Acid-Catalyzed Rearrangements between Cyclic Oligomers of 3,4-Dihydro-2*H*-1,5-benzodiazocine. Crystal and Molecular Structures of Mono- and Dinuclear Copper(II) Complexes of Tetraaza (16-Membered), Hexaaza (24-Membered), and Octaaza (32-Membered) Macrocycles

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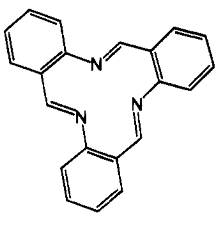
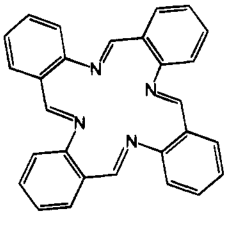
Propylene-1,3-diamine and 2-chlorobenzaldehyde react together in the presence of copper and formic acid to produce the 32-membered octaaza−tetraimine macrocycle 7,8,16,17,18,27,28,36,37,38-decahydrotetrabenzo[*g*,*o*,*w*,*aw*][1,5,9,13,17,21,25,29]octaazacyclodotriacontine (**8**) in 26% yield. Reduction of **8** with cyanoborohydride in acetic acid−methanol produces the corresponding 32-membered octaaza−octaamine 7,8,9,10,16,17,18,19,20,27,28,29,30,36,37,38,39,40-octadecahydrotetrabenzo[*g*,*o*,*w*,*ae*][1,5,9,13,17,21,25,29]octaazacyclodotriacontine (**9**). In chloroform **8** rearranges into an equilibrium mixture of the 16-membered cyclic tetraaza−diimine 5,7,8,16,17,18-pentahydrodibenzo[*g*,*o*][1,5,9,13]tetraazacyclotetradecine (**4**) and the 24-membered hexaaza−triimine 7,8,16,17,18,27,28-heptahydrotribenzo[*g*,*o*,*w*][1,5,9,13]hexaazacyclotetracosine (**6**). The macrocycle **4** was separated as its nickel(II) thiocyanate derivative and subsequently displaced with cyanide. Reduction of **4** with cyanoborohydride afforded the 16-membered tetraaza−tetraamine 7,8,9,10,16,17,18,19,20-nonahydrodibenzo[*g*,*o*][1,5,9,13]tetrazacyclotetradecine (**5**). The hexaaza−triimine **6** was trapped by precipitation, isolated by fractional crystallization, and subsequently converted into the 24-membered hexaaza−hexaamine 7,8,9,10,16,17,18,19,20,27,28,29,30-tridecahydrotribenzo[*g*,*o*,*w*][1,5,9,13,17,21]hexaazacyclotetracosine (**7**) by reduction with cyanoborohydride. The structures of the paramagnetic salts $[Cu_2(\mathbf{9})](CF_3SO_3)_4{\cdot}3H_2O$ and $[Cu(\mathbf{7}\text{-}H)](CF_3SO_3)_3{\cdot}MeOH{\cdot}2H_2O$ have been determined. Data for $[Cu_2(\mathbf{9})](CF_3SO_3)_4{\cdot}3H_2O$: space group $P2_1/n$, $a = 14.940(3)$ Å, $b = 9.825(2)$ Å, $c = 20.456(2)$ Å, $\beta = 97.58(1)°$, $R = 0.058$, $R_w = 0.064$. Data for $[Cu(\mathbf{7}\text{-}H)](CF_3SO_3)_3{\cdot}MeOH{\cdot}2H_2O$: space group $P1$ (No. 2), $a = 11.509(3)$ Å, $b = 12.172(3)$ Å, $c = 18.129(4)$ Å, $\alpha = 82.23°$, $\beta = 83.58°$, $\gamma = 72.47°$, $Z = 2$, $R = 0.059$, $R_w = 0.069$. The copper ions in each structure have regular square-planar geometries.

Introduction

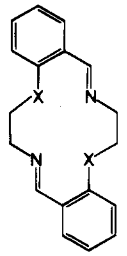
Syntheses of macrocyclic aza−imines are generally brought about by metal-template Schiff-base condensations.[1] In the self-condensation of 2-aminobenzaldehyde in the presence of nickel(II), the products are the nickel(II) complexes of the 16-membered cyclic tetraimine tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecine (TAAB) and the 12-membered triimine tribenzo[*b*,*f*,*j*][1,5,9]triazacycloduodecine (TRI).[2] The polycyclic bis- and tris-anhydro-oligomers formed by the self-condensation of 2-aminobenzaldehyde in the absence of metal ions rearrange in the presence of nickel(II) to produce the complexes of TAAB and TRI.[3,4] The diimines **1** (where X = CH_2,[5] S,[6] O,[7] or AsMe[8]) can also be synthesized in high yields in the absence of metal ions. In each case the 14-membered *trans*-diimines spontaneously rearrange into the corresponding more stable 7-membered monoimines **2** in the presence of traces of acid.



TRI



TAAB



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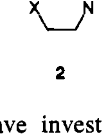

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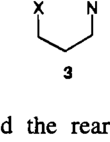

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Recently we have investigated the rearrangement of the tetraaza macrocycle **1** (where X = NH[9]) in chloroform.[10] This compound also rearranges under acidic conditions, but unlike

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⊗ Abstract published in *Advance ACS Abstracts*, November 1, 1994.

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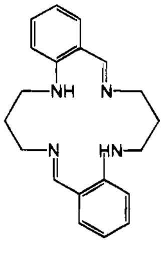
its congeners, the 14-membered tetraaza–diimine macrocycle is the more stable species at equilibrium and the 7-membered monoimine **2** can be isolated as the kinetic product only.

In the case of the 8-membered benzodiazocine **3**, although the 16-membered tetraaza–diimine **4** is reported to be the more stable product,[9] we find the equilibrium also involves the 24-membered hexaaza–triimine **6** and the 32-membered octaaza–tetraimine **8** in the presence of acid, with **8** being the least soluble and most readily isolated product. We report here details for the isolation of the cyclic oligomers **4**, **6**, and **8** and their reduction products, the corresponding polyaza–amines **5**, **7**, and **9**; the isolation and structural characterization of the copper(II) complexes of **5**, **7**, and **9** are also described.



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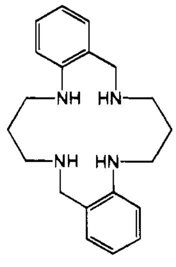

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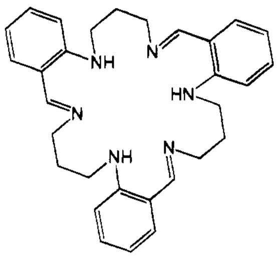

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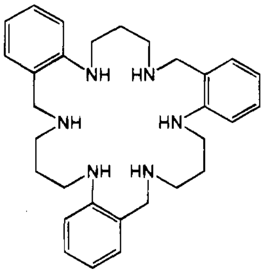

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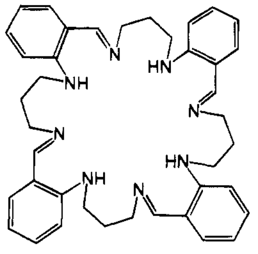

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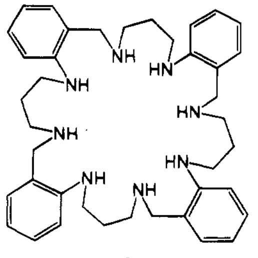

9

Results and Discussion

Syntheses of Imino Ligands 4, 6, and 8. The reaction of 2-chlorobenzaldehyde with propylene-1,3-diamine in boiling toluene in the presence of copper powder and formic acid, according to the method given in ref 9, afforded an orange oil that was not amenable to crystallization. The oil, when dissolved in ethanol and diluted with diethyl ether, however, gave a solution from which the octaaza–tetraimine macrocycle **8** began to crystallize after 3–4 days; after 1 month the yield of **8** was 26%. The crude product was purified by Soxhlet extraction into chloroform whereupon fine needles of the pure material having mp 252–254 °C were obtained. The mass spectrum of this solid contained a prominent peak at *m/e* 640.3 amu consistent with the tetrameric structure. It was further characterised by reduction to the corresponding octaaza–octaamine **9**.

The tetraimine **8** is poorly soluble in most solvents, including dimethyl sulfoxide, but a sample of sufficient concentration in chloroform-d_1 was obtained for NMR spectroscopy. The ^{1}H NMR spectrum of **8** in this solvent displays a weak but distinctive azamethine resonance at δ 8.20, as well as sets of multiplets for the aromatic and aliphatic protons. Over 1–2 days in chloroform-d_1, the azamethine signal at δ 8.20 for **8** decreased in intensity and was replaced by similar signals at δ 8.24 (80%) and δ 8.38 (20%). Over the same period the propylene proton multiplets of **8** were replaced by new sets of multiplets of similar profile. However, removal of solvent from the solution after rearrangement regenerated **8**. Gas chromatography/mass spectral (GC/MS) experiments on chloroform-d_1 solutions of **8** indicated that if tested within 5 min of preparation, solutions contained extremely small quantities of the monomer **3** and dimer **4** in almost equal amounts. After being stood for 3–4 h, the same solutions contained **4** in substantially increased amounts as the predominant species detected. The tetramer was not observed by this technique.

These experiments suggested that, upon dissolution in chloroform, **8** commenced a rearrangement into two cyclic oligomers with ^{1}H NMR azamethine resonances at δ 8.24 and δ 8.38 and that one of these was the dimer **4** while the other was not observed by GC/MS; the rearrangement appeared to involve the intermediacy of barely detectable amounts of the monomer **3**. These conclusions were validated by the isolation of the oligomers **4** and **6** as described below and confirmation that their ^{1}H NMR azamethine resonances appeared at δ 8.24 (**4**) and δ 8.38 (**6**) in chloroform-d_1; the propylene proton resonances were similarly consistent with those obtained after the monitored rearrangement of **8**.

A sample of **8** was extracted into chloroform, and the solution was stood for 3 days, whereafter it was carefully concentrated and added to a large volume of *n*-heptane. This led to the precipitation of the two lower oligomers predominantly. The ^{1}H NMR spectrum of the precipitate, taken immediately after dissolution in chloroform-d_1, indicated **4**:**6**:**8** = 70:25:5, according to the intensities of the azamethine resonances. Careful fractional recrystallization of the precipitate from dichloromethane–diethyl ether, under acid-free conditions, gave first

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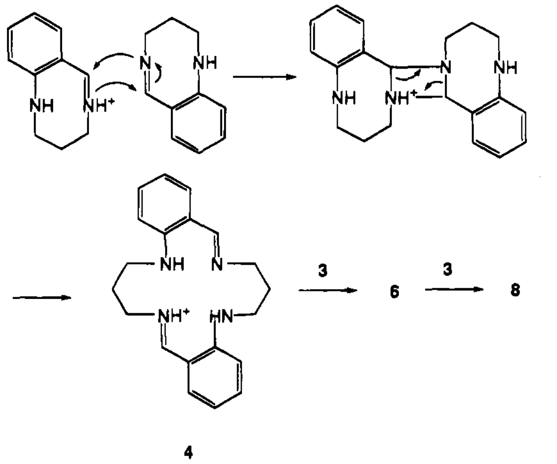
Scheme 1



a small quantity of **8**, but then pure **6** was obtained. This was characterized by reduction to the corresponding hexaaza–hexaamine **7**. The tetraaza–diimine **4** was isolated from the original extract by treatment with aqueous nickel(II) chloride containing potassium thiocyanate. The addition of the metal salts led to selective precipitation of microcrystalline [Ni(**4**)]-$(SCN)_2$ from which the ligand was liberated with cyanide and extracted into dichloromethane. Incidentally, cyanide appeared to be an effective proton scavenger and minimized rearrangement of the oligomers in dichloromethane.

Chloroform solutions of **4** or **6** spontaneously, and rapidly, precipitated **8** when concentrated. All rearrangements occurred in the absence of metal ions and were accelerated by an increase in trace acidity, indicating that **3**, **4**, **6**, and **8** exist simultaneously in a facile acid-catalyzed equilibrium in solution.

As suggested for the acid-catalyzed rearrangement between 4,5-dihydro-3*H*-2-benzazepine and its dimer,[5] and related molecules,[6-8] a stepwise mechanism involving 1,3-diazetidine intermediates is suggested for rearrangements between **4**, **6**, and **8** (Scheme 1). The direct dimerization of **4** to **6** by this mechanism is also possible.

Synthesis of Amino Ligands 5, 7, and 9. The addition of a 1:1 mixture of acetic acid–methanol to a mixture of $Na(CN)BH_3$ and **4**, **6**, or **8**, followed by neutralization with saturated NaOH solution, produced high yields of the amino ligands **5**, **7**, and **9**, respectively. The amino ligands are strongly basic, especially **5**. In the reduction of **4** below 5 °C, the tetraacetic acid salt **5**·4HAc crystallized from the reaction mixture during the neutralization step and could be extracted into dichloromethane from which it was subsequently isolated by the addition of diethyl ether. At 30–40 °C, the diacetic acid salt **5**·2HAc precipitated during the neutralization step and was extracted into dichloromethane and isolated by concentration and the addition of diethyl ether. Both salts afforded the free amine **5** upon neutralization and extraction into dichloromethane or precipitation of [Ni(**5**)]$(SCN)_2$ followed by liberation with cyanide. Thermal decomposition of the acetic acid salts at 120–130 °C (0.1 mmHg) also yielded the tetraamine **5**, which formed colorless crystals from methanol.

Copper(II) Triflates of the Amino Ligands 5, 7, and 9. The addition of copper(II) triflate in methanol to the amino ligands **5**, **7**, or **9** in dichloromethane produced deep green solutions from which the respective copper(II) complexes were isolated in high yield. For **5** and **7**, 1 equiv of copper(II) triflate afforded the complexes [Cu(**5**)]$(CF_3SO_3)_2$ and [Cu(**7**-H)]$(CF_3SO_3)_3$·MeOH·$2H_2O$; the octaaza–tetraamine **9** sequestered 2 equiv of copper(II) triflate to form the dinuclear complex [Cu_2(**9**)]$(CF_3SO_3)_4$, which was isolated as the trihydrate. Each complex was paramagnetic having a moment consistent with regular square-planar geometries around the copper ions.[11] As expected the complexes each exhibited broad electronic transitions due to d–d transitions in the region of 650 nm.[12]

Table 1. Crystal Parameters and Experimental Data for X-ray Diffraction Measurements on [Cu_2(9)]$(CF_3SO_3)_4$·$3H_2O$ and [Cu(7-H)]$(CF_3SO_3)_3$·MeOH·$2H_2O$[a]

	[Cu_2(**9**)]$(CF_3SO_3)_4$· $3H_2O$	[Cu(**7**-H)]$(CF_3SO_3)_3$· MeOH·$2H_2O$
empirical formula	$C_{44}H_{56}Cu_2F_{12}N_8O_{15}S_4$	$C_{34}H_{51}CuF_9N_6O_{12}S_2$
fw	1420.28	1066.52
cryst dimens, mm	0.10 × 0.09 × 0.20	0.10 × 0.20 × 0.09
lattice type	primitive	primitive
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	14.940(3)	11.059(3)
b, Å	9.825(2)	12.172(3)
c, Å	20.456(2)	18.129(4)
α, deg	90.00	82.23(2)
β, deg	97.58(1)	83.58(2)
γ, deg	90.00	72.47(2)
V, Å^3	2976.3(8)	2299.2(10)
Z	2	2
ϱ_{calcd}, gcm^{-3}	1.585	1.54
$F(000)$	1452.00	1102.0
μ, cm^{-1}	31.41	28.4
data collcn instrum	Rigaku AFC6R	Rigaku AFC6R
radiation (graphite monochromated)	Cu Kα	Cu Kα
λ (radiation), Å	1.541 78	1.541 78
T, °C	23	23
transmissn factors	0.63–0.78	0.68–0.82
R, R_w[b]	0.058, 0.064	0.059, 0.069

[a] The estimated standard deviation in the least significant digit is shown in parentheses for each entry in this and subsequent tables. [b] $R = (\sum|F_o| - |F_c|)/\sum|F_o|)$; $R_w = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$.

Crystal and Molecular Structures: [Cu_2(9)]$(CF_3SO_3)_4$·$3H_2O$ and [Cu(7-H)]$(CF_3SO_3)_3$·MeOH·$2H_2O$. Crystal data, information relating to data collection, and refinement details for [Cu_2(**9**)]$(CF_3SO_3)_4$·$3H_2O$ and [Cu(**7**-H)]$(CF_3SO_3)_3$·MeOH·$2H_2O$ are given in Table 1. Important bond distances are given in Table 2, and atomic coordinates for the two compounds are given in Table 3 and 4, respectively. Complete data are available as supplementary material.

The molecular structure of the dinuclear complex [Cu_2(**9**)]$(CF_3SO_3)_4$·$3H_2O$ is shown in Figure 1. The dinuclear cation has a center of symmetry with a water-*O* atom having half-occupancy near the inversion center. The copper ions in the complex are each located in approximately square-planar coordination environments; there is tetrahedral distortion around each copper with N(1) and N(3) lying slightly below the plane [0.026(7) and 0.027(4) Å, respectively] and N(2) and N(4) slightly above the plane [0.031(5) and 0.027(4) Å, respectively]. The Cu–N distances range between 2.026 and 2.100 Å and are similar to those found in [Cu(**7**-H)]$(CF_3SO_3)_3$·MeOH·$2H_2O$ (see below) which are typical for copper(II)–amine complexes. The Cu–Cu distance in the complex is 6.912(1) Å. The aromatic rings of the ligand alternate above and below the plane in the centrosymmetric structure. The pairwise arrangement of the N*H* atoms in the structure gives two copper units of opposite helicity in the centrosymmetric dimer.

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Table 2. Selected Bond Lengths and Angles

$[Cu_2(\mathbf{9})](CF_3SO_3)_4\cdot 3H_2O$		$[Cu(\mathbf{7}\text{-H})](CF_3SO_3)_3\cdot MeOH\cdot 2H_2O$	
	Bond Lengths (Å)		
Cu(1)−N(1)	2.100(4)	2.088(9)	Cu(1)−N(1)
Cu(1)−N(2)	2.026(4)	2.023(7)	Cu(1)−N(2)
Cu(1)−N(3)	2.089(4)	2.069(9)	Cu(1)−N(3)
Cu(1)−N(4)	2.042(4)	2.019(7)	Cu(1)−N(4)
	Bond Angles (deg)		
N(1)−Cu(1)−N(2)	91.8(2)	92.6(3)	N(1)−Cu(1)−N(2)
N(1)−Cu(1)−N(4)	90.5(2)	90.5(3)	N(1)−Cu(1)−N(4)
N(1)−Cu(1)−N(3)	173.0(2)	84.2(3)	N(1)−Cu(1)−N(3)
N(2)−Cu(1)−N(4)	175.7(2)	175.6(3)	N(2)−Cu(1)−N(4)
N(2)−Cu(1)−N(3)	85.2(2)	84.2(3)	N(2)−Cu(1)−N(3)
N(3)−Cu(1)−N(4)	92.1(2)	92.8(3)	N(3)−Cu(1)−N(4)
Cu(1)−N(1)−C(1)	115.2(3)	113.6(6)	Cu(1)−N(1)−C(1)
Cu(1)−N(3)−C(10)	110.5(3)	112.4(7)	Cu(1)−N(3)−C(10)
Cu(1)−N(4)−C(18)	116.4(3)	114.8(5)	Cu(1)−N(4)−C(18)
Cu(1)−N(1)−C(20)	114.5(3)	112.9(6)	Cu(1)−N(1)−C(30)
Cu(1)−N(2)−C(7)	115.2(3)	117.0(6)	Cu(1)−N(2)−C(7)
Cu(1)−N(4)−C(17)	109.3(3)	111.4(6)	Cu(1)−N(4)−C(17)
C(18)−C(10)−C(20)	115.1(5)	109.8(7)	C(18)−C(19)−C(20)
N(4)−C(18)−C(19)	114.6(5)	115.1(7)	N(4)−C(18)−C(19)

Table 3. Atomic Coordinates and Isotropic Displacement Parameters for $[Cu_2(\mathbf{9})](CF_3SO_3)_4\cdot 3H_2O$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu(1)	0.60585(5)	0.07471(8)	0.36395(4)	3.54(4)
N(1)	0.4696(3)	0.1006(4)	0.3764(2)	3.5(2)
N(2)	0.5990(3)	0.2265(5)	0.2964(2)	3.7(2)
N(3)	0.7357(3)	0.0420(4)	0.3397(2)	3.5(2)
N(4)	0.6158(3)	−0.0877(5)	0.4268(2)	3.4(2)
C(1)	0.4104(4)	0.1397(6)	0.3175(3)	3.8(3)
C(2)	0.3327(4)	0.0676(7)	0.2980(3)	5.0(3)
C(3)	0.2753(5)	0.1076(9)	0.2433(4)	6.8(4)
C(4)	0.2959(5)	0.218(1)	0.2073(4)	7.5(5)
C(5)	0.3752(5)	0.2890(8)	0.2251(3)	5.9(4)
C(6)	0.4338(4)	0.2498(7)	0.2803(3)	4.3(3)
C(7)	0.5212(4)	0.3228(6)	0.2972(3)	4.5(3)
C(8)	0.6048(4)	0.1740(6)	0.2293(3)	4.2(3)
C(9)	0.6985(4)	0.1186(6)	0.2232(3)	4.2(3)
C(10)	0.7316(4)	0.0043(6)	0.2689(3)	4.0(3)
C(11)	0.7992(4)	−0.0446(6)	0.3814(2)	3.3(2)
C(12)	0.8901(4)	−0.0108(6)	0.3917(3)	4.3(3)
C(13)	0.9508(4)	−0.0944(7)	0.4290(3)	4.8(3)
C(14)	0.9213(4)	−0.2092(7)	0.4563(3)	5.0(3)
C(15)	0.8315(4)	−0.2429(6)	0.4464(3)	4.1(3)
C(16)	0.7684(4)	−0.1611(5)	0.4085(2)	3.2(2)
C(17)	0.6707(4)	−0.1972(6)	0.4001(3)	3.7(3)
C(18)	0.6481(4)	−0.0580(6)	0.4975(3)	4.0(3)
C(19)	0.6383(4)	−0.1764(6)	0.5445(3)	4.5(3)
C(20)	0.5457(4)	−0.1904(6)	0.5669(3)	4.3(3)

[a] $B_{eq} = (8/3)\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

The geometry around the copper ion in $[Cu(\mathbf{7}\text{-H})](CF_3SO_3)_3\cdot MeOH\cdot 2H_2O$ is approximately square-planar with N(1) and N(3) having distances of 0.038(7) and 0.045(7) Å below the coordination plane, respectively; for N(2) and N(4) the distances are respectively 0.041(7) and 0.040(7) Å above the plane (Figure 2). The Cu−N bond distances range between 2.019(7) and 2.088(9) Å with the *N* atoms of the chiral amine-*N* stereocenters at the end of the loop being arranged syn to one another and anti to the inner pair of coordinated *N* atoms. Polyaza macrocycles are spontaneously protonated in solutions containing water, which substantially decreases rates of metal chelation.[1] In the present system it is likely that the proton is delocalized between the free amino groups of the ligand in solution. In the solid state there is no evidence of association of the proton with one or the other of the uncoordinated amino groups, however.

Table 4. Atomic Coordinates and Isotropic Displacement Parameters for $[Cu(\mathbf{7}\text{-H})](CF_3SO_3)_3\cdot MeOH\cdot 2H_2O$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu(1)	0.2498(1)	−0.0871(1)	0.20326(7)	4.40(4)
N(1)	0.1707(7)	−0.1873(6)	0.1494(4)	4.4(2)
N(2)	0.2311(7)	0.0370(6)	0.1156(4)	4.3(2)
N(3)	0.3220(7)	0.0210(6)	0.2526(5)	5.3(2)
N(4)	0.2822(7)	−0.2104(6)	0.2912(4)	4.3(2)
N(5)	0.0148(7)	−0.3781(6)	0.3920(4)	4.9(2)
N(6)	−0.0997(7)	−0.3570(7)	0.2426(4)	5.5(2)
C(1)	0.2078(8)	−0.1862(9)	0.0692(5)	4.3(3)
C(2)	0.2544(10)	−0.2886(9)	0.0411(7)	6.0(3)
C(3)	0.287(1)	−0.290(1)	−0.351(7)	7.1(4)
C(4)	0.273(1)	−0.188(1)	−0.0799(6)	7.2(4)
C(5)	0.2288(10)	−0.0857(10)	−0.0504(6)	5.5(3)
C(6)	0.1941(9)	−0.828(9)	0.0256(6)	4.6(3)
C(7)	0.1489(9)	0.0327(9)	0.0569(5)	5.3(3)
C(8)	0.3555(10)	0.0472(8)	0.0832(5)	5.5(3)
C(9)	0.419(1)	0.0962(9)	0.1333(6)	6.8(3)
C(10)	0.440(1)	0.0374(9)	0.2118(6)	6.8(3)
C(11)	0.3344(9)	0.0007(10)	0.3328(5)	4.8(3)
C(12)	0.309(1)	0.0976(10)	0.3701(7)	6.7(4)
C(13)	0.322(1)	0.081(1)	0.4472(8)	8.6(5)
C(14)	0.361(1)	−0.033(1)	0.4819(7)	8.0(4)
C(15)	0.386(1)	−0.125(1)	0.4453(7)	6.4(4)
C(16)	0.3730(9)	−0.1111(10)	0.3698(6)	5.2(3)
C(17)	0.3980(9)	−0.2136(8)	0.3277(5)	4.8(3)
C(18)	0.1691(9)	−0.2094(8)	0.3444(5)	4.9(3)
C(19)	0.1915(9)	−0.3063(8)	0.4093(5)	4.7(3)
C(20)	0.0654(10)	−0.3230(8)	0.4423(5)	5.7(3)
C(21)	−0.1006(10)	−0.4049(8)	0.4130(6)	5.0(3)
C(22)	−0.170(1)	−0.3817(9)	0.4797(6)	6.0(3)
C(23)	−0.287(1)	−0.404(1)	0.4948(6)	6.7(4)
C(24)	−0.334(1)	−0.450(1)	0.4455(8)	7.1(4)
C(25)	−0.265(1)	−0.4765(9)	0.3803(7)	6.7(4)
C(26)	−0.1498(10)	−0.4543(8)	0.3626(6)	5.0(3)
C(27)	−0.0822(10)	−0.4758(8)	0.2870(6)	5.6(3)
C(28)	−0.016(1)	−0.3573(9)	0.1730(6)	6.2(3)
C(29)	−0.0333(9)	−0.2382(9)	0.1326(5)	5.9(3)
C(30)	0.0259(9)	−0.1574(8)	0.1642(5)	5.3(3)

[a] $B_{eq} = (8/3)\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Single crystals of $[Cu(\mathbf{5})](CF_3SO_3)_2$ were isolated from various solvent mixtures but were found to be twinned in every case. Refinement of X-ray data corrected on this compound to *R* = 0.20 revealed approximately square-planar coordination of the ligand around the centrosymmetrical copper(II) ion (Figure 3).

Experimental Section

^1H NMR and ^{13}C spectra were recorded at 20 °C on a Varian Gemini 300 spectrometer operating at 299.96 MHz. Chemical shifts are quoted as δ values in chloroform-d_1 relative to internal Me_4Si unless otherwise stated. Magnetic moments were measured with a Princeton Applied Research vibrating magnetometer (Model 155) at 10 kG and 20 °C. Corrections for diamagnetism and temperature independent paramagnetism were made. Infrared spectra were recorded on a Perkin-Elmer Model 1800 FTIR spectrometer. Elemental analyses and molecular weight measurements were performed by the staff within the Research School of Chemistry. The names of the macrocycles are consistent with Chemical Abstracts nomenclature.

7,8,16,17,18,27,28,36,37,38-Decahydrotetrabenzo[*g*,*o*,*w*,*aw*][1,5,9,13,17,21,25,29]octaazacyclodotriacontine−0.3-Water ($\mathbf{8}\cdot 0.3H_2O$). *Caution*: *2-Chlorobenzaldehyde is an extreme irritant which may be harmful by inhalation or skin absorption.* A mixture of propane-1,3-diamine (126.4 g, 6-fold excess), formic acid (4.5 mL), and copper powder (18.0 g, 0.284 g atom) was heated under reflux in toluene (300 mL) for 30 min. To this mixture, under reflux, a solution of 2-chlorobenzaldehyde (40.0 g, 0.284 mol) in toluene (150 mL) was slowly added over 4 h (directly into the reaction mixture via a second condenser with maintainence of a slow flow of inert gas in the direction

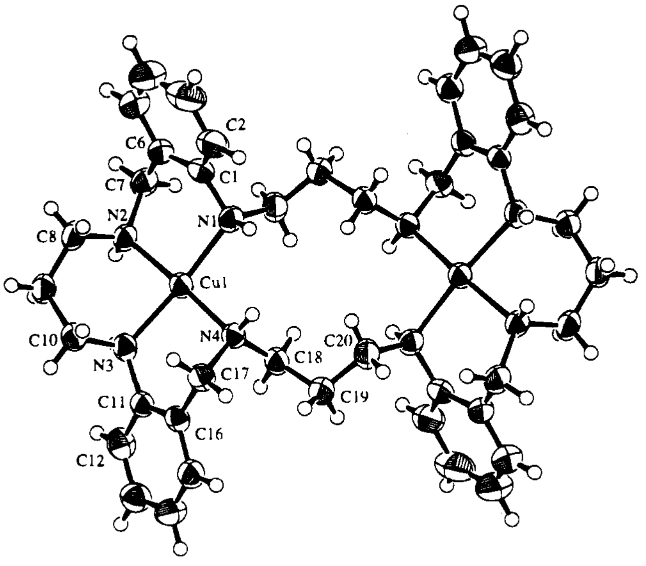

Figure 1. ORTEP view of $[Cu_2(\mathbf{9})](CF_3SO_3)_4{\cdot}3H_2O$ showing the atom-labeling scheme for non-hydrogen atoms in the centrosymmetrical dimer. Thermal ellipsoids enclose 50% probability levels.

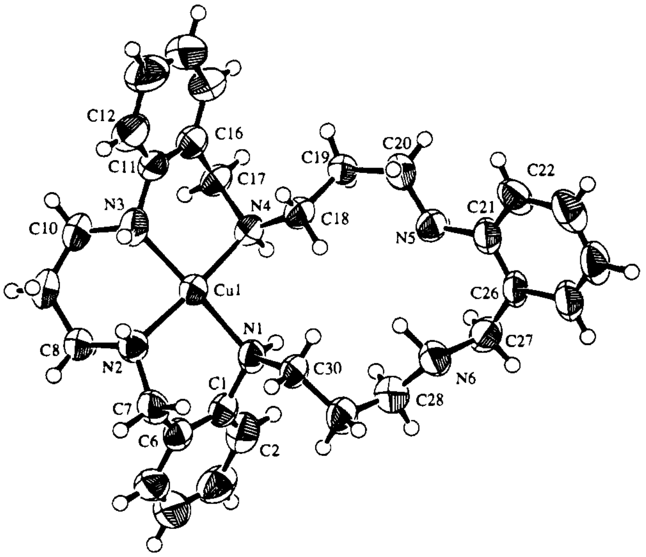

Figure 2. ORTEP view of $[Cu(\mathbf{7}\text{-H})](CF_3SO_3)_3{\cdot}MeOH{\cdot}2H_2O$ showing the atom-labeling scheme for non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels.

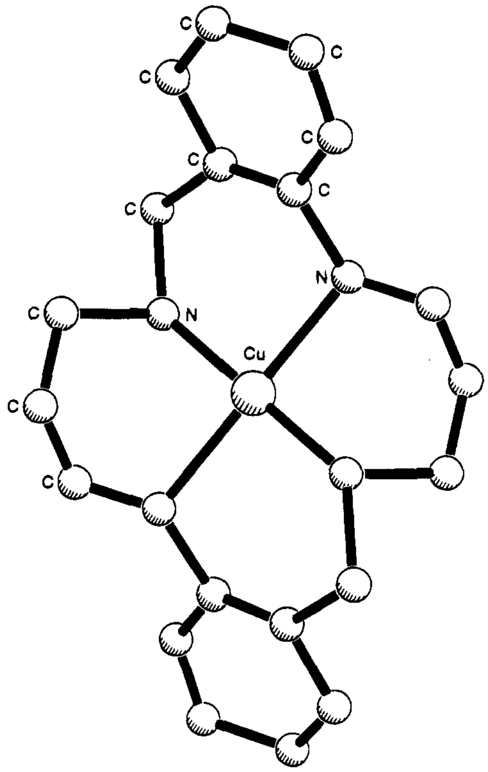

Figure 3. Perspective view of the cation of $[Cu(\mathbf{5})](CF_3SO_3)_2$ refined to $R = 0.20$.

of the falling drops to prevent condensation of the aldehyde with the diamine in the vapor phase). The mixture was then heated under reflux for 12 h. The unreacted copper was removed by filtration from the hot solution, and the upper yellow and lower blue layers were separated. The lower layer was extracted with toluene, and the combined organic fractions were then washed with water, dried over $MgSO_4$, and evaporated under reduced pressure to yield an orange oil. The oil was taken up in a small quantity of ethanol, to which diethyl ether or water was added. The crude product began to separate as a colorless precipitate after 3–4 days and continued to precipitate over several months. Yield: ca. 4.5 g after 1 week; 12 g after 1 month. The material was collected and washed with 20 mL portions of methanol, diethyl ether, and *n*-pentane. Additional product precipitated from the washings. The crude product was purified by extraction into a small volume of chloroform in a Soxhlet apparatus whereupon the pure product crystallized as whispy, colorless needles with 0.3 water of crystallization after drying for 2 h at 200 °C and 0.1 mmHg: mp 252–254 °C. Anal. Calcd for $C_{40}H_{48}N_8{\cdot}0.3H_2O$: C, 74.3; H, 7.6; N, 17.3. Found: C, 74.4; H, 7.5; N, 17.3. ^1H NMR: δ 1.60 (b, 0.3 H_2O), 1.97 (t, 8 H, $^3J_{HH} = 5.1$ Hz, $C-CH_2-C$), 3.26 (t, 8 H, $^3J_{HH} = 5.1$ Hz, $-CH_2-$), 3.55 (t, 8 H, $^3J_{HH} = 5.1$ Hz, $-CH_2-$), 5.59 (m, 4 H, Ar H), 6.65 (m, 4 H, Ar H), 7.15 (m, 4 H, Ar H), 7.25 (m, 4 H, Ar H), 8.20 (s, 4 H, ArCH=N), 9.17 (b, 4 H, NH). Mass spectrum (*m/e*): 640.3, $[M]^+$. IR (KBr disk): 1631 cm^{-1} ($\nu_{C=N}$).

7,8,9,10,16,17,18,19,20,27,28,29,30,36,37,38,39,40-Octadecahydrotetrabenzo[*g,o,w,ae*][1,5,9,13,17,21,25,29]octaazacyclo-dotriacontine (9). A mixture of the tetraimine **8** (5.0 g, 7.8 mmol) and $Na(CN)BH_3$ (3.9 g, 62.0 mmol) was treated with a mixture of anhydrous acetic acid–methanol (1:1, 500 mL). Hydrogen was evolved as the solids dissolved to give a pale yellow solution. After 1 h the solution was cooled to 0 °C and saturated sodium hydroxide solution (500 mL) was slowly added. The mixture was then extracted with dichloromethane (3 × 100 mL), and the extract was dried over $MgSO_4$. Concentration *in vacuo* left a pale yellow oil. Addition of dichloromethane–diethyl ether to the oil produced the amine as colorless microcrystals: mp 139–140 °C; yield 4.80 g (95%). Anal. Calcd for $C_{40}H_{56}N_8$: C, 74.0; H, 8.7; N, 17.3. Found: C, 74.4; H, 9.0; N, 17.2. ^1H NMR: δ 1.80 (q, 8 H, $^3J_{HH} = 7.1$ Hz, $C-CH_2-C$), 2.65 (t, 8 H, $^3J_{HH} = 7.1$ Hz, $-CH_2-$), 3.10 (t, 8 H, $^3J_{HH} = 7.1$ Hz, $-CH_2-$), 3.73 (s, 8 H, $Ar-CH_2-N$), 6.60 (m, 8 H, Ar H), 6.90 (d, 4 H, $^2J_{HH} = 7.1$ Hz, Ar H), 7.13 (m, 4 H, Ar H). ^{13}C NMR: δ 29.72, 41.39, 47.07, 53.75, 109.88, 115.95, 123.56, 128.47, 129.57, 148.46. Mass spectrum (*m/e*): 648.6, $[M]^+$. Molecular weight (osmometry in CH_2Cl_2): calcd (found) 648.9 (652). IR (KBr disk): 3249 cm^{-1} (ν_{NH}).

5,7,8,16,17,18-Pentahydrodibenzo[*g,o*][1,5,9,13]tetraazacyclotetradecine (4). Crude **8** (5.0 g) was extracted into chloroform (250–300 mL, Soxhlet apparatus) over 3 days; the extract was filtered and heated under reflux for a further 2 days. The solution was then reduced in volume to ca. 30 mL *in vacuo*, being careful to avoid crystallization, and the concentrated solution was slowly poured into *n*-heptane (250 mL) with vigorous stirring. The mixture was concentrated to half-volume, and additional *n*-heptane (150 mL) was added. This solution was reduced to dryness, and the residue was redissolved in dry dichloromethane (100 mL). The solution, including some undissolved solid, was stirred briefly with a solution of sodium cyanide (3 g) in water (40 mL). The organic layer was separated, filtered (to remove **8**), and added to a solution of nickel(II) chloride (3.70 g) and potassium thiocyanate (3.0 g) in methanol–water (1:1, 30 mL). The brown microcrystalline complex $[Ni(\mathbf{7})(NCS)_2]$ was collected (4.35 g). The filtrate was retained for use in the preparation of **9**. After being washed with methylene chloride and diethyl ether, the solid was suspended in dichloromethane (60 mL) and stirred overnight with a solution of sodium cyanide (5 g) in water (60 mL), during which time the solid dissolved. The aqueous layer was separated and washed with dichloromethane. The combined organic fractions were washed with water, dried over $MgSO_4$, and concentrated. Upon the addition of diethyl ether to the concentrate the product crystallized as colorless needles. Successive recrystallizations did not significantly improve the melting point of the material (120−140 °C), although analytical and spectroscopic data indicated high purity. Filtration through a short column of silica gel (activity I) using diethyl ether as eluent produced a sample having mp 236−238 °C (lit.[9] mp 236−238 °C), yield 2.53 g (90%). Anal. Calcd for $C_{20}H_{24}N_4$: C, 75.0; H, 7.6, N: 17.5. Found: C, 74.9; H, 7.7; N, 17.3. ^{1}H NMR: δ 2.17 (m, 4 H, C−CH_2−C), 3.36 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, −CH_2−), 3.72 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, −CH_2−), 6.59 (m, 4 H, Ar H), 7.08 (m, 2 H, Ar H), 7.20 (m, 2 H, Ar H), 8.24 (s, 2 H, ArCH=N−), 9.02 (b, 4 H, NH). ^{13}C NMR: δ 29.73, 42.46, 62.33, 109.55, 113.83, 131.18, 134.04, 149.00, 164.20. Mass spectrum (*m*/*e*): 320.2, $[M]^+$. Molecular weight (osmometry in CH_2Cl_2): calcd (found); 320.4 (321). IR (KBr disk): 1632 cm^{-1} ($\nu_{C=N}$).

7,8,9,10,16,17,18,19,20-Nonahydrodibenzo[*g*,*o*][1,5,9,13]tetrazacyclotetradecine (5). Pure **4** (5.0 g) was mixed with Na(CN)BH_3 (3.92 g) and treated with anhydrous acetic acid−methanol (1:1, 500 mL) to produce a clear yellow solution. After I h the solution was cooled to 0 °C and saturated sodium hydroxide solution (500 mL) was slowly added. The nature of the product was dependent upon the temperature of the addition. For example, at temperatures below 5 °C the tetraacetic acid salt crystallized (along with sodium acetate) from the reaction mixture during the neutralization step; at 35−40 °C the diacetic acid salt crystallized. At higher temperatures the free amine was isolated. Extraction with dichloromethane (3 × 100 mL), drying of the extracts over $MgSO_4$, and concentration to a small volume followed by the addition of diethyl ether produced the respective products as colorless crystals. **5**: mp 103 °C; yield 4.75 g (94%). Anal. Calcd for $C_{20}H_{28}N_4$: C, 74.0; H, 8.7; N, 17.3. Found: C, 74.4; H, 9.3; N, 17.5. ^{1}H NMR: δ 1.78 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, C−CH_2−C), 2.72 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, −CH_2−), 3.16 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, −CH_2−), 3.73 (s, 4 H, Ar−CH_2−N), 6.58 (m, 4 H, Ar H), 7.00 (d, 2 H, $^2J_{HH}$ = 7.1 Hz, Ar H), 7.15 (m, 2 H, Ar H). ^{13}C NMR: δ 28.90, 42.46, 49.10, 54.44, 109.64, 115.46, 123.68, 128.42, 129.90, 148.20. Mass spectrum (*m*/*e*): 324.3, $[M]^+$. Molecular weight (osmometry in CH_2Cl_2): calcd (found) 324.47 (331). IR (KBr disk): 3324 cm^{-1} (ν_{NH}).

5·2HAc: mp 144−147 °C; yield 5.27 g (76%). Anal. Calcd for $C_{20}H_{28}N_4 \cdot 2CH_3CO_2H$: C, 64.8; H, 8.2; N, 12.6. Found: C, 64.5; H, 8.3; N, 12.4. ^{1}H NMR: δ 1.50 (s, 6 H, CH_3CO_2H), 2.12 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, C−CH_2−C), 3.18 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, −CH_2−), 3.32 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, −CH_2−), 3.94 (s, 4 H, Ar−CH_2−N), 6.64 (m, 4 H, Ar H), 7.04 (d, 2 H, $^2J_{HH}$ = 7.1 Hz, Ar H), 7.27 (m, 2 H, Ar H). ^{13}C NMR: δ 26.15, 42.37, 49.88, 51.66, 23.29, 111.10, 116.53, 130.51, 131.22, 146.94, 178.10.

5·4HAc: mp 130 °C; yield 6.78 g (77%). Anal. Calcd for $C_{20}H_{28}N_4 \cdot 4CH_3CO_2H$: C, 59.56; H, 7.9; N, 9.9. Found: C, 59.3; H, 7.8; N, 9.9. ^{1}H NMR: δ 1.75 (b, 12 H, CH_3CO_2H), 2.17 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, C−CH_2−C), 3.34 (t, 8 H, $^3J_{HH}$ = 5.1 Hz, Ar−CH_2−N and −CH_2−), 4.01 (t, 4 H, $^3J_{HH}$ = 5.1 Hz, −CH_2−), 6.64 (m, 4 H, Ar H), 7.05 (d, 2 H, $^2J_{HH}$ = 7.1 Hz, Ar H), 7.27 (m, 2 H, Ar H). ^{13}C NMR: δ 22.40, 25.40, 42.44, 50.10, 51.20, 111.50, 117.11, 130.90, 131.70, 147.00, 178.00.

7,8,16,17,18,27,28-Heptahydrotribenzo[*g*,*o*,*w*][1,5,9,13]hexaazacyclotetracosine−0.3-Water (6·0.3H_2O). The red dichloromethane filtrate from the separation of $[Ni(\mathbf{4})](SCN)_2$ in the preparation of **4** contained mainly **6**. The solution was concentrated to ca. 40 mL and stirred with sodium cyanide (2 g) in water (40 mL) for 2 h. The colorless organic layer was then separated, washed with water, dried over $MgSO_4$, and reduced to ca. 5 mL. The careful addition of diethyl ether to this solution produced **6** as colorless needles. After filtration, the remaining solution was concentrated and diethyl ether was added. Several successive crystallizations in this way produced a total of 0.53 g (ca. 30%) of **6**. Crystallizations were complete within 20−30 min of addition of the ether; longer periods produced material contaminated with 10−30% of **8**, whereas rapid recrystallizations led to contamination with **4**. The imine **6** crystallized with 0.3 water after drying for 2 h at 60 °C and 0.1 mmHg: mp 170−172 °C. Anal. Calcd for $C_{30}H_{36}N_6 \cdot 0.3H_2O$: C, 74.1; H, 7.6; N, 17.3. Found: C, 73.9; H, 7.6; N, 17.3. ^{1}H NMR: δ 1.60 (H_2O), 2.12 (t, 6 H, $^3J_{HH}$ = 7.1 Hz, −CH_2−), 3.32 (t, 6 H, $^3J_{HH}$ = 7.1 Hz, −CH_2−), 3.68 (t, 6H, $^3J_{HH}$ = 7.1 Hz, −CH_2−), 6.67 (m, 6 H, Ar H), 7.20 (m, 6 H, Ar H), 8.38 (s, 3 H, ArCH=N), 9.33 (b, 3 H, NH). ^{13}C NMR: δ 31.64, 40.56, 58.88,109.86, 114.10, 131.17, 133.63, 164.14. Mass spectrum (*m*/*e*): 480.2, $[M]^+$. Molecular weight (osmometry in CH_2Cl_2): calcd (found) 480.66 (485). IR (KBr disk): 1632 cm^{-1} ($\nu_{C=N}$).

7,8,9,10,16,17,18,19,20,27,28,29,30-Tridecahydrotribenzo[*g*,*o*,*w*]-[1,5,9,13,17,21]hexaazacyclotetracosine (7). Pure **6** (0.53 g) was mixed with Na(CN)BH_3 (0.42 g) and treated with anhydrous acetic acid−methanol (1:1, 53 mL). After 1 h the clear yellow solution was cooled to 0 °C and a saturated sodium hydroxide solution (53 mL) was slowly added. Extraction of the mixture with dichloromethane (3 × 75 mL), followed by drying of the extracts, and concentration of the solution to near dryness followed by addition of diethyl ether produced colorless crystals of the product: mp 140−142 °C; yield 0.50 g (93%). Anal. Calcd for $C_{30}H_{42}N_6$: C, 74.0; H, 8.7; N, 17.3. Found: C, 73.8; H, 8.9; N, 16.7. ^{1}H NMR: δ 1.82 (t, 6 H, $^3J_{HH}$ = 7.1 Hz, −CH_2−), 2.70 (t, 6 H $^3J_{HH}$ = 7.1 Hz, −CH_2−), 3.12 (t, 6 H, $^3J_{HH}$ = 7.1 Hz, −CH_2−), 3.79 (s, 6 H, Ar−CH_2−N), 6.60 (m, 6 H, Ar H), 6.95 (m, 3 H, Ar H), 7.17 (m, 3 H, Ar H). ^{13}C NMR: δ 29.72, 41.60, 46.61, 53.23, 109.94, 115.96, 123.34, 128.43, 129.54, 148.58. Mass spectrum (*m*/*e*): 486.4, $[M]^+$. Molecular weight (osmometry in CH_2Cl_2): calcd (found) 486.70 (479). IR (KBr disk): 3264 cm^{-1} (ν_{NH}).

[*SP*-4]-(7,8,9,10,16,17,18,19,20,27,28,29,30,36,37,38,39,40-Octadecahydrotetrabenzo[*g*,*o*,*w*,*ae*][1,5,9,13,17,21,25,29]octaazacyclodotriacontine-*N*^{5},*N*^{9},*N*^{15},*N*^{19},*N*^{25},*N*^{29},*N*^{35},*N*^{39})dicopper(II) Triflate−3-Water ($[Cu_2(\mathbf{9})](SO_3CF_3)_4 \cdot 3H_2O$) (10). A solution of **9** (0.40 g) in dichloromethane (5 mL) was added to a solution of copper(II) triflate (0.60 g) in methanol (0.5 mL). The green solution was stood in an open vessel overnight, yielding the product as blue microcrystals that were separated and washed with *n*-pentane. Yield: 0.75 g (94%). Anal. Calcd for $C_{44}H_{56}Cu_2F_{12}N_8O_{12}S_4 \cdot 3H_2O$: C, 37.1; H, 4.4; N, 7.9. Found: C, 37.2; H, 4.1; N, 7.7. Magnetic moment: $\mu_{eff} = 1.84\ \mu_B$ per Cu (25 °C). IR (KBr disk): 3242 cm^{-1} (ν_{NH}). Electronic spectrum (MeOH): 246, 248, 298, 400, 646 nm.

[*SP*-4]-(7,8,9,10,16,17,18,19,20,27,28,29,30-Tridecahydrotribenzo-[*g*,*o*,*w*][1,5,9,13,17,21]hexaazacyclotetracosine-*N*^{5},*N*^{9},*N*^{15},*N*^{19},*N*^{25},*N*^{29})copper(II) Triflate−1-Methanol−2-Water ($[Cu(\mathbf{7}\text{-}H)](SO_3CF_3)_3 \cdot MeOH \cdot 2H_2O$) (11). A solution of **7** (0.10 g) in dichloromethane (5 mL) was added to a solution of copper(II) triflate (0.15 g) in methanol (0.5 mL). The intensely colored green solution was filtered, and diethyl ether was added; the product separated from the solution as purple crystals. Yield: 0.13 g (71%). Anal. Calcd for $C_{30}H_{43}CuF_9N_6O_9S_3 \cdot CH_3OH \cdot 2H_2O$: C, 38.3; H, 4.8; N, 7.9. Found: C, 38.6; H, 4.3; N, 7.9. Magnetic moment: $\mu_{eff} = 1.83\ \mu_B$ (25 °C). IR (KBr disk): 3253 cm^{-1} (ν_{NH}). Electronic spectrum (MeOH): 251, 302, 399, 670 nm.

[*SP*-4]-(7,8,9,10,16,17,18,19,20-Nonahydro[*g*,*o*][1,5,9,13]tetraazacyclotetradecine-*N*^{5},*N*^{9},*N*^{15},*N*^{19})copper(II) Triflate ($[Cu(\mathbf{5})](SO_3CF_3)_2$) (12). A solution of **5** (0.50 g) in dichloromethane (5 mL) was added to a solution of copper(II) triflate (0.73 g) in methanol (0.5 mL). An immediate dark green color developed. Addition of diethyl ether and a few drops of *n*-pentane to the solution produced, over 12 h, tetragonal green crystals of the product which were filtered off, washed with *n*-pentane, and dried. Yield: 0.89 g (84%). Anal. Calcd for $C_{22}H_{28}CuF_6N_4O_6S_2$: C, 38.5; H: 4.1; N, 8.2. Found: C, 38.6; H, 4.1; N, 8.0. Magnetic moment: $\mu_{eff} = 1.84\ \mu_B$ (25 °C). IR (KBr disk): 3228 cm^{-1} (ν_{NH}). Electronic spectrum (MeOH): 207, 270, 320, 390, 664 nm.

Structural Analyses. Single crystals of $[Cu_2(\mathbf{9})](SO_3CF_3)_4 \cdot 3H_2O$, $[Cu(\mathbf{7}\text{-}H)](SO_3CF_3)_3 \cdot MeOH \cdot 2H_2O$, and $[Cu(\mathbf{5})](SO_3CF_3)_2$ were isolated as described above. The calculations were performed with the teXsan crystallographic software of the Molecular Structure Corp.[13] In the calculations, neutral atom scattering factors were taken from Table 2.2A of ref 14 and mass attenuation coefficients and values for $\Delta f'$ and $\Delta f''$ were taken from Tables 4.2.4.3 and 4.2.6.8 of ref 15, respectively. Anomalous dispersion effects were included in F_c.[16]

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(13) *teXsan*: *Single Crystal Structure Analysis software, Version 1.6c*; Molecular Structure Corp.: The Woodlands, TX, 1993.

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

For [Cu_2(**9**)](SO_3CF_3)$_4$·$3H_2O$ the complex was solved using Fourier techniques.[17] All non-hydrogen atoms were refined anisotropically, with the exception of minor disordered components for a CF_3 group of one counterion. One of the oxygens of the water molecules was refined with half-occupancy near the center of symmetry. Hydrogen atoms were included in calculated positions but not refined. Water hydrogens were not located. For [Cu(**7**-H)](SO_3CF_3)$_3$·MeOH·$2H_2O$, the crystal structure was solved by a heavy-atom Patterson method[18] and expanded using Fourier techniques.[17] All non-hydrogen atoms were refined anisotropically, with the exception of the minor component of one disordered triflate CF_3 group, which was refined isotropically as a rigid group. Hydrogen atoms were included in calculated positions and held fixed, but those attached to N(5) and N(6) were located from a difference map calculated with (sin θ)/λ cutoff of 60°. Methanol and water hydrogens were not located.

Further crystal data, information relating to data collection, and refinement details are summarized in Table 1. The atomic coordinates are given in Tables 3 and 4.

Supplementary Material Available: For [Cu_2(**9**)](SO_3CF_3)$_4$·$3H_2O$ and Cu(**7**-H)](SO_3CF_3)$_3$·MeOH·$2H_2O$ tables of bond distances and angles, torsion angles, complete atomic coordinates and isotropic displacement parameters, anisotropic displacement parameters, nonbonded contacts, selected least-square planes, and hydrogen bond data (55 pages). Ordering information is given on any current masthead page.

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(15) *International Tables for X-Ray Crystallography*; Kluwer Academic Press: Boston, MA, 1992; Vol. C.

(16) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(17) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *DIRDIF92, The DIRDIF Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

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