonal bipyrimidial) and an "axial" bond angle of 167° versus 180° for trigonal bipyramidal. Finally, all three copper atoms are collinear, and the two pyrazine moieties are still available for further metal coordination, making **6a** a potential building block for coordination oligomers.

Related copper(II) trinuclear species have been reported for copper(II) complexes of 1,4,8,11-tetraazacyclotetradecane-2,3-dione[20] and bis(3-aminopropyl)oxamide.[21] In these cases, the bridging copper atom is coordinated to the two adjacent carbonyl groups of the oxamide. A less closely related tetracopper species involving linkage through a single coordinated amide carbonyl group of a 5,12-dioxocyclam has also recently been reported.[22]

For comparison purposes, the C_2 symmetric cyclam **3b** was also capped with pyrazine (eq 3). In this case, the two



(3)

faces of the cyclam are diastereotopic rather than enantiotopic, and the two possible diastereoisomers were obtained in 67% yield as a 1:4.5 mixture of diastereoisomers. Copper was introduced into the major (capping from the methyl face) diastereoisomer **4b** as shown in eq 3, giving a bright green complex, **5b**.

Although copper(II) preferred amide coordination over pyrazine coordination in the formation of **6a**, the free nitrogen in the pyrazine ring of complex **5a** was capable of additional

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(19) For recent examples, see: (a) Pickardt, J.; Staub, B. *Z. Naturforsch., B.: Chem. Sci.* **1997**, *52*, 1456−1460. (b) Dong, Y.-B.; Smith, M. D.; Layland, R. C.; zur Loye, H.-C. *Inorg. Chem.* **1999**, *38*, 5027. (c) Kwiatkowski, E.; Romanowski, G.; Nowicki, W.; Suwinska, K. *Polyhedron* **2001**, *20*, 1097.

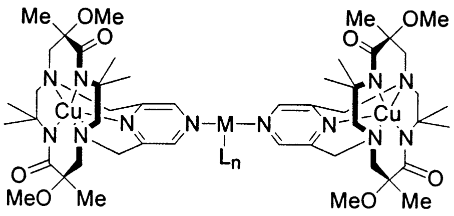
(20) Cronin, L.; Mount, A. R.; Parsons, S.; Robertson, N. *J. Chem. Soc., Dalton Trans.* **1999**, 1925.

(21) Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1986**, *25*, 439.

(22) Goeta, A. E.; Howard, J. A. K.; Maffeo, D.; Puschmann, H.; Williams, J. A.; Gareth, Yufit, D. S. *J. Chem. Soc., Dalton Trans.* **2000**, 1873. Trinuclear copper(II) complexes are also known for their distantly related bis-oximato ligands (Gao, E.-Q.; Zhao, Q.-H.; Tang, D.-Z.; Jiang, Z.-H.; Yan, S.-P. *J. Chem. Soc., Dalton Trans.* **2001**, 1537) and dithiooxamido ligands (Veit, R.; Girerd, J.-J.; Kahn, O.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 4175).

coordination. Treatment of **5a** with $RuCl_2(DMSO)_4$ or $Rh_2(OAc)_4$ produced tri- and tetrametallic complexes **7** and **8** with Ru or Rh bridging two units of complex **5a** through the 4-position of pyrazine (eq 4). The Cu_2Ru complex **7** was

$$\mathbf{5a} + \begin{matrix} RuCl_2(DMSO)_4 \\ \text{or} \\ Rh_2(OAc)_4 \end{matrix} \longrightarrow \qquad \textbf{(4)}$$



7 $ML_n = RuCl_2(DMSO)_2$
8 $ML_n = Rh_2(OAc)_4$

characterized mainly by its mass spectrum, which had a parent peak cluster at m/z 1405 with the intensity pattern calculated for the assigned structure having two copper atoms and one ruthenium atom. Fragment clusters at m/z 1343 (p-Me_2S), m/z 1327 (p-DMSO), and m/z 539 (complex **5a**) all were consistent with the assigned structure. The Cu_2Rh_2 complex **8** crystallized as dichroic brown−green crystals. The X-ray crystal structure of **8** is shown in Figure 3, with bond lengths and angles in Table 3. Again, since racemic **5a** was used, diastereoisomers are expected. Again, the centrosymmetric diastereoisomer crystallized.[29]

In contrast to complex **6a**, which displayed profound structural changes in the pyrazine-capped copper dioxocyclam unit relative to complex **5a**, that same unit in complex **8** remained virtually unchanged. All bond lengths in the copper unit of **8** are within 0.04 Å of those in unbound **5a**, and the biggest bond angle difference is 3°. Even the copper−pyrazine nitrogen bond length remained unchanged notwithstanding the fact that the pyrazine is now complexed to two metals. The pyrazine nitrogen−rhodium bond length (2.249 Å) is very close to that (2.231 Å) observed in the simple bis-pyridine adduct of $Rh_2(OAc)_4$,[23] and the rhodium−rhodium bond lengths are very similar (2.389 Å for **8** vs 2.396 Å).[24]

Spectroscopic Studies. The spectroscopic parameters for compounds **4**−**8** are presented in Table 4; crystallographic details for **5**−**8** are available in Table 5.

The most significant feature of the infrared spectra is the carbonyl stretching frequency for the amide group. For the uncomplexed ligands, this falls in the range 1653−1667 cm^{-1} and includes the uncapped cyclams **3a**,**3b**, the pyrazine-capped cyclams **4a**,**4b**, and the corresponding pyridine-capped centrosymmetric ligand analogue of **4a**.[15] Introduction of copper(II) into these ligands shifts this absorption to the range 1575−1590 cm^{-1}. Further complexation of the exocyclic nitrogen of the pyrazine (complexes **6**−**8**) causes only a minor shift, from 1590 to 1575 cm^{-1}. As might be expected, the most profound changes were observed for complex **6a**, in which one of the amide carbonyl groups is coordinated through oxygen to another copper. In this instance, two carbonyl absorptions were observed, at 1725 and 1575 cm^{-1}. Little information concerning the relative donor−acceptor capabilities of the various capping species

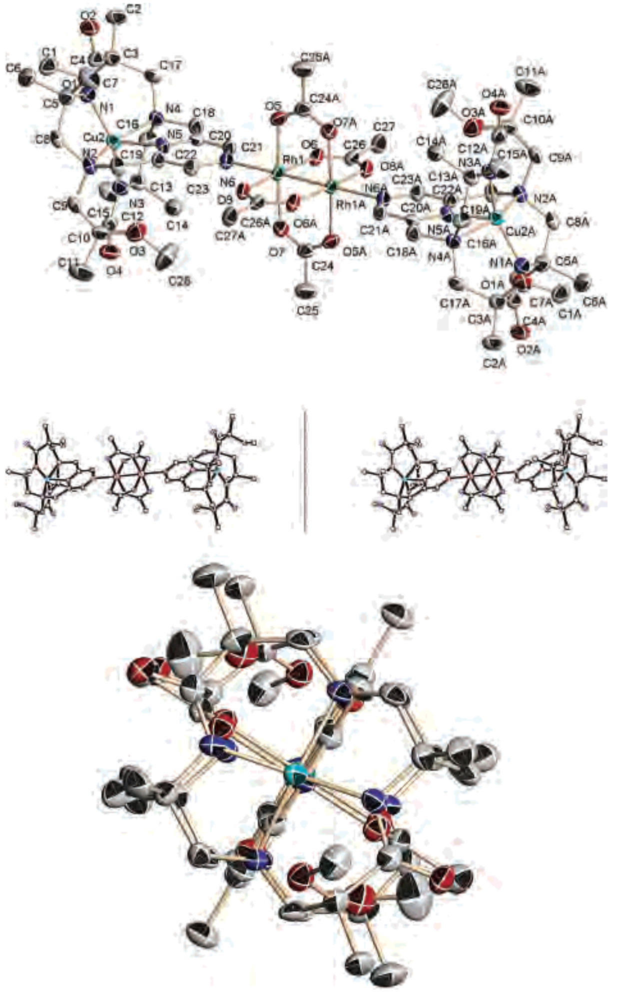


Figure 3. ORTEP diagram and stereoview of complex **8**.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **8** with Estimated Standard Deviations in Parentheses

N(1)−Cu(2)	1.945(5)	N(1)−Cu(2)−N(2)	85.70(18)
N(2)−Cu(2)	2.112(4)	N(3)−Cu(2)−N(2)	99.21(18)
N(3)−Cu(2)	1.935(5)	N(3)−Cu(2)−N(4)	84.75(18)
N(4)−Cu(2)	2.103(4)	N(1)−Cu(2)−N(4)	99.85(18)
N(5)−Cu(2)	2.122(4)	N(3)−Cu(2)−N(1)	155.92(19)
C(4)−O(2)	1.243(6)	N(4)−Cy(2)−N(2)	157.23(17)
C(12)−O(4)	1.239(7)	N(1)−Cu(2)−N(5)	104.81(18)
N(6)−Rh(I)	2.249(4)	N(2)−Cu(2)−N(5)	78.52(16)
Rh(I)−Rh(1A)	2.389(1)	N(3)−Cu(2)−N(5)	99.27(18)
		N(4)−Cu(2)−N(5)	78.71(16)
		N(6)−Rh(I)−Rh(1A)	178.31(12)

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(23) Koh, Y. B.; Christoph, G. G. *Inorg. Chem.* **1978**, *17*, 2590. For Rh(II) dimer bridged pyridyl porphyrins, see: Schaivo, S. L.; Serroni, S.; Puntoriero, F.; Tresoldi, G.; Piraino, P. *Eur. J. Inorg. Chem.* **2002**, 79. For pyrazine-bridged rhodium(II) carboxylates, see: Mori, W.; Hoshino, H.; Nishimoto, Y.; Takamizawa, S. *Chem. Lett.* **1999**, 331.

(24) Rhodium(II) acetate also complexes isonitriles: Eagle, C. T.; Farrar, D. G.; Pfaff, C. U.; Davies, J. A.; Kluwe, C.; Miller, L. *Organometallics* **1998**, *17*, 4523. It also complexes nitriles: Miyasaka, H.; Campos-Fernandez, C. S.; Galan-Mascaros, J.; Dunbar, K. R. *Inorg. Chem.* **2000**, *39*, 5870.

Table 4. Spectroscopic Properties for Compounds **3**−**8**

compd	IR, $\nu_{\text{cm}^{-1}}$	λ_{max}, nm (ϵ)[b]	ESR[a] g_{iso}	A_{iso}	G, cm^{-1}
3a	1664				
3b	1667				
3a−Cu(II)	1575	522(75)	2.1241	97	(9.47 × 10^{-3})
3b−Cu(II)	1583	631(183)	2.1139	100	(9.76 × 10^{-3})
4a	1660				
4b	1653				
5a	1590	407(sh) 684(116)	2.1368	103	(1.00 × 10^{-2})
5b	1586	400(s) 756(119)	2.1553	82	(8.00 × 10^{-3})
6a	1725 1575	407(sh) 558(637)			
7	1575	504(668) 632(239)	2.1360	90	(8.78 × 10^{-3})
8	1575	436(739) 534(340) 658(222)	2.1347	100	(9.76 × 10^{-3})

[a] Spectra run in 3:1 CH_2Cl_2/PhH. [b] Spectra run in methanol.

Table 5. Crystallographic Data

	5	**6**	**8**
empirical formula	$C_{24}H_{38}CuN_6O_4$	$C_{32}H_{50}CuN_6O_{10}Rh$	$C_{25}H_{41}B_2Cu_{1.5}F_8N_6O_5$
fw	538.14	845.23	742.80
T (K)	298(2)	183(2)	298(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
unit cell dimensions			
a (Å)	9.2796(6)	9.533(3)	11.2129(16)
b (Å)	15.0482(10)	14.048(5)	13.640(2)
c (Å)	18.7680(11)	14.153(5)	21.933(3)
α (deg)	89.117(2)	96.406(6)	90
β (deg)	90.000(2)	93.866(6)	97.366(3)
γ (deg)	72.0410(10)	104.369(6)	90
V (Å^3), Z	2492.8(3), 4	1815.7(10), 2	3326.8(8), 4
d_{calcd} (Mg/m^3)	1.434	1.546	1.483
abs coeff (mm^{-1})	0.919	1.103	0.745
GOF of F^2	1.112	0.967	1.042
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.1025, wR2 = 0.1866	R1 = 0.0467, wR2 = 0.1132	R1 = 0.0426, wR2 = 0.1106
R indices (all data)	R1 = 0.1831, wR2 = 0.2317	R1 = 0.0744, wR2 = 0.1238	R1 = 0.0561, wR2 = 0.1171

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum[w(F_o - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$.

can be inferred from the infrared data because of the substantial changes in geometry about copper caused by a rigid bridge between the two amine nitrogens.

The visible spectra also showed responses to changes in geometry about copper. The copper complex of centrosymmetric ligand **3a** was pale violet and had a broad, weak (ϵ = 75) absorption around 522 nm. In contrast, the copper complex of C_2 symmetric ligand **3b** was dark purple and had a more intense (ϵ = 183) absorption at 631 nm. The bright green pyrazine-capped complexes **5a** and **5b** had pronounced shoulders at 407 and 400 nm, respectively, and moderate absorptions at 684 nm (ϵ = 116) and 756 nm (ϵ = 119), respectively. This large red shift may be, in part, due to alkylation of the amine nitrogens, weakening in-plane bonding to copper,[25] but a substantial portion of it must be due to the presence of the cap. For comparison, the green *pyridine*-capped version of **5a**[15] has an absorption at 678 nm (ϵ = 72). The bright blue tris-copper complex **6a** had a shoulder at 407 nm and a fairly strong absorption at 558 nm (ϵ = 637). Although UV spectra were not reported for the related[20,21] 2,3-dione tris-copper complexes already discussed, they are likely to have quite different visible spectra since they are reported to be deep red in both the crystalline state and in solution. The ruthenium-bridged complex **7** had an intense absorption at 504 nm (ϵ = 668) (vs 495 nm [(ϵ = 573) for Ru(dmso)$_4$Cl$_2$]) and a weaker one at 632 nm (ϵ = 239), indicating that both partners were affected by additional coordination. The dirhodium bridged complex **8** had three absorptions, at 436 nm (ϵ = 739), 534 nm (ϵ = 340), and 658 nm (ϵ = 222) vs 364 nm (sh) and 546 nm for Rh$_2$(OAc)$_4$.

The isotropic ESR spectra of the above copper complexes are also informative.[26] The uncapped copper complexes of **3a** and **3b** had very similar ESR spectra, typical[27] for square planar copper(II) complexes, with four equally spaced absorptions due to the interaction with the copper(II) nucleus (J = $^3/_2$). Hyperfine structure was seen on the high field peaks, but not the low field peaks. The ESR spectrum of C_2 symmetric pyrazine capped complex **5b** similarly had four equally spaced absorptions but lacked any hyperfine structure. In sharp contrast, centrosymmetric analogue **5a** had a single broad absorption (g_{iso} = 2.1368, A_{iso} = 103) with a slight shoulder downfield from the main peak, and no features upfield. This is virtually identical to the centrosymmetric *pyridine*-capped complex (g_{iso} = 2.1367). Both of these complexes have ESR spectra that stand in contrast to those observed for copper(II) complexes of 5,7-dioxocyclams having a quinoline[25a] (four peaks, g_{iso} = 2.094) or a pyridine[25b] (four peaks, g_{iso} = 2.096) pendant from one of the cyclam ring amine nitrogens. Complexation of the pyrazine to ruthenium(II) (complex **7**) or rhodium(II) (complex **8**) caused very little change in the ESR spectrum of **5a**. The ESR spectrum of complex **7** is similarly broad (g_{iso} = 2.1360) with slight shoulders both up and downfield of the main absorption, while that of complex **8** (g_{iso} = 2.1347) had a weak downfield absorption in place of the downfield shoulder of complex **5a**.

Electrochemical Studies. The electrochemistry of copper(II)−cyclam and −oxocyclam complexes has been studied extensively by Kimura et al.[28] Although the parent cyclam−copper(II) complex undergoes irreversible oxidation, systematic replacement of amine groups by *amide* groups results in increasing net stabilization of the +3 oxidation state of copper. As a consequence, the monooxocyclam−copper(II) complex has a quasireversible oxidation wave at +0.86 V

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(25) (a) Bu, X.-H.; An, D. L.; Chen, Y. T.; Shinoyo, M.; Kimura, E. *J. Inclusion Phenom.* **1997**, *27*, 245. This paper reports a red shift from 516 to 576 nm for related pendant quinoline−copper dioxocyclam complexes. See also: (b) Bu, X.-H.; An, D. L.; Cao, X.-C.; Zhang, R. H.; Clifford, T.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1998**, 2247. (c) Bu, X.-H.; Cao, X.-C.; An, D. L.; Zhang, R. H.; Thomas, C.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1998**, 433.

(26) Full ESR spectra are contained in the Supporting Information associated with this paper.

(27) Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Surfside: Gainesville, FL, 1992; p 590. From: Hasty, E. F.; Colburn, T. J.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 2414.

(28) Kimura, E.; Koike, T.; Machida, R.; Nagai, R.; Kodama, M. *Inorg. Chem.* **1984**, *23*, 4181.

(29) For a detailed discussion of stereoisomerism in capped bis-cyclams, see ref 15.

(vs SCE), while the 1,3-dioxocyclam copper complex oxidizes at +0.64 V and the 1,3,7-trioxocyclam oxidizes at +0.43 V. Both the increased donor ability of deprotonated amides over amines, and the preference of square planar geometry of copper(III) species, accounts for this dramatic decrease in oxidation potential.

Appending a 2-pyridylmethyl[25b] or an 8-quinolylmethyl[25a] group to an amine nitrogen of the 1,3-dioxocyclam copper(II) complex produced five-coordinate distorted square pyramidal complexes. This resulted in an increase in the oxidation potential to +0.83 V (vs SCE) and +0.78 V, respectively. The coordination of the pendant heterocycle stabilizes the +2 oxidation state. However, copper(III) tends to adopt square planar coordination in preference to five-coordination, resulting in decoordination of the apical heterocycle upon oxidation and increasing the oxidation potential.

The copper(II) complexes reported herein showed substantially different electrochemical behavior. The complex of uncapped C_2 symmetric ligand **3b** had a reversible oxidation wave at +0.49 V (vs SCE) similar to that observed for the 1,3-dioxocyclam already discussed.[28] Surprisingly, the complex of the uncapped centrosymmetric ligand **3a** underwent irreversible oxidation. Similarly, the pyridine-capped copper(II) complexes of **3a** and **3b**, the pyrazine-capped copper(II) complexes of the same ligands, and polymetallic complexes **5**, **7**, and **8**, all underwent irreversible oxidation. This is consonant with the increase in oxidation potential caused by pendant ligands already discussed.[25a,b] The difference here is that, because of the rigid two-point attachment of the capping ligand, decomplexation to form a stabilized square planar copper(III) complex is not possible, and this oxidation state becomes inaccessible. Tricopper complex **6a** showed an irreversible reduction peak at −0.99 V (vs Ag/AgO) with an associated oxidation peak at −0.58 V. This is very similar to that observed with the literature tricopper species already cited,[20] which was attributed to reduction of only the central copper ion, with deposition on the electrode in a two electron process, followed by reoxidation to generate a copper(I) species. Neither oxidation nor reduction of the cyclam-bound copper was observed.

Magnetic Properties. Magnetic Behavior of 6a. The copper(II) cyclam complex, **6a**, resembles the cyclam complexes of Kahn[21] and Robertson[20] and the trinuclear Cu(II) complexes of Gao;[22] however, **6a** is unable to form a strong dimeric complex across the central copper atoms due to the methanol ligands coordinated in the solid state. Consequently, there is no Cu(2)−Cu(2) intermolecular separation near 3.2 Å as in their complexes. It was therefore anticipated that little or no intermolecular antiferromagnetic (AF) communication would be observed. However, the data at low temperatures do suggest that there is still a weak anitferromagnetic coupling between molecules in the crystal ($J' < 10$ cm^{-1}).

The plot of susceptibility, χ, versus T, showed typical Curie−Weiss paramagnetic behavior with a room-temperature moment, $\mu_{\mathrm{eff}} = 3.07\ \mu_{\mathrm{B}}$, and a Weiss constant, $\theta = -1.4$, indicating a weak AF communication among centers. (A plot of χT versus T is shown in Figure 4.) This value is reasonable compared to a classical three-center $S = {}^1/_2$, $\mu_{\mathrm{eff}} = 2.996\ \mu_{\mathrm{B}}$. The plot shows that the moment decreases with temperature until about 100 K where the moment levels to 2.10 μ_{B}. This value is a bit high compared with a $S = {}^1/_2$ AF coupled system where $\mu_{\mathrm{eff}} = 1.73\ \mu_{\mathrm{B}}$. Nevertheless, the data are consistent with what others have observed for similar Cu(II) systems.[20−22] At very low temperatures, an abrupt downturn in the χT data was observed, suggesting that there is a lower-lying AF state that is likely due to intermolecular interactions. This hypothesis is based on Kahn's model for a weakly AF system with a low-lying coupling between two trinuclear copper complexes. Kahn's coupling constant was $J = -2.9$ cm^{-1}; therefore, we conclude that the intermolecular coupling constant in our system is equally small. However, we have not been able to adequately model our data using the equations reported earlier[21] to model J', the intermolecular coupling constant.

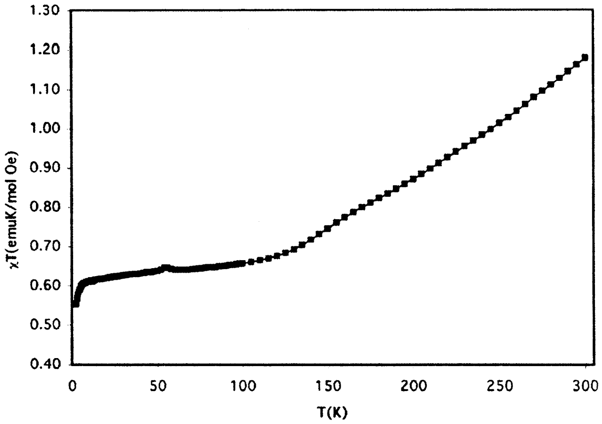

Figure 4. Plot of χT versus T for complex **6a**.

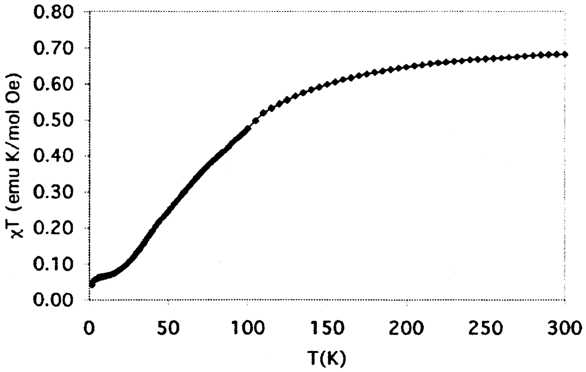

Figure 5. Plot of χT versus T for complex **8**.

Magnetic Studies of 8. The magnetic susceptibility of **8** is displayed in Figure 5 as χT versus T. The sample showed classic Curie−Weiss behavior at low temperatures, with a very weak AF Weiss constant, $\theta = -40$ K. The χT plot illustrates a moment of $\mu_{\mathrm{eff}} = 2.41\ \mu_{\mathrm{B}}$ at room temperature. This value is very close to the expected value for two $S = {}^1/_2$ systems with one unpaired electron on each site and is consistent with the picture of two Cu(II) d^9 atoms not coupled through the Rh−Rh dimer, where the theoretical moment should be $\mu_{\mathrm{eff}} = 2.440\ \mu_{\mathrm{B}}$. This suggests that the localized, paired δ^* electrons are not involved in any superexchange process at room temperature, unlikely in any event as the symmetry of the HOMO is not consistent with superexchange.[30] At temperatures below 100 K, a downturn in the moment, nearly reaching zero at 25 K, was observed, suggesting that there is some coupling between the copper atoms either through the rhodium dimer or through space with other molecules in the unit cell. We are currently engaged in low-temperature ac susceptibility measurements to determine the nature of the low-temperature behavior in **8** and an attempt to model this magnetic data in an effort to evaluate the level of Cu−Cu coupling through the rhodium dimer.

Summary

In summary, a pyrazine-capped 5,12-dioxocyclam was synthesized. Complexation to copper produced the expected mononuclear copper complex **5a** under thermal conditions but the unusual tricopper species **6a** under microwave irradiation. The remote pyrazine nitrogen of **5a** can coordinate to other metals, allowing **5a** to be utilized as a subunit in coordination oligomers. This was demonstrated by the synthesis of tri- and tetrametallic complexes **7** and **8**. Current studies are centering on the synthesis of bis-pyrizine−bis-cyclam ligands and complexes for the ultimate synthesis of more extended coordination oligomers.

Acknowledgment. Support for this research under Grant CHE-9908661 from the National Science Foundation is gratefully acknowledged. Mass spectra were obtained on instruments supported by National Institutes of Health shared instrumentation Grant GM 49631. Professor David Shultz, North Carolina State University, is acknowledged for his assistance in interpreting the magnetic measurements.

Supporting Information Available: ESR spectra for complexes **3a**, **3b**, **5a**, **5b**, **7**, and **8**, and tables of crystal data, structure solutions and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **5a**, **6a**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.