Synthesis and Structural Studies of 1,8-Pyridine-Capped 5,12-Dioxocyclams

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Abstract: 5,12-Dioxocyclams and bis-dioxocyclams were capped across the 1,8-secondary amino groups with 2,6-bis(bromomethyl)pyridine to give pyridine-capped mono- and bis-dioxocyclams. The copper(II) complex of capped monocyclam **5b** was prepared and characterized by X-ray crystallography. Treatment of dioxocyclams with 2,3,5,6-tetrakis(bromomethyl)pyrazine produced bis-cyclams connected through their secondary amino groups through the 2,3- and 5,6-positions of the pyrazine.

Introduction

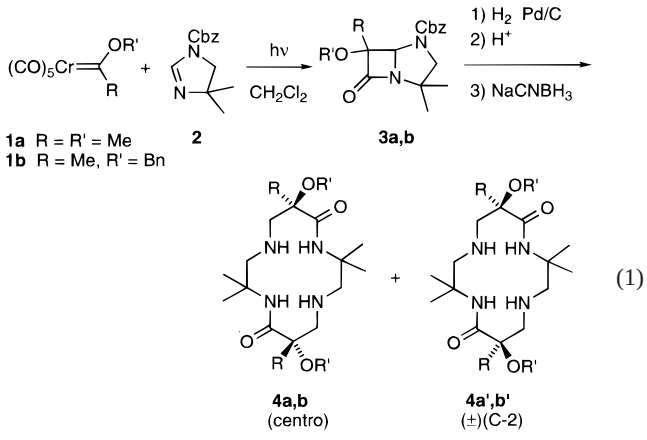
Cyclams are a class of 14-membered tetraazacycloalkanes with the ability to complex with a wide range of metal ions including both main group and transition metals,[1] as well as lanthanides.[2] Cyclam−metal complexes have been developed as catalysts for both laboratory[3] and biological[4] processes, as magnetic imaging agents,[5] and as DNA cleaving agents.[6] Dioxocyclams are a subclass of tetraazacycloalkane in which two of the amine groups have been replaced by two amide groups. They are intermediate in their metal complexation properties between cyclic peptides and cyclic polyamines. The most common types of dioxocyclams are prepared from 5,7-dicarbonyl compounds,[7] but dioxocyclams having 5,12-disposed carbonyl groups are also known.[8]

In addition to their ability to coordinate metals, the secondary amine groups of cyclams can be alkylated or acylated. By using appropriate bis-electrophiles they can be either capped[9] or bridged,[9,10] giving macrobi- or tricyclic compounds having both unusual coordination sites for metals and well-defined cavities with the potential to act as selective receptors for specific molecules.

Recently, an efficient synthesis of functionalized dioxocyclams having 5,12-disposed carbonyl groups has been reported from these laboratories. They are produced by the acid-catalyzed dimerization of azapenams, which are in turn produced by photolysis of chromium carbene complexes in the presence of protected imidazolines.[11] The use of optically active imidazolines results in the production of optically active dioxocyclams[12] while the use of bis-carbene complexes leads to bis-dioxocyclams.[13] These ligands provide square-planar coordination sites for transition metals, and the bis-dioxocyclams provide cavities, the dimensions of which vary with the chain length of the linkers. The synthesis of capped mono- and bis-dioxocyclams utilizing recently reported[9] capping procedures, and metal-complexation studies of the resulting capped ligand systems, are reported below.

Results and Discussion

The requisite dioxocyclams were synthesized as previously described (eq 1).[11] With achiral imidazoline **2**, an easily separated 1:1 mixture of the centrosymmetric (**4a**,**4b**) and C_2-symmetric (**4a′**,**4b′**) diastereoisomers was obtained. Capping of



(1)

these dioxocyclam amino groups with 2,6-bis(bromomethyl)-pyridine converts the amine nitrogens to chiral centers, since the rigid capping group prevents inversion at nitrogen. Thus,

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(4) For a review, see: Kimura, E. *Tetrahedron* **1992**, *48*, 6175.

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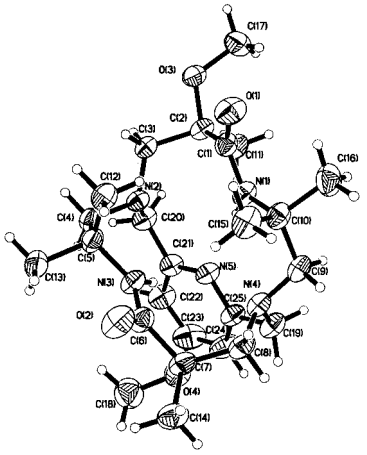


Figure 1. ORTEP diagram of compound **5a**. Hydrogens are omitted for clarity.

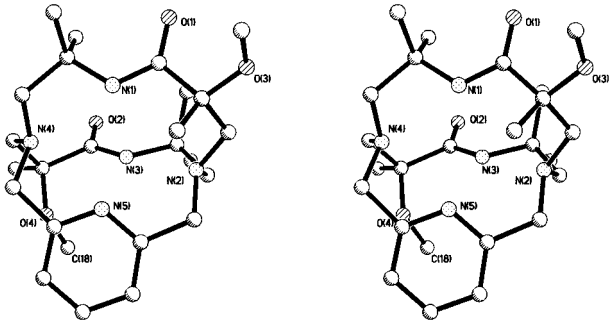
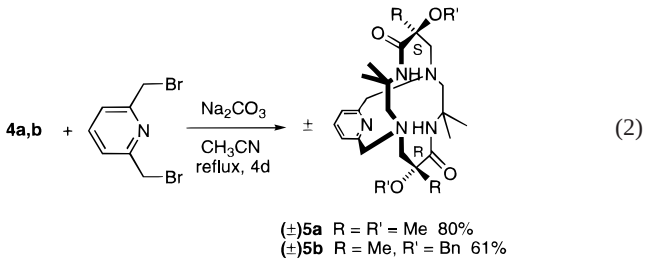


Figure 2. Stereoview of compound **5a**. Hydrogens are omitted for clarity.

treatment of the achiral centrosymmetric diastereoisomers **4a**,**b** with 2,6-bis(bromomethyl)pyridine produced capped, racemic dioxocyclams **5a**,**5b** in excellent yield (eq 2).

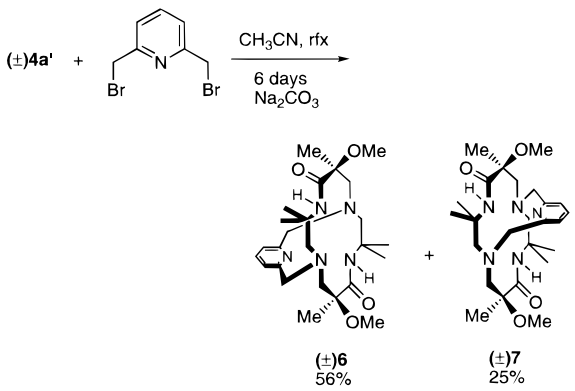


(±)**5a** R = R' = Me 80%
(±)**5b** R = Me, R' = Bn 61%

(2)

The most significant feature of the ^{1}H NMR spectrum of the (methyl)(methoxy)dioxocyclam **5a** was the difference in chemical shifts for the two different OCH_3 signals. One was strongly shielded, appearing at δ 2.52, almost 1 ppm upfield from the other, which appeared at the expected δ 3.50. The upfield signal was assigned to the OCH_3 group syn to the capping pyridine group, which is held in the shielding cone of the aromatic ring. An X-ray crystal structure of **5a** (Figure 1) confirmed that capping across the secondary amines had occurred, producing a ligand with five potentially coordinating nitrogens: two amines, two amides, and a pyridine. The 14-membered ring is far from planar, a situation similar to that observed with uncapped dioxocyclams.[11,12] A stereoview of the structure (Figure 2) confirms the placement of the syn methoxy group (C(18)) over the face of the capping pyridine, accounting for its upfield shift in the ^{1}H NMR spectrum.

Because capping of the dioxocyclams generates chiral tertiary amines which cannot invert because they are held in a rigid cyclic environment, *enantiomers* are produced with the centrosymmetric systems **5a**,**5b**. However, with the racemic C_2-symmetric dioxocyclam **4a′**, capping could, in principle, produce two racemic diastereoisomers, resulting from capping from the face occupied by the two methoxy groups or the face occupied by the two methyl groups, respectively. Treatment of C_2-symmetric (methyl)(methoxy)dioxocyclam **4a′** with bis(bromomethyl)pyridine produced two diastereoisomers in 56% and 25% isolated yields, respectively (eq 3). The major isomer had

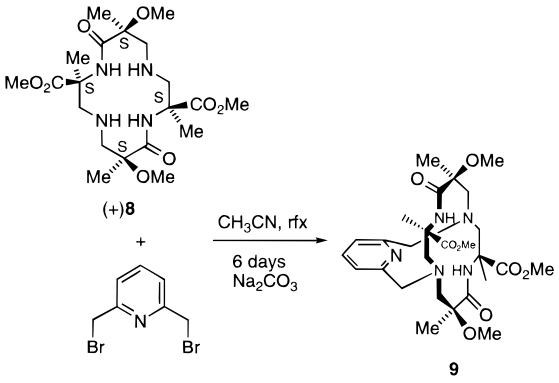


(±)**6** 56% (±)**7** 25%

(3)

a singlet at δ 3.36 for the two methoxy groups, while the minor one had a singlet at δ 2.72 for these same groups. Based on the shielding arguments presented above, the major isomer resulted from capping of the face syn to the methyl groups, while the minor one resulted from capping of the face syn to the methoxy groups. Since **4a′** was racemic, the diastereoisomer **6** and **7** are also racemic.

Optically active dioxocyclams are available by starting with an optically active imidazoline.[12] Reaction of optically active (+)-dioxocyclam **8** with bis(bromomethyl)pyridine proceeded only very slowly, producing 45% of capped product **9** after 6 days at reflux in acetonitrile, along with recovered **8** (eq 4). Again, two (optically active) diastereoisomers could be formed

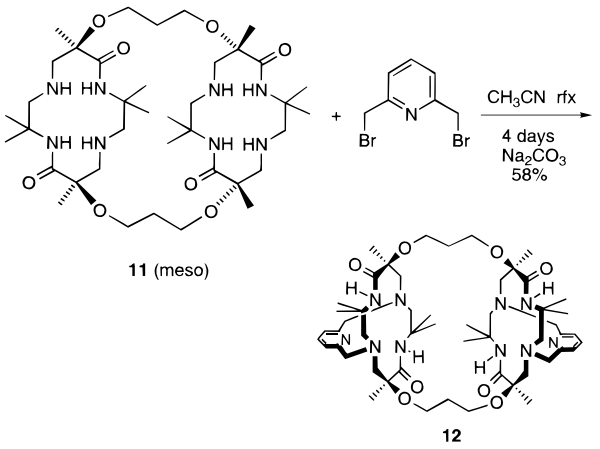


(4)

in this reaction. However, a single product was obtained. Based on the ^{1}H NMR spectrum, capping occurred exclusively from the face syn to the methyl groups and anti to the methoxy and the ester groups. The signal for the methoxy groups (δ 3.35) was virtually unchanged from that of **8**, while the signal for the methyl group was shifted slightly upfield (δ 1.10 vs 1.36).

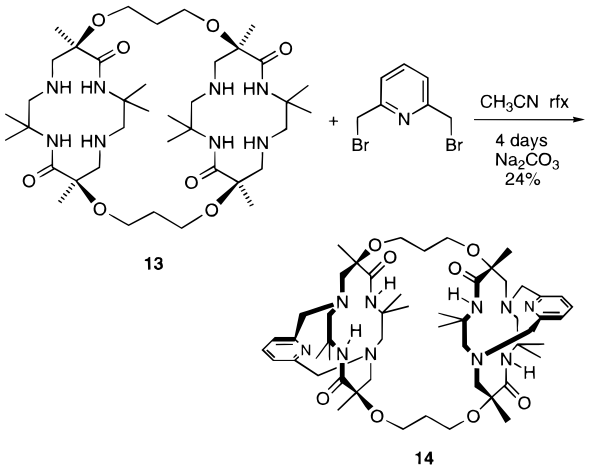
Finally, centrosymmetric dioxocyclam **4a** was capped with α,α′-dibromo-*m*-xylene. A low (30%) yield of capped dioxocyclam (**10**), corresponding to **5a**, but with benzene replacing the pyridine group, was produced. As with **5a**, the ^{1}H NMR spectrum had an upfield signal (δ 3.06) for one methoxy group and a "normal" (δ 3.39) signal for the other.

Bis-dioxocyclams are readily available by the reaction shown in eq 1 by starting with bis-carbene complexes.[13] Capping of these with bis(bromomethyl)pyridine should produce unusual ligands having two potentially five-coordinate sites in addition to a well-defined cavity, the dimensions of which could be varied by varying bridging chain length. In *meso*-bis-dioxocyclam **11**, the two dioxocyclam rings are held strictly in a face-to-face, eclipsed orientation, about 6−7 Å apart.[13] Capping with bis(bromomethyl)pyridine produced the bis-capped, bis-dioxocyclam **12** in fair yield (eq 5). Capping was assumed to occur



(5)

from the face opposite the bridge, since the bridge face is very sterically hindered. This is consistent with the ^{1}H NMR spectrum, for which the bridging OCH_2 signals have the same chemical shift as in the uncapped bis-dioxocyclam, while the methyl groups at the bridging position are shifted slightly upfield (≈0.2 ppm). Similar capping of the (racemic) D_2-symmetric bis-dioxocyclam **13** gave a low yield of the bis-capped D_2-symmetric bis-dioxocyclam **14** (eq 6).



(6)

The bis-dioxocyclams discussed above arose from starting with bis-carbene complexes linked through the alkoxy groups. An alternative approach is to couple mono-dioxocyclams with a bis-linking agent. This approach has some serious stereochemical consequences. Capping a mono-dioxocyclam generates two new chiral centers at the capped amine groups, since these can no longer invert due to the rigid cyclic nature of the system. The least complex example would be to couple a C_2-symmetric dioxocyclam which only caps on a single face, such as (+)-**8** (eq 4). This should, and does, lead to a single, optically active bis-dioxocyclam when treated with tetrakis(bromomethyl)-

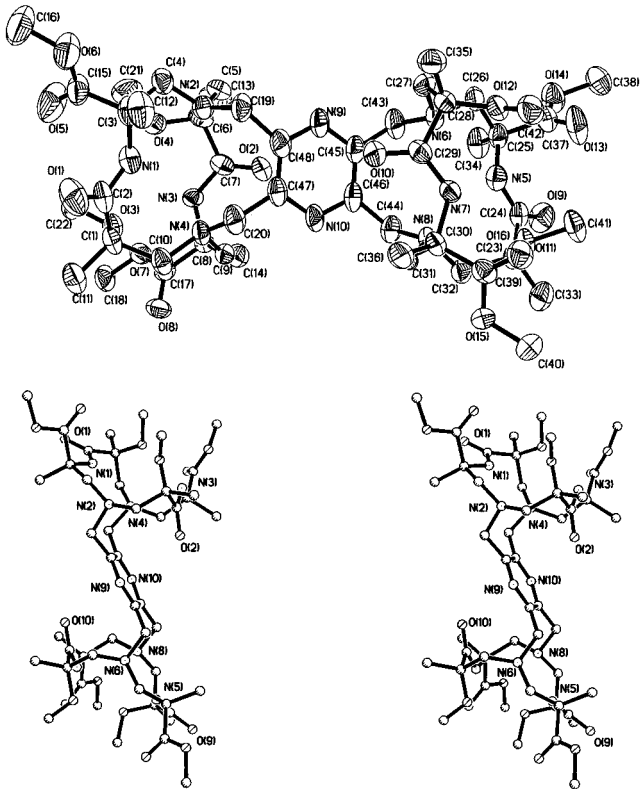
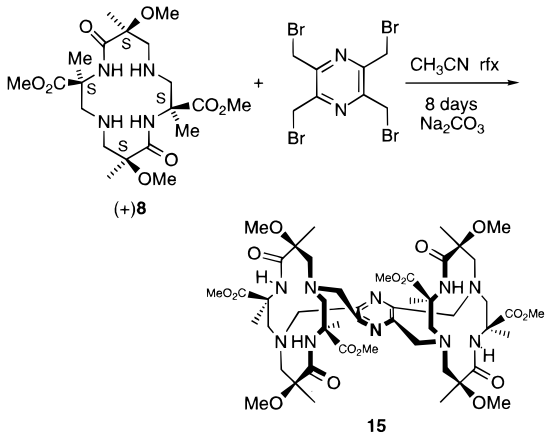


Figure 3. ORTEP diagram and stereoview of **15**. Hydrogen atoms and solvent molecules have been removed for clarity.

pyrazine (eq 7). Capping/linking occurred exclusively in an ortho



(7)

(1,2) manner from the face opposite the methoxy and ester groups, giving a bis-dioxocyclam with the pyrazine nitrogens perpendicular to the dioxocyclam coordination spheres. This is probably a consequence of the flexibility of the dioxocyclam ring, placing the two reacting ring amines in close proximity. The structure was confirmed by X-ray crystallography (Figure 3) and shows two dioxocyclams, linked back-to-back by a bridging pyrazine, and held at an acute angle to the pyrazine bridge.

This type of bridging for the centrosymmetric dioxocyclam **4a** is potentially considerably more complex. Two aspects determine the stereochemistry of the resulting product: (1) the face of the cyclam which undergoes reaction (e.g., the configuration generated at the bridgehead nitrogens) and (2) the relative orientation of the two cyclam rings (e.g., the alignment of the chiral centers on each ring relative to the other). The possibilities are presented in Figure 4. Because the two chiral

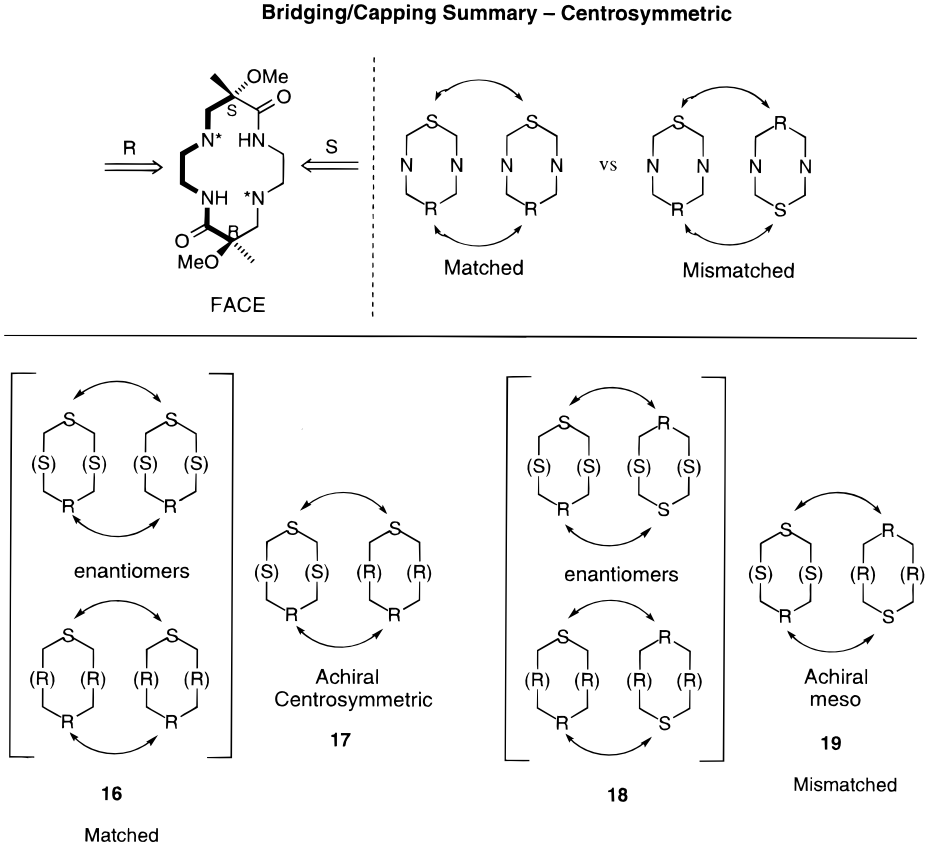


Figure 4. Possible stereoisomers from bridging of centrosymmetric **4a**.

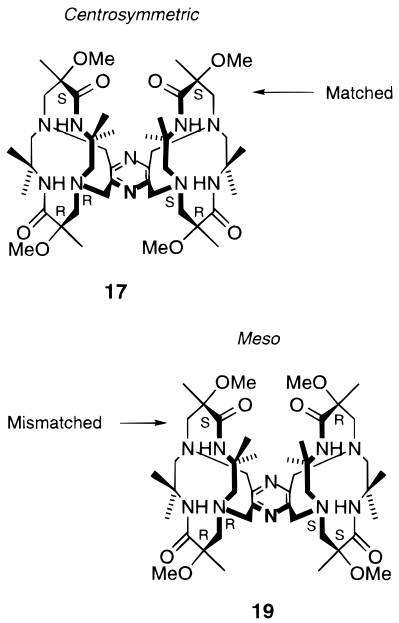
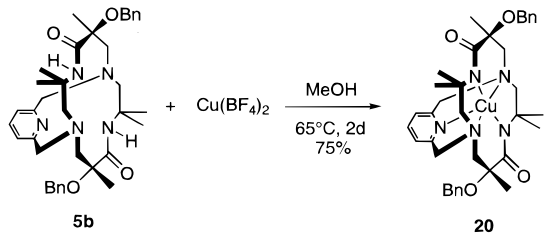


Figure 5. Structures of compounds **17** and **19**.

centers in **4a** are of opposite configuration, in the bis-cyclam they can either be aligned (matched) or opposite (mismatched) one another. For each series (matched, mismatched), three possible diastereoisomers can result, depending upon which prochiral face of the cyclam reacts. For the matched series, a pair of enantiomers and a *centrosymmetric* achiral diastereoisomer can form, while for the mismatched series, a pair of enantiomers and a *meso* achiral diastereoisomer can be formed. In the event, treatment of **4a** with tetrakis(bromomethyl)pyrazine gave a mixture of achiral diastereomers in overall 72% yield. Careful selective crystallization allowed separation of these (**17** and **19**) (Figure 5). X-ray crystal structures of sufficient resolution to determine connectivity and stereochemistry were obtained for **17** and **19**. However, they were not of sufficient quality to provide accurate bond angles and bond lengths (wR > 0.20). Surprisingly, the two pairs of racemates (**16** and **18**) were not observed.

Pyridine-capped dioxocyclams provide approximate square pyramidal coordination sites for the complexation of metals. Recently reported syntheses and structural studies of copper(II) complexes of 13-membered tetraazamacrocycles with 7,5-disposed carbonyl groups with a pendant quinoline,[14] the closely related 14-membered dioxo-macrocycles with one- and two-pendant pyridines,[15] and the 14-membered dioxo-macrocycles with two-pendant quinolines[16] provide an excellent basis for comparison with copper(II) complexes of **5** in which the pyridine is fixed into position for coordination. Treatment of **5b** with copper(II) tetrafluoroborate in methanol produced blue complex **20** in good yield (eq 8).



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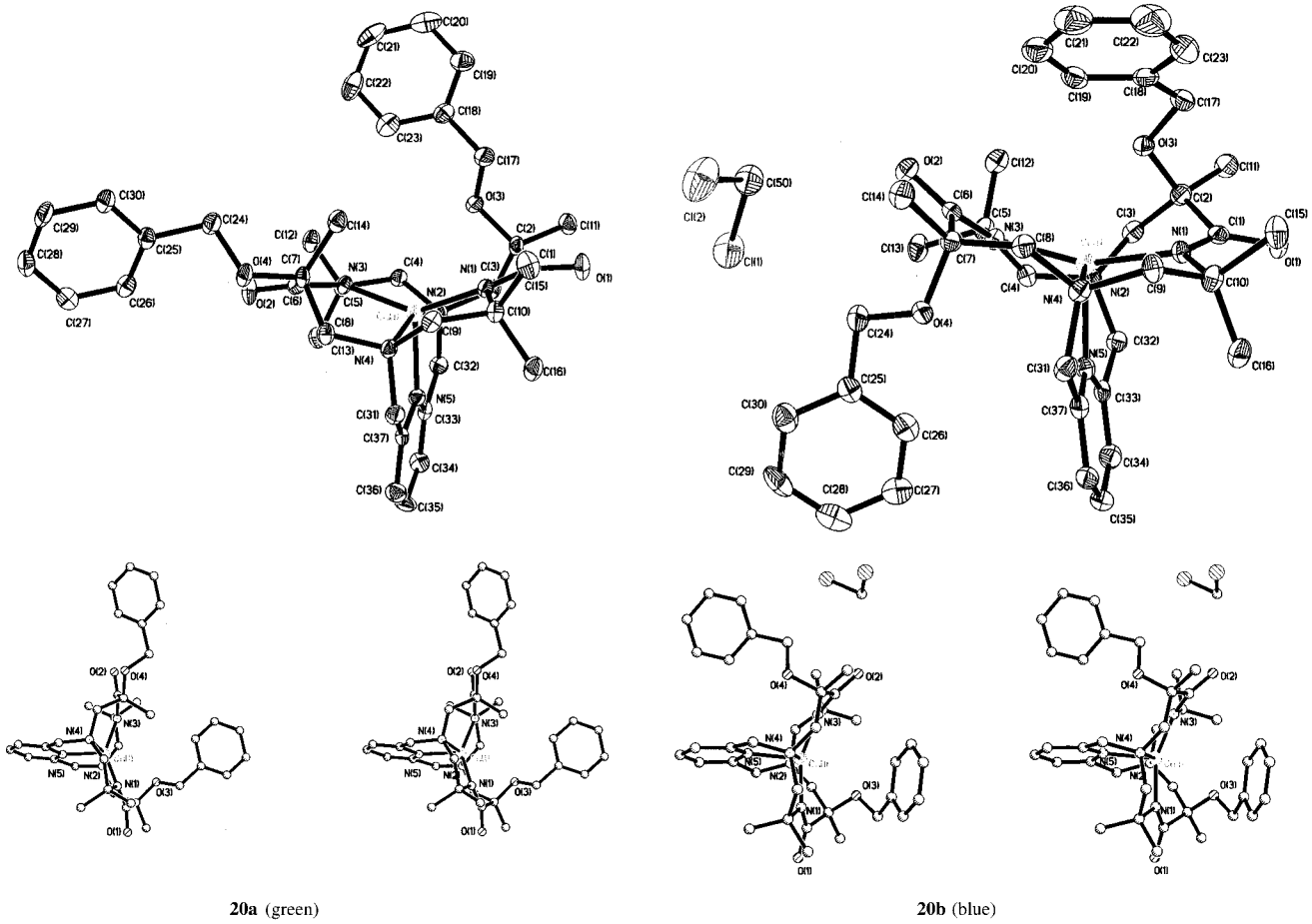

20a (green) **20b** (blue)

Figure 6. ORTEP diagram and stereoviews of **20a** and **20b**.

Recrystallization from methylene chloride−hexane gave green crystals (**20a**) and blue crystals (**20b**). The X-ray crystal structures of **20a** and **20b** are shown in Figure 6, along with isolated structural features highlighting the differences between these two compounds (Figure 7). Selected bond lengths and angles are shown in Tables 1 and 2.

The copper is clearly five-coordinate in both modifications of **20**, and the copper−amide bond lengths (1.95 Å, 1.96 Å, **20a**; 1.94 Å, 1.95 Å **20b**), copper−amine bond lengths (2.12 Å, 2.14 Å **20a**; 2.10 Å, 2.10 Å **20b**), and the copper−pyridine bond lengths (2.12 Å **20a**; 2.13 Å **20b**) are virtually identical between these two complexes and very similar to those found in Kimura's[14] 13-membered β-dioxocyclam copper complex with a pendant quinoline group (copper−amide bond lengths 1.94 Å, 1.93 Å; copper−amine bond lengths 2.03 Å, 2.03 Å; copper−quinoline bond length 2.27 Å). The major structural difference between **20a** and **20b** is the degree of distortion from square-pyramidal geometry the copper suffers, resulting from (or causing) major conformational differences between the dioxocyclam rings of **20a** and **20b**.

In dioxocyclam complexes, the metal is part of two six-membered rings and two five-membered rings as a consequence of the disposition of the four coordinating nitrogens about the 14-membered cyclam ring. Complexes **20a** and **20b** differ primarily by the conformation of one of the six-membered rings in which copper participates. In **20a**, this six-membered ring is in a half-boat conformation with the O-benzyl group equatorial, while in **20b**, it is in a chair conformation, with the O-benzyl group axial. These changes in conformation of this six-membered ring are not independent, but rather are coupled to the rest of the macrocyclic periphery. Isolating the coordination sphere of the metal from the periphery (Figure 7) shows that green complex **20a** is strongly distorted toward trigonal-bipyramidal geometry, with "equatorial" N−Cu−N angles of 142.8°, 110.3°, and 106.8° (vs 120° for trigonal bipyramidal), while blue complex **20b** is more nearly square pyramidal with angles of 157.9°, 105.0°, and 96.9° (vs 180°, 90°, and 90° for square pyramidal).

It should be noted that complex **20b** contains a molecule of methylene chloride in the crystal lattice, which might, in principle, account for the structural difference between **20a** and **20b**. However, methylene chloride solutions of **20** are green (λ_{max} 260, 368, 660 nm), while methanol solutions are blue (λ_{max} 258, 340, 654 nm), implying that these structural differences remain in solution and are solvent-dependent. The fact that it is the *blue* form (**20b**) that has a molecule of methylene chloride in the crystal lattice, but the solution of **20** is *green* in methylene chloride, suggests that the solvent of crystallization is not responsible for the different conformation of **20**.

In summary, a series of pyridine-capped mono- and bis-dioxocyclams have been synthesized and characterized. They provide unusual coordination sites for metals in addition to well-defined cavities for potential host−guest interactions and selective catalysis. Studies of these properties are the subject of current studies.

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp apparatus and are uncorrected. The 300-Hz ^{1}H NMR and 75.5-MHz ^{13}C NMR spectra were obtained on a Varian Inova-300 spectrometer, and the 400-MHz ^{1}H NMR and 100.6-MHz ^{13}C NMR spectra were obtained on a Varian Inova-400 spectrometer. Chemical shifts are given in ppm relative to $(CH_3)_4Si$ (0 ppm, ^{1}H) or $CDCl_3$ (77.23 ppm, ^{13}C)

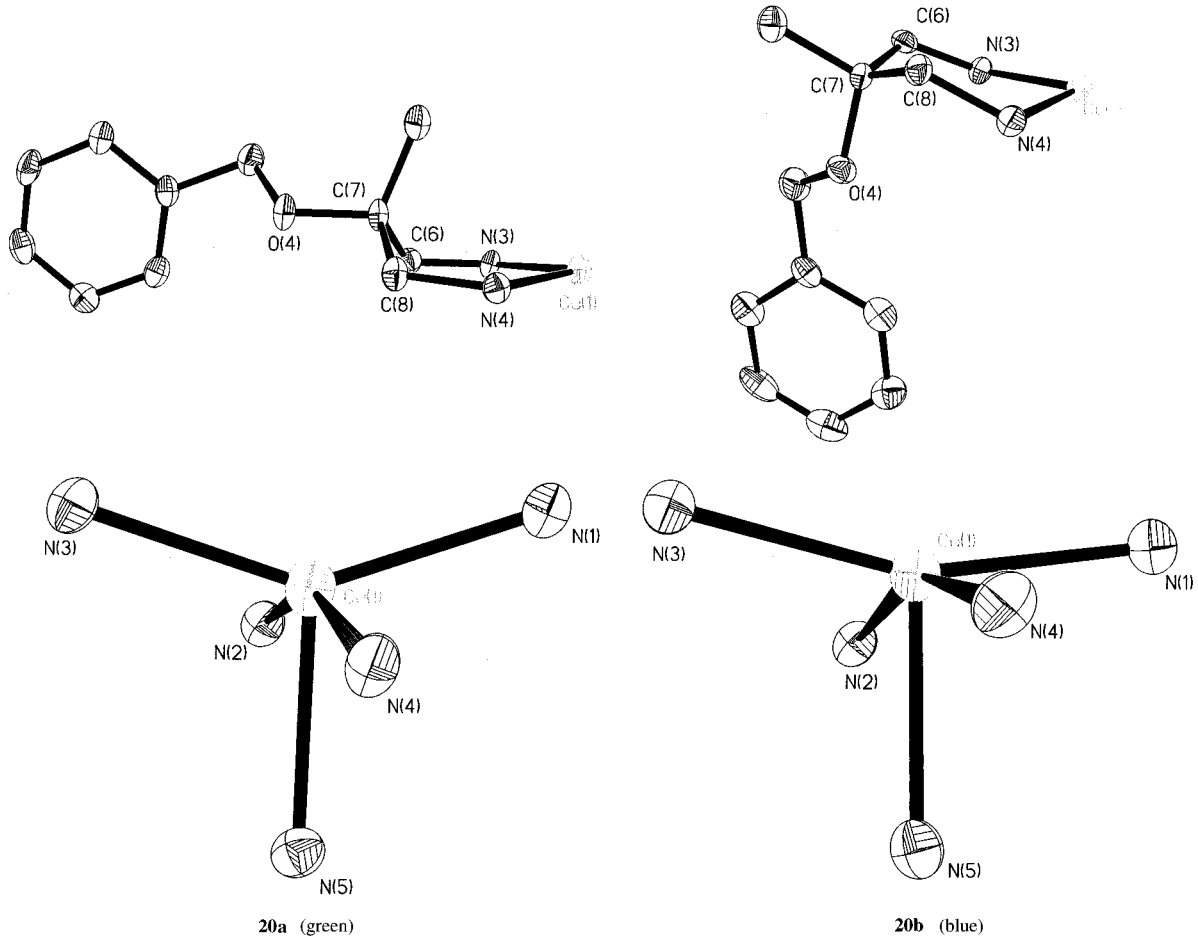

Figure 7. Isolated structural features for **20a** and **20b**.

unless otherwise noted. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. X-ray crystallographic studies were performed on a Bruker Smart CCD diffractometer, and the intenisty of the data set was integrated using Bruker SAINT software. The structures were solved using Bruker SHELXTL version 5.03 software. Column chromatography was performed on silica gel (Silicycle 230−400 mesh). Radial chromatography was performed on silica gel (EM Science silica gel 60 PF_{254} containing gypsum) plates 1−2 mm in thickness.

Acetonitrile (Fisher certified ACS grade) was used without further purification. Methanol (Fisher, ACS grade) was dried over 3-Å molecular sieves. CH_2Cl_2 (technical grade) was distilled from CaH_2. $CHCl_3$ (Fisher), Et_3N (Fisher stored over KOH), and Et_2O (Fisher) were used without further purification. Hexanes for crystallization purposes was distilled at ambient pressure. Distilled water was used for crystallization purposes.

2,6-Bis(bromomethyl)pyridine and α,α′-dibromo-*m*-xylene were purchased from Aldrich and used without further purification. $Cu(BF_4)_2$ was purchased from Stem chemicals and was dried under high vacuum at room temperature for 2 days and then stored in a desiccator. The following chemicals were prepared according to literature procedures: centrosymmetric (methyl)(methoxy)dioxocyclam **(4a)**,[10] centrosymmetric (methyl)(benzyloxy)dioxocyclam **(4b)**,[10] C_2-symmetric (methyl)-(methoxy)dioxocyclam **(4a′)**,[10] (*S*,+)-(methyl)(methoxy)dioxocyclam **(8)**,[13] *meso*-(C3)-bis-dioxocyclam **(11)**,[12] D_2-symmetric (C3)-bis-dioxocyclam **(13)**,[12] and tetrakis(bromomethyl)pyrazine.[17]

Pyridine-Capped *centro*-(Methyl)(methoxy)dioxocyclam (5a). In a 250-mL three-neck flask equipped with a condenser, 190 mg (0.51 mmol) of centrosymmetric (methyl)(methoxy)dioxocyclam **(4a)** was dissolved in 100 mL of CH_3CN. To this solution was added 216 mg (2.04 mmol, 4.0 equiv) of Na_2CO_3, and the turbid solution was heated to reflux. Next, 135 mg (0.51 mmol) of 2,6-bis(bromomethyl)pyridine in 5 mL of CH_3CN was added over 20 min via a syringe pump. The solution was then allowed to stir at reflux for 4 days, after which the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was purified by radial chromatography on a 1-mm silica gel plate ($CHCl_3$ to 1:9 MeOH/$CHCl_3$) to yield 195 mg (0.41 mmol, 80%) of a white solid. X-ray quality crystals were generated by slow evaporation of CH_2Cl_2, mp > 250 °C. ^{1}H NMR: δ 9.1 (s, 1H), 8.1 (s, 1H), 7.6 (t, 1H, J = 8 Hz), 6.9 (app dd, 2H, J = 8, 3 Hz), 4.1 (m, 4H), 3.4 (s, 3H), 3.2 (d, 1H, J = 14 Hz), 2.9 (m, 5H), 2.6 (m 4H), 2.35 (d, J = 14 Hz), 1.6 (bs, 2H), 1.5 (s, 3H), 1.4 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H), 1.2 (s, 3H), 1.1 (s, 3H). ^{13}C NMR: δ 173.5, 172.9, 162.9, 158.4, 137.2, 119.1, 118.8, 82.7, 79.7, 74.5, 72.8, 69.2, 67.3, 65.7, 64.7, 55.9, 54.9, 51.9, 50.3, 26.3, 25.7, 23.7, 23.5, 19.3. IR (neat): ν 1660 (C=O) cm^{-1}. FAB mass spectrum: m/z 476.2 (M + 1). The structure of **5a** was determined by X-ray analysis, and the results of the study are presented in the Supporting Information.

Pyridine-Capped *centro*-(Methyl)(benzyloxy)dioxocyclam (5b). In a 100-mL three-neck flask equipped with a condenser, 150 mg (0.29 mmol) of centrosymmetric (methyl)(benzyloxy)dioxocyclam **(4b)** was dissolved in 60 mL of CH_3CN. To this solution was added 121 mg (1.14 mmol, 4.0 equiv) of Na_2CO_3, and the turbid solution was heated to reflux. Next, 75 mg (0.29 mmol) of 2,6-bis(bromomethyl)pyridine in 5 mL of CH_3CN was added over 20 min via a syringe pump. The solution was then allowed to stir at reflux for 4 days, after which the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was purified by radial chromatography on a 1-mm silica gel plate ($CHCl_3$ to 1:9 MeOH/$CHCl_3$) and then crystallized from CH_2Cl_2/hexanes to yield 111 mg (0.176 mmol, 61%) of a colorless crystalline solid, mp > 250 °C. ^{1}H NMR: δ 9.15 (s, 1H), 8.85 (s, 1H), 7.4 (m, 3H), 7.2−7.35 (m, 3H), 7.1 (m, 1H), 7.0 (t, 2H, J = 7 Hz), 6.9 (d, 1H, J = 7 Hz), 6.7 (d, 3H, J = 7 Hz), 4.8 (d, 1H, J = 12 Hz), 4.7 (d, 1H, J = 12 Hz), 4.5 (d, 1H,

(17) Ferigo, M.; Bonhote, P.; Marty, W.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1994**, 1549.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **20a**, with Estimated Standard Deviations in Parentheses

Cu(1)−N(1)	1.954(3)	Cu(1)−N(3)	1.957(2)
Cu(1)−N(2)	2.118(3)	Cu(1)−N(5)	2.121(3)
Cu(1)−N(4)	2.138(3)	N(1)−C(1)	1.328(4)
N(1)−C(10)	1.492(4)	N(2)−C(3)	1.499(4)
N(2)−C(4)	1.510(4)	N(2)−C(32)	1.512(4)
N(3)−C(6)	1.347(4)	N(3)−C(5)	1.490(4)
N(4)−C(9)	1.500(4)	N(4)−C(31)	1.506(4)
N(4)−C(8)	1.511(4)	N(5)−C(37)	1.336(4)
N(5)−C(33)	1.341(4)	O(1)−C(1)	1.261(4)
O(2)−C(6)	1.251(4)	O(3)−C(17)	1.432(4)
O(3)−C(2)	1.453(4)	O(4)−C(24)	1.438(4)
O(4)−C(7)	1.445(4)	C(1)−C(2)	1.573(5)
C(2)−C(11)	1.529(4)	C(2)−C(3)	1.535(4)
C(4)−C(5)	1.542(4)	C(5)−C(13)	1.541(4)
C(5)−C(12)	1.544(4)	C(6)−C97)	1.576(5)
C(7)−C(14)	1.531(5)	C(7)−C(8)	1.544(4)
C(9)−C(10)	1.549(4)	C(10)−C(15)	1.544(4)
C(10)−C(16)	1.550(4)		
N(1)−Cu(1)−N(3)	142.84(11)	N(1)−Cu(1)−N(2)	101.22(10)
N(3)−Cu(1)−N(2)	86.66(10)	N(1)−Cu(1)−N(5)	110.33(10)
N(3)−Cu(1)−N(5)	106.82(10)	N(2)−Cu(1)−N(5)	78.58(10)
N(1)−Cu(1)−N(4)	86.23(10)	N(3)−Cu(1)−N(4)	100.73(10)
N(2)−Cu(1)−N(4)	156.76(10)	N(5)−Cu(1)−N(4)	78.19(10)
C(1)−N(1)−C(10)	118.7(3)	C(1)−N(1)−Cu(1)	124.0(2)
C(10)−N(1)−Cu(1)	114.5(2)	C(3)−N(2)−C(4)	111.8(2)
C(3)−N(2)−C(32)	108.4(2)	C(4)−N(2)−C(32)	110.2(2)
C(3)−N(2)−Cu(1)	111.5(2)	C(4)−N(2)−Cu(1)	101.8(2)
C(32)−N(2)−Cu(1)	113.1(2)	C(6)−N(3)−C(5)	118.7(3)
C(6)−N(3)−Cu(1)	122.9(2)	C(5)−N(3)−Cu(1)	113.7(2)
C(9)−N(4)−C(31)	110.0(2)	C(9)−N(4)−C(8)	110.6(2)
C(31)−N(4)−C(8)	108.2(2)	C(9)−N(4)−Cu(1)	103.1(2)
C(31)−N(4)−Cu(1)	112.9(2)	C(8)−N(4)−Cu(1)	112.0(2)
C(37)−N(5)−C(33)	121.2(3)	C(37)−N(5)−Cu(1)	119.3(2)
C(33)−N(5)−Cu(1)	1118.7(2)	C(17)−O(3)−C(2)	115.7(2)
C(24)−O(4)−C(7)	115.8(2)	O(1)−C(1)−N(1)	127.1(3)
O(1)−C(1)−C(2)	116.5(3)	N(1)−C(1)−C(2)	116.4(3)
O(3)−C(2)−C(11)	110.2(3)	O(3)−C(2)−C(3)	105.9(2)
C(11)−C(2)−C(3)	106.0(3)	O(3)−C(2)−C(1)	111.8(3)
C(11)−C(2)−C(1)	109.7(3)	C(3)−C(2)−C(1)	113.0(3)
N(2)−C(3)−C(2)	118.7(2)	N(2)−C(4)−C(5)	113.9(3)
N(3)−C(5)−C(13)	111.6(3)	N(3)−C(5)−C(4)	105.3(2)
C(13)−C(5)−C(4)	113.9(3)	N93)−C(5)−C(12)	112.2(3)
C(13)−C(5)−C(12)	108.5(3)	C(4)−C(5)−C(12)	105.1(3)
O(2)−C(6)−N(3)	127.1(3)	O(2)−C(6)−C(7)	118.8(3)
N(3)−C(6)−C(7)	114.1(3)	O(4)−C(7)−C(14)	110.6(3)
O(4)−C(7)−C(8)	99.5(2)	C(14)−C(7)−C(8)	115.1(3)
O(4)−C(7)−C(6)	109.6(2)	C(14)−C(7)−C(6)	110.9(3)
C(8)−C(7)−C(6)	110.5(3)	N(4)−C(8)−C(7)	117.4(3)
N(4)−C(9)−C(10)	114.5(3)	N(1)−C(10)−C(15)	112.5(3)
N(1)−C(10)−C(9)	106.7(2)	C(15)−C(10)−C(9)	105.2(3)
N(1)−C(10)−C(16)	110.5(3)	C(15)−C(10)−C(16)	108.8(3)
C(9)−C(10)−C(16)	113.1(3)	O(3)−C(17)−C(18)	107.9(3)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **20b**, with Estimated Standard Deviations in Parentheses

Cu(1)−N(1)	1.936(3)	Cu(1)−N(3)	1.948(3)
Cu(1)−N(4)	2.100(3)	Cu(1)−N(2)	2.102(3)
Cu(1)−N(5)	2.125(3)	N(1)−C(1)	1.336(5)
N(1)−C(10)	1.484(4)	N(2)−C(4)	1.493(4)
N(2)−C(3)	1.499(4)	N(2)−C(32)	1.502(4)
N(3)−C(6)	1.329(4)	N(3)−C(5)	1.498(5)
N(4)−C(8)	1.497(4)	N(4)−C(9)	1.502(4)
N(4)−C(31)	1.508(4)	N(5)−C(37)	1.326(5)
N(5)−C(33)	1.337(5)	O(1)−C(1)	1.252(4)
O(2)−C(6)	1.266(4)	O(3)−C(17)	1.436(4)
O(3)−C(2)	1.453(4)	O(4)−C(24)	1.431(4)
O(4)−C(7)	1.459(4)	C(1)−C(2)	1.574(5)
C(2)−C(3)	1.541(5)	C(2)−C(11)	1.535(5)
C(4)−C(5)	1.541(5)	C(5)−C(12)	1.536(5)
C(5)−C(13)	1.546(5)	C(6)−C(7)	1.571(5)
C(7)−C(14)	1.534(5)	C(7)−C(8)	1.545(5)
C(9)−C(10)	1.547(5)	C(10)−C(16)	1.542(5)
C(10)−C(15)	1.546(5)		
N(1)−Cu(1)−N(3)	157.98(12)	N(1)−Cu(1)−N(4)	87.05(11)
N(3)−Cu(1)−N(4)	99.29(11)	N(1)−Cu(1)−N(2)	94.42(11)
N(3)−Cu(1)−N(2)	87.75(11)	N(4)−Cu(1)−N(2)	157.37(11)
N(1)−Cu(1)−N(5)	96.93(11)	N(3)−Cu(1)−N(5)	104.97(11)
N(4)−Cu(1)−N(5)	78.80(11)	N(2)−Cu(1)−N(5)	78.60(11)
C(1)−N(1)−C(10)	121.7(3)	C(1)−N(1)−Cu(1)	122.2(2)
C(10)−N(1)−Cu(1)	114.9(2)	C(4)−N(2)−C(3)	113.7(3)
C(4)−N(2)−C(32)	108.7(3)	C(3)−N(2)−C(32)	108.6(3)
C(4)−N(2)−Cu(1)	101.8(2)	C(3)−N(2)−Cu(1)	113.2(2)
C(32)−N(2)−Cu(1)	110.6(2)	C(6)−N(3)−C(5)	118.9(3)
C(6)−N(3)−Cu(1)	124.9(2)	C(5)−N(3)−Cu(1)	112.5(2)
C(8)−N(4)−C(9)	109.1(3)	C(8)−N(4)−C(31)	111.0(3)
C(9)−N(4)−C(31)	111.8(3)	C(8)−N(4)−Cu(1)	109.6(2)
C(9)−N(4)−Cu(1)	102.0(2)	C(31)−N(4)−Cu(1)	113.0(2)
C(37)−N(5)−C(33)	122.7(3)	C(37)−N(5)−Cu(1)	118.6(2)
C(33)−N(5)−Cu(1)	117.7(2)	C(17)−O(3)−C(2)	114.0(3)
C(24)−O(4)−C(7)	116.0(3)	O(1)−C(1)−N(1)	127.6(3)
O(1)−C(1)−C(2)	118.8(3)	N(1)−C(1)−C(2)	113.4(3)
O(3)−C(2)−C(3)	104.8(3)	O(3)−C(2)−C(11)	110.7(3)
C(3)−C(2)−C(11)	106.5(3)	O(3)−C(2)−C(1)	107.9(3)
C(3)−C(2)−C(1)	115.6(3)	C(11)−C(2)−C(1)	111.1(3)
N(2)−C(3)−C(2)	115.6(3)	N(2)−C(4)−C(5)	115.9(3)
N(3)−C(5)−C(12)	113.2(3)	N(3)−C(5)−C(4)	104.6 (3)
C(12)−C(5)−C(4)	112.6(3)	N(3)−C(5)−C(13)	111.8(3)
C(12)−C(5)−C(13)	109.3(3)	C(4)−C(5)−C(\13)	105.0(3)
O(2)−C(6)−N(3)	126.6(3)	O(2)−C(6)−C(7)	116.5(3)
N(3)−C(6)−C(7)	116.5(3)	O(4)−C(7)−C(14)	109.3(3)
O(4)−C(7)−C(8)	106.8(3)	C(14)−C(7)−C(8)	105.4(3)
O(4)−C(7)−C(6)	107.4(3)	C(14)−C(7)−C(6)	110.1(3)
C(8)−C(7)−C(6)	117.6(3)	N(4)−C(8)−C(7)	119.2(3)
N(4)−C(9)−C(10)	116.2(3)	N(1)−C(10)−C(16)	113.2(3)
N(1)−C(10)−C(15)	112.3(3)	C(16)−C(10)−C(15)	107.0(3)
N(1)−C(10)−C(9)	103.8(3)	C(16)−C(10)−C(9)	115.1(3)
C(15)−C(10)−C(9)	105.3(3)	O(3)−C(17)−C(18)	111.6(3)
C(23)−C(18)−C(17)	119.3(3)		

J = 17 Hz), 4.25 (d, 1H, J = 11 Hz), 4.05 (s, 2H), 3.95−3.85 (m, 2H), 3.4 (d 1H, J = 14 Hz), 3.15−2.8 (m, 5H), 2.4 (dd, 2H, J = 6, 14 Hz), 1.6 (s, 3H), 1.5 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H), 1.2 (s, 3H). ^{13}C NMR: δ 173.7, 173.3, 160.7, 158.4, 140.5, 138.6, 137.4, 128.4, 128.1, 127.6, 127.3, 127.2, 119.4, 118.5, 83.3, 80.8, 73.4, 66.7, 66.4, 66.1, 65.4, 65.4, 55.5, 26.3, 25.8, 25.2, 23.7, 23.7, 20.2. IR (neat) ν 1659 (C═O) cm^{-1}. Anal. Calcd for $C_{37}H_{49}N_5O_4$: C, 70.79; H, 7.87; N, 11.15. Found: C, 70.66; H, 8.00; N, 10.95.

Pyridine-Capped *d,l*-(Methyl)(methoxy)dioxocyclams (6 and 7). In a 100-mL round-bottom flask equipped with a condenser, 125 mg (0.34 mmol) of C_2-symmetric (methyl)(methoxy)dioxocyclam **(4a′)** was dissolved in 60 mL of CH_3CN. To this solution was added 284 mg (2.68 mmol, 8.0 equiv) of Na_2CO_3. The turbid mixture was then allowed to reflux for 1 h, followed by the addition of 88 mg (0.34 mmol) of 2,6-bis(bromomethyl)pyridine. After 6 days at reflux, the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was purified by column chromatography (1:99 Et_3N/CH_2Cl_2 to 1:1:98 $Et_3N/MeOH/CH_2Cl_2$) to yield, after a saturated Na_2CO_3 wash to remove the Et_3N, 90 mg (189 mmol 56%) of the major isomer **6** as a clear wax and a mixture of the minor isomer **7** and the starting C_2 dioxocyclam **4a′**. A second column (2:98 $MeOH/CH_2Cl_2$) yielded 40 mg (84 mmol, 25%) of the minor isomer **7** as a clear wax.

Major isomer **6**. ^{1}H NMR: δ 8.82 (bs, 2H), 7.49 (t, 1H, J = 7.7 Hz), 6.85 (d, 2H, J = 7.7 Hz), 3.94. (dd, 4H, J = 16.8, 10.3 Hz), 3.35 (s, 6H) 3.20 (d, 2H, J = 14.6 Hz), 2.86 (d, 2H, J = 14.3 Hz), 2.84 (d, 1H, J = 13.6 Hz), 2.57 (d, 2H, J = 13.6 Hz), 1.47 (m, 2H), 1.34 (s, 6H), 1.20 (s, 6H), 1.17 (s, 6H). ^{13}C NMR: δ 173.0, 159.2, 136.5, 119.0, 81.8, 71.4, 66.6, 66.1, 54.4, 51.6, 27.1, 25.4, 21.6. IR (neat): ν 1658 (C═O) cm^{-1}. Anal. Calcd for $C_{25}H_{42}N_5O_4$: C, 63.13; H, 8.69; N, 14.72. Found: C, 62.95; H, 8.50; N, 14.68.

Minor isomer **7**. ^{1}H NMR: δ 8.98 (bs, 2H), 7.55 (t, 1H, J = 7.7 Hz), 6.85 (d, 2H, J = 7.7 Hz), 4.36 (d, 2H, J = 16.5 Hz), 3.83 (d, 2H, J = 16.5 Hz), 2.98 (dd, 4H, J = 14.1, 10.6 Hz), 2.88 (d, 1H, J = 14.3 Hz), 2.75 (s, 6H), 2.45 (d, 2H, J = 14.3 Hz), 1.61 (bs, 2H), 1.45 (s, 6H), 1.25 (s, 6H), 1.20 (s, 6H). ^{13}C NMR: δ 173.3, 161.2, 136.7, 118.2, 83.1, 73.4, 67.7, 66.3, 55.4, 50.6, 25.7, 23.7, 19.6. IR (neat): ν 1652 (C═O) cm^{-1}. MS (HR FAB): MW calculated for $C_{25}H_{42}N_5O_4$, 476.3237; found, 476.3222 (Δ = 3.1 ppm) (M + 1).

Pyridine-Capped (+)-(Methyl)(methoxy)dioxocyclam (9). In a 100-mL round-bottom flask equipped with a condenser, 120 mg (0.26 mmol) of (*S*,+)-(methyl)(methoxy)dioxocyclam **(8)** was dissolved in 50 mL of CH_3CN. To this solution was added 220 mg (2.08 mmol, 8 equiv) of Na_2CO_3, and the turbid mixture was then heated at reflux for 1 h. Next, 70 mg (0.26 mmol) of solid 2,6-bis(bromomethyl)pyridine was added. After 6 days at reflux, the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was purified by flash column chromatography, first by eluting (5:95 MeOH/CH_2Cl_2) to remove the dioxocyclam **8** and then with 5:95 Et_3N/CH_2Cl_2 to yield, after a saturated Na_2CO_3 wash to remove the Et_3N, 65 mg (0.12 mmol, 45%) of the capped dioxocyclam **(9)** as a clear wax. X-ray quality crystals of **9** were generated by slow diffusion of water into methanol, mp 187 °C (MeOH/H_2O), $[\alpha]^{21}_D$ +57° (c = 1.03, $CHCl_3$). ^{1}H NMR: δ 8.56 (bs, 2H), 7.56 (t, 1H, J = 7.7 Hz), 6.86 (d, 2H, J = 7.7 Hz), 3.72 (dd, 4H, J = 14.4, 10.9 Hz), 3.71 (s, 6H), 3.27 (s 6H), 3.14 (dd, 4H, J = 11.0, 4.0 Hz) 3.16 (d, 2H, J = 15.0 Hz), 3.12 (d, 2H, J = 12.8 Hz), 2.91(d, 2H, J = 13.1 Hz), 2.78 (d, 2H, J = 15.0 Hz), 1.54 (s, 6H), 1.12 (s, 6H). ^{13}C NMR: δ 175.1, 172.0, 158.6, 136.1, 119.5, 82.4, 65.9, 62.7, 61.9, 61.4, 52.1, 50.1, 21.6, 19.3. IR (neat): ν 1738, 1648 (C═O) cm^{-1}. MS (HR FAB): MW calculated for $C_{27}H_{42}N_5O_8$, 564.3033; found, 564.3030 (Δ = 0.8 ppm) (M + 1). The structure of **5a** was determined by X-ray analysis, and the results of the study are presented in the Supporting Information.

***m*-Xylene-Capped *centro*-(Methyl)(methoxy)dioxocyclam (10).** In a 100-mL round-bottom flask equipped with a condenser, 100 mg (0.26 mmol) of *centro*-(methyl)(methoxy)dioxocyclam **(4a)** was dissolved in 45 mL of CH_3CN, along with 100 mg (1.04 mmol, 4.0 equiv) of Na_2CO_3. This turbid solution was heated to reflux, followed by the addition of 68 mg (0.26 mmol, 1 equiv) of α,α′-dibromo-*m*-xylene. The solution was allowed to stir at reflux for 4 days, after which the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was purified by radial chromatography ($CHCl_3$ to 5% MeOH/$CHCl_3$) and then crystallized from toluene to yield 37 mg (0.078 mmol 30%) of a white powder. ^{1}H NMR: δ 9.21 (bs, 1H), 7.45 (bs, 1H), 7.08 (t, 1H, J = 7 Hz), 6.8 (m, 2H), 5.9 (bs, 1H), 4.0 (d, 1H, J = 13.8 Hz), 3.78 (dd, 2H, J = 20.9, 17.2 Hz), 3.78 (d, 2H, J = 7.7 Hz), 3.11 (m, 3H), 3.06 (s, 3H), 2.90 (s, 2H), 2.84 (d, 1H, J = 14.6 Hz), 2.34 (d, J = 12.7 Hz), 1.70 (m, 1H), 1.35 (s, 6H), 1.34 (s, 3H), 1.27 (s, 3H), 1.21 (s, 3H), 1.08 (s, 3H). ^{13}C NMR: δ 173.7, 172.9, 142.2, 140.3, 131.8, 127.1, 122.5, 122.5, 83.0, 82.9, 72.5, 69.1, 67.9, 63.1, 62.7, 62.5, 55.1, 53.3, 51.5, 49.8, 30.4, 28.1, 27.6, 24.6, 20.6, 20.3. MS (HR FAB): MW calculated for $C_{26}H_{43}N_4O_4$, 475.3284; found, 475.3278 (Δ = 1.2 ppm) (M + 1).

Bis-Capped *meso*-(C3)-Bis-dioxocyclam (12). In a 50-mL round-bottom flask equipped with a condenser, 70 mg (0.09 mmol) of *meso*-(C3)-bis-dioxocyclam **(11)** was dissolved in 20 mL of CH_3CN. To this solution was added 75 mg (0.72 mmol, 8.0 equiv) of Na_2CO_3, and this turbid solution was heated to reflux. Next, 47 mg (0.18 mmol, 2 equiv) of 2,6-bis(bromomethyl)pyridine was added. The solution was allowed to stir at reflux for 5 days, after which the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was dissolved in 20 mL of CH_2Cl_2 and washed 3 times with 10 mL of water. The CH_2Cl_2 was dried with Na_2SO_4, and the solvent was removed in vacuo. The resulting clear wax was crystallized by slow diffusion of Et_2O into CH_2Cl_2 to yield 50 mg (0.051 mmol, 58%) of **11** as white powder, mp > 250 °C. ^{1}H NMR: δ 7.81 (bs, 4H), 7.38 (t, 2H, J = 7.3 Hz), 6.75 (d, 4H, J = 7.3), 3.74 (s, 8H), 3.54 (dt, 4H, J = 5.9, 10.3 Hz), 3.36 (dt, 4H, J = 5.1, 10.3 Hz), 3.10 (d, 4H, J = 15.0 Hz), 2.77 (d, 4H, J = 15.0), 2.70 (dd, 8H, J = 13.3, 7.7 Hz), 1.97 (m, 2H), 1.83 (m 2H), 1.30 (s, 12H), 1.19 (s, 12H), 1.17 (s, 12H). ^{13}C NMR: δ 172.6, 158.7, 135.9, 118.8, 84.1, 68.5, 66.6, 66.3, 60.9, 54.1, 33.3, 28.6, 25.3, 21.1. IR (neat): ν 1651 (C═O) cm^{-1}. Anal. Calcd for $C_{52}H_{82}N_{10}O_8$: C, 64.04; H, 8.47; N, 14.36. Found: C, 64.37; H, 8.35; N, 14.39.

Bis-Capped D_2-Symmetric (C3)-Bis-dioxocyclam (14). In a 50-mL round-bottom flask equipped with a condenser, 83 mg (0.11 mmol) of D_2-symmetric (C3)-bis-dioxocyclam **(13)** was dissolved in 20 mL of CH_3CN. To this solution was added 75 mg (0.42 mmol, 4.0 equiv) of Na_2CO_3, and this turbid solution was heated to reflux. Next, 56 mg (0.21 mmol, 2 equiv) of 2,6-bis(bromomethyl)pyridine was added. After 6 days at reflux, the cooled reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was crystallized from $CHCl_3$ to yield 25 mg (0.026 mmol, 24%) of **13** as white powder. ^{1}H NMR (CD_3OD): δ 8.47 (t, 2H, J = 8.1 Hz), 7.80 (d, 4H, J = 7.7), 7.31 (s, 4H), 4.28 (dd, 8H, J = 7.3, 18.3 Hz), 3.81 (m, 8H), 3.45 (d, 4H, J = 15.7 Hz), 3.00 (d, 4H, J = 13.2 Hz), 2.98 (d, 4H, J = 15.4 Hz), 2.82 (d, 4H, J = 13.5 Hz) 2. 29 (m, 4H), 1.46 (s, 12H), 1.38 (s, 12H), 1.30 (s, 12H). ^{13}C NMR: δ 175.7, 154.7, 148.3, 125.2, 85.8, 68.0, 65.6, 63.2, 62.3, 55.9, 34.5, 29.7, 26.1, 21.4. IR (neat): ν 1664 (C═O) cm^{-1}. MS (HR FAB): MW calculated for $C_{52}H_{83}N_{10}O_8$, 975.6395; found, 975.6379 (Δ = 1.7 ppm) (M + 1).

Pyrazine-Bridged *S*-(Methyl)(methoxy)bis-dioxocyclam (15). In a 100-mL round-bottom flask equipped with a condenser, 259 mg (0.56 mmol) of (*S*,+)-(methyl)(methoxy)dioxocyclam **((+)8)** was dissolved in 50 mL of CH_3CN. To this solution was added 238 mg (2.25 mmol, 8.0 equiv) of Na_2CO_3, and this turbid solution was heated to reflux. Next, 56 mg (0.21 mmol, 2 equiv) of tetrakis(bromomethyl)pyrazine was added. The solution was allowed to stir at reflux for 6 days, after which the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was purified by flash column chromatography, first by eluting (5:95 MeOH/CH_2Cl_2) to remove the dioxocyclam (**8**) and then with 5:95 Et_3N/CH_2Cl_2 to yield, after a saturated Na_2CO_3 wash to remove the Et_3N, 59 mg (0.17 mmol, 10%) of the bridged bis-dioxocyclam **(15)** as a clear wax. X-ray quality crystals of **15** were generated by slow diffusion of water into methanol, mp 160 °C dec, $[\alpha]^{21}_D$ +20.4° (c = 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, −10 °C): δ 9.34 (s, 2H), 7.49 (s, 2H), 4.30 (d, 2H, J = 12.1 Hz), 4.03 (d, 2H, J = 10.5 Hz), 3.83 (d, 2H, J = 10.5 Hz), 3.75 (s, 6H), 3.70 (s, 6H), 3.47 (m, 4H), 3.28 (s, 6H), 3.25 (m, 8H), 3.09 (d, 2H, J = 15.4 Hz), 3.00 (m, 4H), 2.86 (d, 2H, J = 12.5 Hz), 2.77 (d, 2H, J = 15.3 Hz), 2.46 (d, 2H, J = 14.3 Hz), 2.00 (s, 6H), 1.29 (s, 6H), 1.13 (s, 6H), 1.05 (s, 6H). ^{13}C NMR: δ 174.6, 174.5, 173.5, 172.4, 150.3, 150.0, 81.9, 79.0, 77.4, 68.6, 66.1, 62.2, 61.5, 59.7, 57.3, 56.9, 56.1, 52.8, 52.5, 51.2, 25.7, 23.7, 18.6, 17.5. IR (neat): ν 1741, 1667 (C═O) cm^{-1}. The structure of **14** was determined by X-ray analysis, and the results of the study are presented in the Supporting Information.

Pyrazine-Bridged *centro*-(Methyl)(methoxy)bis-dioxocyclam (20 and 22). In a 100-mL three-neck flask equipped with a condenser, 247 mg (0.66 mmol, 2.0 equiv) of *centro*-(methyl)(methoxy)dioxocyclam **(4a)** was dissolved in 50 mL of CH_3CN. To this solution was added 280 mg (2.64 mmol, 8.0 equiv) of Na_2CO_3, and this turbid solution was heated to reflux. Next, 50 mg (0.33 mmol) of tetrakis(bromomethyl)pyrazine was added. The solution was allowed to stir at reflux for 6 days, after which the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The resulting yellow oil was recrystallized from MeOH/H_2O. The first crop of crystals yielded 30 mg of capped monomer. The mother liquor was allowed to evaporate, and a second crop of crystals was collected (177 mg, 0.20 mmol, 61%) as a 3:4 mixture of diasteriomers. ^{1}H NMR (400 MHz, $CDCl_3$, −30 °C): δ 9.91 (s, 2H), 9.77 (s, 2H), 8.53 (s, 2H), 8.37 (s, 2H), 5.24 (d, 2H, J = 12.5 Hz), 5.20 (d, 2H, J = 12.8 Hz), 4.25 (d, 2H, J = 11.7 Hz), 4.14 (d, 2H, J = 11.7 Hz), 3.63 (d, 2H, J = 11.7 Hz), 3.46 (d, 2H, J = 11.7 Hz), 3.37 (m, 8H), 3.16 (d, 2H, J = 13.6 Hz), 3.00 (m, 8H), 2.84 (d, 2H, J = 14.4 Hz), 2.82 (d, 2H, J = 13.6 Hz), 2.62 (m, 8H), 2.15 (d, 2H, J = 14.0 Hz), 2.03 (d, 2H, J = 14.0 Hz), 1.52 (s, 12H), 1.49 (s, 12H), 1.28 (s, 6H), 1.27 (s, 6H), 1.24 (s, 12H), 1.18 (s, 6H), 1.14 (s, 6H), 1.02 (s, 6H), 1.01 (s, 6H). ^{13}C NMR: δ 171.3, 171.2, 170.1, 169.5, 151.5, 150.7, 150.5, 149.3, 81.0, 80.8, 80.3, 79.8, 70.2, 66.6, 66.0, 63.9, 63.4, 63.1, 62.6, 58.6, 53.4, 53.3, 53.1, 51.1, 51.0, 50.8, 28.6, 28.3, 27.6, 27.2, 25.7, 24.9, 19.7, 19.3, 18.9, 18.9. IR (neat): ν 1671 (C═O) cm^{-1}.

Cu(II) Complex of *centro*-(Methyl)(benzyloxy)-capped Dioxocyclam (20). To 5 mL of CH_2Cl_2 in a pressure tube was added 70 mg (0.11 mmol) of **5b** along with 187 mg (0.55 mmol, 5.0 equiv) of $Cu(BF_4)_2 \cdot 6H_2O$ and 76 mg (0.55 mmol, 5.0 equiv) of K_2CO_3. The pressure tube was capped, and the reaction was heated to 65 °C for 2 days. The green reaction mixture was then filtered through a pad of Celite, and the solvent was removed in vacuo. The resulting green tar was dissolved in CH_2Cl_2, and the organic layer was extracted with water. During the

Table 3. Crystallographic Data

	5a	**15**·0.5MeOH,1.7H_2O	**20a**	**20b**·CH_2Cl_2
formula	$C_{25}H_{41}N_5O_4$	$C_{48.50}H_{76}N_{10}O_{18.20}$	$C_{37}H_{47}CuN_5O_4$	$C_{38}H_{47}Cl_2CuN_5O_4$
fw	475.63	1096.40	689.34	772.25
space group	*Cc*	*P*1	*P*1	*P*1
cryst syst	monoclinic	triclinic	triclinic	triclinic
a (Å)	17.5675(7)	9.6559(2)	11.6459(3)	11.0870(3)
b (Å)	14.4967(5)	12.7467(3)	12.15910(10)	12.68930(10)
c (Å)	10.2831(4)	12.7602(3)	12.8298(3)	13.6631(3)
α (deg)	90	90.25(10)	72.12(10)	80.00(10)
β (deg)	102.12(10)	108.44(10)	85.22(10)	75.73(10)
γ (deg)	90	98.40(10)	71.91(10)	85.18(10)
V (Å^3)	2560.5(2)	1471.81(6)	a1643.36(6)	1832.86(7)
Z	4	1	2	2
D_{calcd} (Mg/m^3)	1.234	1.237	1.393	1.399
F(000)	1032	586	730	810
μ(Mo Kα) (mm^{-1})	0.085	0.095	0.714	0.789
temp (K)	298(2)	298(2)	173(2)	163(2)
no. of reflns collected	8292	9808	7579	8434
no. of unique reflns	5523	8008	4647	5184
R^a	$R1 = 0.0546$	$R1 = 0.0676$	$R1 = 0.0410$	$R1 = 0.0431$
$R_w{}^b$	$R_w2 = 0.1105$	$R_w2 = 0.1688$	$R_w2 = 0.0905$	$R_w2 = 0958$
GOF	0.984	0.983	1.030	1.052

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

extraction, the aqueous layer turned blue. The blue aqueous layers were combined, and the water was removed in vacuo. The resulting blue tar was recrystallized from CH_2Cl_2/hexanes to give 57 mg (0.082 mmol, 75%) of separate green and blue crystals. UV/vis: (MeOH, blue solution) λ 339, 658 nm; (CH_2Cl_2, green solution) λ 368, 659 nm. FAB mass spectrum: *m*/*z* 689.2 (M + 1). IR (neat): ν 1573 (C═O) cm^{-1}. The structures of **20a** and **20b** were determined by X-ray analysis, and the results of the studies are presented in the Supporting Information. Crystallographic data for **5a**, **15**·0.5MeOH·1.7H_2O, **20a**, and **20b**·CH_2Cl_2 are given in Table 3.

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Supporting Information Available: Tables of crystal data, structure solutions and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **5a**, **15**, **20a**, and **20b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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