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Binuclear Copper(II) Complexes of Bis(1,4,7-triazacyclononane) Ligands Containing Tri- and Tetramethylene Bridging Groups. An Equilibrium and Structural Study

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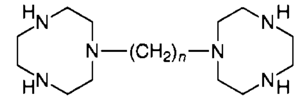
Two members of a homologous series of bis(triazacyclononane) ligands, 1,3-bis(1,4,7-triaza-1-cyclononyl)propane, EM3, and 1,4-bis(1,4,7-triaza-1-cyclononyl)butane, EM4, form stable 1:1 and 2:1 Cu(II)-L complexes. Dissociation constants for the acid salts of the compounds and equilibrium studies with copper(II) in aqueous 0.1 M KNO_3 at 25 °C are reported. $Cu(EM3)^{2+}$ is more stable than $Cu(EM4)^{2+}$ while $Cu_2(EM4)^{4+}$ is slightly more stable than $Cu_2(EM3)^{4+}$. Probable reasons for this behavior are discussed in light of the 1:1 complexes existing in solution as monomeric species. Binuclear copper(II) complexes of each ligand have been isolated and their structures determined by X-ray crystallography. $Cu_2(EM3)Cl_4{\cdot}2H_2O$ crystallizes in space group *P2/c* with unit cell dimensions $a = 12.607(3)$ Å, $b = 7.589(2)$ Å, $c = 12.948$ Å, and $\beta = 93.71(3)°$. $Cu_2(EM4)Cl_4$ crystallizes in space group $P2_1/c$ with unit cell dimensions $a = 11.919(2)$ Å, $b = 8.468(2)$ Å, $c = 11.508(2)$ Å, and $\beta = 99.06(3)°$. In both complexes the copper(II) is 5-coordinate with two secondary amine N atoms of a [9]aneN_3 group and two Cl^- occupying sites at the base and the tertiary N atom of the same moiety at the apex of a square pyramid. The structures have somewhat different conformations. The pair of Cl^- attached to the two Cu(II) are approximately *syn* for $Cu_2(EM3)Cl_4{\cdot}2H_2O$ and *anti* for $Cu_2(EM4)Cl_4$.

Introduction

The synthesis of molecules that contain two or more spatially separated metal centers is an active area of research. In numerous studies binuclear metal complexes have been modeled as active sites of polynuclear metal-containing proteins, receptors for organic substrates and studied for multi-metal-centered catalysis and multi-electron redox properties.[1] When a series of such molecules can be prepared where the relative positions of the metals can be adjusted there exists the possibility of selective control of electronic properties and interaction with substrate. The series of bis(macrocycles) that contain two covalently-linked pentaaza crown units provides an example of such molecules.[2] Another series of compounds that may form binuclear metal complexes are the bis(triazacycloalkanes). Until recently, likely due to their difficulty of synthesis, these compounds have received little attention. However, a convenient method is now available where triazacycloalkanes can be joined via polymethylene chains to form bis(triazacycloalkanes). Because metal complexes of triazacycloalkanes are thermodynamically stable and kinetically inert, complexes of bis(triazacycloalkanes) appear particularly well-suited to produce binuclear metal reaction centers.[3,4] Further, these complexes should contain metal centers that are coordinatively unsaturated and capable of binding other ligands at two or three sites on each metal.



bis(triazacycloalkane) with [9]aneN_3, as the aza-crown

Although bis(triazacycloalkanes) were previously reported,[5,6] it was not until 1985 that the first metal complexes of an early homologue of the series, 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane, EM2[7] , were isolated and characterized by Wieghardt and co-workers.[8] Since 1990 several publications have appeared which indicate that bis(triazacycloalkanes) readily form polymetallic complexes with metals such as Fe(III)[9] and Ru(III).[10] Binuclear metal complexes containing derivatives of the bis(triazacycloalkanes) have also recently been reported.[11]

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In this paper we report the synthesis of two bis(triazacycloalkanes): 1,3-bis(1,4,7-triaza-1-cyclononyl)propane, EM3, and 1,4-bis(1,4,7-triaza-1-cyclononyl)butane, EM4. The compounds both contain 1,4,7-triazacyclononane, [9]aneN$_3$, as the aza-crown. The method used is that reported by Weisman[12] that employs alkylation of a tricyclic orthoamide derivative with α,ω-diiodoalkanes followed by base hydrolysis to give the bis(triazacycloalkanes). Pure hydrochloride salts of EM3 and EM4 were prepared and the acid dissociaton constants determined at 25 °C in aqueous 0.1 M KNO$_3$. Equilibrium studies of both compounds with Cu(II) were made at the same conditions. These bis(triazacycloalkane) ligands form stable 1:1 and 2:1 Cu(II)−L complexes. In solution several protonated and hydrolyzed species are stable as well. X-ray structure determinations of the complexes [Cu$_2$(EM3)Cl$_4$·2H$_2$O] and [Cu$_2$(EM4)Cl$_4$] are also reported. Both structures are binuclear containing 5-coordinate Cu(II) with one [9]aneN$_3$ moiety bonded to each metal.

Experimental Section

1,4,7-Triazacyclononane, [9]aneN$_3$, was either prepared by published methods[13] or purchased from Aldrich. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR. NMR spectra were recorded on a Brucker AC 200 and mass spectra on a Finnigan 8200 instrument.

1,4,7-Triazatricyclo[5.2.1.0^{4,10}]decane (1).[14] A solution containing 691 mg (5.80 mmol) of *N,N*-dimethylformamide dimethyl acetal in 40 mL acetonitrile was added to 749 mg (5.80 mmol) [9]aneN$_3$ in 60 mL dry acetonitrile. The solution was stirred and heated to 85 °C for 3 h. The solvent was removed by evaporation in vacuo. The product, a light brown oil, 790 mg (5.68 mmol, 98%) was used in the next step without further purification. ^{1}H NMR (CDCl$_3$): δ 5.01 (1H, s, CH), 2.52−3.25 (12H, m, AA′BB′). Lit.[14] δ 5.05, 2.50−3.25.

1,1′-(Tetramethylene)bis(1-azoniatricyclo[2.2.2.1^{1,4}]decane) diiodide (2a).[12,15] To a stirred solution under nitrogen containing 790 mg (5.68 mmol) **1** in 100 mL acetonitrile was added 884 mg (2.85 mmol) 1,4-diiodobutane in 30 mL acetonitrile. The solution was stirred in a nitrogen atmosphere for 5 days. The off-white solid which formed was removed by filtration (1.33 g, 2.26 mmol, 79%). Mp: 271−273 °C dec; lit.[15] 271−273 °C dec. IR (KBr, cm^{-1}): 2943 s, 2884 s, 1467 s, 1384 s, 1161 s, 1084 s, 709 s, Lit.[15] 2945 s, 2890 s, 1470 s, 1338 s, 1164 s, 1098 s, 708 s.

1,1′-(Trimethylene)-bis-(1-azoniatricyclo[2.2.2.1^{1,4}]decane) diiodide, (2b). This compound was synthesized in a similar manner to **2a** except 1,3-diiodopropane was used as a reactant. Yield: 60%. Mp: 226−228 °C dec, IR (KBr, cm^{-1}): 2937 s, 2880 s, 1468 s, 1385 s, 1176 s, 1066 s, 730 s.

1,4-Bis(1,4,7-triaza-1-cyclononyl)butane, EM4, (3a).[12,15] The diiodide salt **2a** (1.33 g, 2.26 mmol) was refluxed under nitrogen in 50 mL of water for 2 h and then 1.2 g (30 mmol) of NaOH was cautiously added. Refluxing was continued for an additional 8 h. After cooling, the reaction mixture was extracted four times with 25-mL portions of CHCl$_3$. The combined extracts were dried over Na$_2$SO$_4$ (anhydrous). After filtering and removal of solvent in vacuo a light yellow oil remained which solidified on standing. This material was Kugelrohr distilled (160 °C, 0.050 mmHg), giving a colorless oil which slowly solidified. Yield: 596 mg, 85%. ^{1}H NMR: δ 1.40 (4H, br, (−CH$_2$)$_2$), 2.20−2.35 (4H, br (NH)), 2.46−2.50 (12 H, m, N(−CH$_2$)$_3$), 2.62−2.66 (16 H, m, (H−N−CH$_2$)$_4$); lit.[9a] δ 1.43, 2.46−2.55, 2.64−2.74, 2.85. (Although ^{1}H NMR agrees well with reported chemical shifts the position of the NH protons appear to be concentration dependent and are upfield from those reported.) ^{13}C NMR: δ 25.81, 46.62, 46.74, 52.95, 57.56; lit.[9a] δ 25.62, 46.24, 46.47, 52.58, 57.27. EI MS *m/e* 312.4 (M$^+$) (calcd for C$_{16}$H$_{36}$N$_6$ *m/e* 312.3).

1,3-Bis(1,4,7-triaza-1-cyclononyl)propane, EM3, (3b). The diiodide salt **2b** was hydrolyzed according to the procedure given above. Yield: 80%. ^{1}H NMR δ 1.53 (2H, m, CH$_2$), 2.31−2.36 (4H, br, NH), 2.44−2.50 (12H, m, N(−CH$_2$)$_3$), 2.59−2.63 (16H, m, (HN−CH$_2$)). ^{13}C NMR: δ 26.38, 46.68, 46.76, 53.06, 55.65; EI MS: *m/e* 298.3 (M$^+$) (calcd for C$_{15}$H$_{34}$N$_6$ *m/e* 298.3).

Table 1. Acid Dissociation Constants for Protonated Forms of the Ligands EM3 and EM4 at 25.0 °C in 0.10 mol dm^{-3} KNO$_3$

	−log K_a	
reaction	EM3	EM4
$HL^+ \rightleftharpoons L + H^+$	11.08(5)	11.21(3)
$H_2L^{2+} \rightleftharpoons HL^+ + H^+$	10.38(4)	10.48(3)
$H_3L^{3+} \rightleftharpoons H_2L^{2+} + H^+$	6.47(2)	6.57(3)
$H_4L^{4+} \rightleftharpoons H_3L^{3+} + H^+$	5.77(2)	5.87(2)

[a] Estimated standard deviations in parentheses.

Hydrochloride Salts of 3a and 3b. Dry HCl(g) was carefully passed through a cold solution containing 2 mmol of the amine in 60 mL of absolute ethanol. The white solid was removed by filtration and dissolved in 10 mL of water containing a small amount of decolorizing charcoal. The solution was heated to boiling and filtered while hot. Addition of 10 mL concentrated HCl to the filtrate gave the white hydrochloride salt in greater than 90% yield. The salts were dried in a vacuo at 80 °C. Anal. calcd for C$_{16}$H$_{45}$N$_6$Cl$_6$O$_{1.5}$ (mol wt 558.3) (EM4·6HCl·1.5H$_2$O): C, 34.42; H, 8.12; N, 15.05; Cl, 38.10. Found: C, 34.48; H, 8.12; N, 14.96; Cl, 37.29. Anal. Calcd for C$_{15}$H$_{41}$N$_6$Cl$_6$O$_{0.5}$ (mol wt 525.8) EM3·6HCl·0.5H$_2$O: C, 34.24; H, 7.35; N, 15.97; Cl, 40.42. Found: C, 34.36; H, 7.65; N, 16.06; Cl, 40.23.

Cu$_2$(EM4)Cl$_4$ and Cu$_2$(EM3)Cl$_4$·2H$_2$O. To a solution containing 7 mmol of the amine hydrochloride in 10 mL of water was added 14 mmol of Cu(NO$_3$)$_2$·3H$_2$O. The pH was adjusted to 6−7 with 0.1 M NaOH, and on slow evaportation blue plate-like crystals suitable for X-ray studies were obtained. Elemental analysis verified that the copper to ligand ratio was 2:1.

pH Potentiometric Titrations. All pH measurements were made with a Beckman Model Φ71 pH meter fitted with Fisher glass and Ag/AgCl reference electrodes. Titrations were performed in a sealed thermostated (25.0 °C) cell under a blanket of presaturated nitrogen. The meter−electrode system was calibrated with 4.008 buffer at 25.0 °C. Meter correction was made by measuring the pH of a 0.00100 M HCl which was 0.1 M in KNO$_3$. The value measured was used to compute a correction factor by assuming that the pH of 0.00100 M H$^+$ was 3.000. At times the linearity was checked with 0.0100 M HCl and 0.0100 M NaOH solutions both 0.1 M in KNO$_3$. The value of pK_w was 13.797.

Aqueous stock solutions (∼0.02 M) of each ligand were prepared from the hydrochloride salts. Solution concentration was determined by titrating aliquots of these solutions with standard NaOH. The mmol of base required from the first to the second inflection of the titration curve is equivalent to half the mmol of ligand present. The acid dissociation constants for the protonated ligands at the conditions specified above were determined from these titrations (Table 1). At least 10 separate titrations using ligand from several different preparations were used as data sources for the equilibrium calculations.

Aqueous solutions of Cu(II) were prepared from analytical grade nitrate or perchlorate salts and contained a small excess of acid to prevent hydrolysis. These solutions were standardized by titration with primary standard Na$_2$EDTA solution using murexide indicator.[16]

Titrations of Cu(II)-ligand solutions with 0.1000 M NaOH in 0.1 M KNO$_3$ at 25 °C contained concentrations of Cu(II) and ligand hydrochloride salt ranging from 1.8×10^{-3} to 1.2×10^{-2} M. Molar ratios of Cu(II) to ligand ranged from 2:1 to 1:1.2 and typical solution volume was 15 mL. The time required to reach equilibrium, especially in the pH range 3.5−8, was often >1 h.

Equilibrium Calculations. Analysis of the pH potentiometric data was done with both SCOGS2[17] and SUPERQUAD.[18] Equilibrium

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Table 2. Formation Constants for Copper(II) Complexes of the Ligands EM3 and EM4 at 25.0 °C in 0.10 mol dm^{-3} KNO_3[a]

reaction	log β EM3	log β EM4
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	24.90(3)	23.02(6)
$Cu^{2+} + H^+ + L \rightleftharpoons CuHL^{3+}$	27.4(1)	27.0(2)
$Cu^{2+} + 2H^+ + L \rightleftharpoons CuH_2L^{4+}$	31.64(5)	32.02(9)
$2\ Cu^{2+} + L \rightleftharpoons Cu_2L^{4+}$	29.08(7)	29.61(6)
$2\ Cu^{2+} + L \rightleftharpoons Cu_2LOH^{3+} + H^+$	22.5(2)[b]	22.9(2)[b]
$2\ Cu^{2+} + L \rightleftharpoons Cu_2L(OH)_2{}^{2+} + 2\ H^+$	17.0(1)[b]	17.98(9)[b]

[a] Estimated standard deviation in parentheses. [b] For hydrolysis reactions the notation for β is written as the product βK_w which is the standard format in computer programs such as SCOGS2 and SUPERQUAD.

Table 3. Equilibrium constants for Copper(II) Complexes of the Ligands EM3 and EM4 at 25.0 °C in 0.1 mol dm^{-3} KNO_3 Calculated from Constants in Tables 1 and 2

	reaction	log K EM3	log K EM4
$K_a(CuH_2L)$	$CuH_2L^{4+} \rightleftharpoons CuHL^{3+} + H^+$	−4.2	−5.0
$K_a(CuHL)$	$CuHL^{3+} \rightleftharpoons CuL^{2+} + H^+$	−2.5	−4.0
K_2	$Cu^{2+} + CuL^{2+} \rightleftharpoons Cu_2L^{4+}$	4.2	6.6
$K_a(Cu_2L)$	$Cu_2L^{4+} \rightleftharpoons Cu_2LOH^{3+} + H^+$	−6.6	−6.7
$K_a(Cu_2LOH)$	$Cu_2LOH^{3+} \rightleftharpoons Cu_2L(OH)_2{}^{2+} + H^+$	−5.5	−5.0

Table 4. Electronic Absorption Spectra of Cu(II) Complexes in Aqueous Solution at 20 °C

complex	absorbance maxima (λ in cm^{-1}, ϵ in dm^3 mol^{-1} cm^{-1})
$CuEM3^{2+}$	15520 (53), 9430 (15)
Cu_2EM^{4+}	15450 (102), 9430 (41)
$CuEM4^{2+}$	15310 (53), 9300 (17)
Cu_2EM4^{4+}	15500 (112), 9480 (50)

modeling of both Cu(II)−ligand systems was complicated by the presence of dicopper(II) species including hydrolysis products and several protonated forms of the monocomplex. Initial estimates for formation constants of the dicopper(II) species were provided by analysis of the data from titrations containing 2:1 Cu(II)− ligand stoichiometry. These constants were then used as initial estimates in further refinement of titration data with different Cu(II) to ligand ratios. The formation constants presented in Table 2 were computed with data from at least 10 different titrations with each ligand. Average values of the constants are given along with the standard deviations. Standard deviations of constants for a single titration were always smaller than those given in the table. Statistical data from both SCOGS2 and SUPERQUAD were well within acceptable limits.

Crystallographic Studies. Cell dimensions and intensity data were measured with a Syntex P2$_1$ diffractometer using monochromated MoKα radiation and $\theta-2\theta$ scans. Cell dimensions were determined by least-squares refinement of 24 reflections ($25 < 2\theta < 40$). Two control reflections collected every 50 reflections during data collection showed no significant trends. Intensities were corrected for Lorentz and Polarization effects. An absorption correction from ψ scans of six reflections with χ near 90° were applied for $Cu_2(EM3)Cl_4{\cdot}2H_2O$. Both structures were solved by direct methods and refined using full-matrix least-squares techniques. All hydrogens were found in difference maps, during the final stages of refinement they were introduced in calculated positions (0.96 Å for C−H and 0.90Å for N−H bonds) and refined isotropically in the "ride approximation" with fixed $U = 0.08$ Å. Final difference Fourier maps showed largest deviations of + 1.02 and −0.66 eÅ^{-3} and + 1.38 and −1.45 e Å^{-3} all near Cu(II) and Cl for $Cu_2(EM4)Cl_4$ and $Cu_2(EM3)Cl_4{\cdot}2H_2O$, respectively. The remainder of the maps were essentially featureless. All calculations were performed with the SHELXTL PLUS suite of computer programs.[19]

Table 5. Crystallographic Data

	$Cu_2(EM4)Cl_4$	$Cu_2(EM3)Cl_4{\cdot}2H_2O$
formula	$Cu_2C_{16}H_{36}N_6Cl_4$	$Cu_2C_{15}H_{38}N_6Cl_4O_2$
fw	581.4	605.4
space group	$P2_1/c$	$P2/c$
a, Å^3	11.919(2)	12.607(3)
b, Å^3	8.468(2)	7.589(2)
c, Å^3	11.508(2)	12.948(3)
β, deg	99.06(3)	93.71(3)
V, Å^3	1147.0(6)	1236.2(6)
Z	2	2
cryst size, mm^3	0.30 × 0.38 × 0.12	0.32 × 0.30 × 0.12
T, °C	20	20
$\varrho_{\text{calcd, g/cm}^3}$	1.683	1.621
ϱ_{meas}, g/cm^3	1.67	1.60
h,k,l range collcd	$0 \le h \le 17, -12 \le k \le 0, -16 \le l \le 16$	$0 \le h \le 17, 0 \le k \le 10, -18 \le l \le 18$
μ, cm^{-1}	23.36	21.76
min/max transm factors		0.33/0.37
no. of unique reflns	3843	3638
no. of reflns with ($F > 4.0\sigma(F)$)	2709	2393
no. of params	181	132
R[a]	0.059	0.053
R_w[b]	0.048	0.058
GOF	2.59	1.93

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

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Cu_2(EM3)Cl_4]{\cdot}2H_2O$[a]

	x	y	z	U, Å^2
Cu	−2746(1)	665(1)	5357(1)	21(1)
Cl(1)	−3425(1)	−688(2)	6745(1)	41(1)
Cl(2)	−1870(1)	−1787(2)	4800(1)	41(1)
O(1)	−4191(4)	2151(9)	8554(4)	65(2)
N(1)	−1549(3)	2512(5)	6138(3)	21(1)
N(2)	−2335(3)	1983(6)	4058(3)	24(1)
N(3)	−3758(3)	2714(6)	5474(3)	23(1)
C(1)	−1053(4)	3483(7)	5310(4)	26(1)
C(2)	−1203(4)	2486(8)	4274(4)	31(2)
C(3)	−3063(5)	3466(7)	3810(4)	30(2)
C(4)	−4062(4)	3243(8)	4392(4)	30(2)
C(5)	−3254(4)	4171(7)	6110(4)	28(1)
C(6)	−2246(4)	3609(7)	6748(4)	24(1)
C(7)	−759(4)	1539(6)	6820(4)	23(1)
C(8)	0	2677(10)	7500	32(2)

[a] Estimated standard deviations are given in parentheses. Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Unit cell parameters and summary of data collection and refinement are given in Table 5. The final atomic coordinates (non-hydrogen atoms) for the structures are listed in Tables 6 and 7.

Results and Discussion

The trend in acidity of H_6EM3^{6+} and H_6EM4^{6+} parallels that of $H_3[9]aneN_3{}^{3+}$.[20] There exist three regions of the titration curve consisting of two overlapping acid dissociations which are strong, moderately weak and weak. The pK_as for these reactions are listed in Table 1. The similarity of magnitude of the measured pK_as of the bis(triazacycloalkanes) indicates that the strong acid protons are probably associated with the tertiary amine nitrogens since variation in the carbon chain has little effect on the acidity constants. When dissociating protons reside on nitrogen atoms separated by two to five methylene groups there is a significant effect on the acidity. For example, the stepwise decrease in the first acid dissociation for the series of

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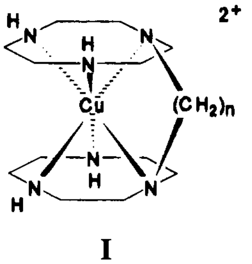
(19) Sheldrick, G., SHELXTL-PLUS. Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990.

(20) (a) Yang, R.; Zompa, L. *Inorg Chem.* **1976**, *15*, 1499. (b) Zompa, L. *Inorg. Chem.* **1978**, *17*, 2531.



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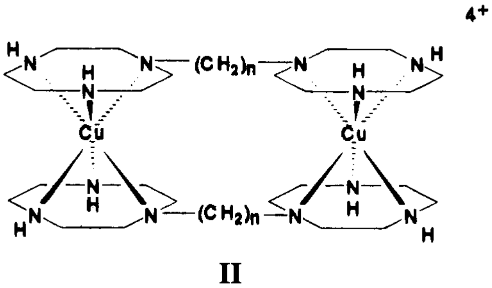

II

diprotonated diamines ethylenediamine to pentamethylenediamine (pK_a range 7.3−10.0) and the third acid dissociation in the series EDTA to pentamethylenediaminetetraacetic acid (pK_a range 6.2−9.5).[21] Therefore, the acid−base behavior of these ligands and, in fact, the entire series of bis(triazacycloalkanes) from $n = 2-6$ (where n is the number of carbon atoms of the methylene chain) essentially resembles that of two isolated [9]-aneN_3 moities.[22]

The titration curves of Cu(II)−H_6EM3^{6+} and Cu(II)−H_6EM4^{6+} with NaOH appear similar when the molar ratio of Cu(II) to ligand exceeds 1:1. For example, the 2:1 titration curves both show well defined inflections at **a** values (**a** = mol of base per mol of ligand) of 6 and 8. Analysis of the titrimetric data agrees well the presence of a binuclear copper(II) species, Cu_2L^{4+}, and CuH_2L^{4+} (L = EM3 or EM4) when **a** < 6. Thus, when base is first added to the solution containing a 2:1 molar ratio of Cu(II) to L the two strong acid protons are titrated. As the pH is increased slightly the concentration of CuH_2L^{4+} and then Cu_2L^{4+} increases until at **a** = 6 (pH ~ 4) the predominant complex species in solution is Cu_2L^{4+}. Continued addition of base where 6 < **a** < 8 agrees with the formation of hydrolysis products Cu_2LOH^{3+} and $Cu_2L(OH)_2^{4+}$ in overlapping equilibrium steps. Although titration of equimolar mixtures of Cu(II) and each ligand show inflections at **a** = 4 and 6, there is considerable difference in the shape of the curves. The Cu(II)−EM4 curve has a distinct inflection at **a** = 6, whereas, the Cu(II)−EM3 curve has a barely perceptible inflection at the same point. Data analysis agrees well with CuH_2L^{4+} as the predominant complex species in the region of the titration where **a** < 4 and nearly exclusive CuL^{2+} formation when **a** > 4. There also exists a small concentration of $CuHL^{3+}$ near the inflection at **a** = 4 (pH ~ 5).

Both EM3 and EM4 form extremely stable 1:1 and 2:1 Cu(II):L complexes. $Cu(EM3)^{2+}$ is more stable than $Cu(EM4)^{2+}$ by nearly 2 orders of magnitude. If the structures of CuL^{2+} are monomeric (**I**), $Cu(EM3)^{2+}$ will contain a 6-membered chelate ring formed by Cu(II), the tertiary amine nitrogens and the bridging chain, whereas, $Cu(EM4)^{2+}$ will have a less stable 7-membered ring. Although there is no direct supporting evidence that the CuL^{2+}(aq) species are monomeric rather than dimeric (**II**) or oligomeric, the decrease in stability as the bridging chain is lengthened suggests a monomeric structure for $Cu(EM3)^{2+}$ and probably for $Cu(EM4)^{2+}$. The magnitude of the acid dissociation constants for CuH_2L^{4+} and $CuHL^{3+}$ supports these arguments (Table 3). In most cases a protonated complex species of type CuH_2L^{2+} is a stronger acid than $CuHL^{3+}$. However, in the process of forming the monomeric species, CuL^{2+}, from $CuHL^{3+}$ proton loss is accompanied by chelate ring formation. This might explain why $CuHL^{3+}$ is the stronger acid (Scheme 1). The difference in $K_a(CuH_2L)$ and $K_a(CuHL)$ for EM3 and EM4, 1.7 and 1.0 log K units respectively, appears to show the greater stability in forming 6- versus 7-membered chelate rings.

Although complexes **I** and **II** as well as CuL^{2+} in Scheme 1 have been drawn with six nitrogen donors, it is well-known that Cu(II) amine complexes in aqueous media form four or five strong bonds with considerably weaker interaction at the sixth donor nitrogen. Therefore, one of the Cu(II)−N bonds might be expected to be weak or possibly even displaced from the coordination sphere. For example, $Cu([9]aneN_3)_2^{2+}$ tends to dissociate or partially dissociate in aqueous solution.[20a,23] For the monomeric bis(triazacyclononane) complexes studied here the presence of an additional chelate ring apparently enhances their stability. The absence in aqueous solution of detectable amounts of CuH_3L^{5+} and Cu_2HL^{5+} appears to favor a structure where the sixth N atom may be weakly coordinated. The behavior of [9]aneN_3 with most metals involves the ligand functioning in a tridentate fashion or not being bound to the metal at all.[3,20] Notable exceptions are Pd(II) and Pt(II) complexes where structures are square planar and [9]aneN_3 is bidentate.[24]

The formation constants of the dicopper(II) complexes with EM3 and EM4 differ by only 0.5 log K unit. EM3 forms a more stable 1:1 complex, but the addition of another mole of Cu(II) to form the Cu_2L^{4+} species favors EM4 by 2.4 log K units (K_2 in Table 3). Provided both CuL^{2+} species are monomeric this can be explained by the energy required in breaking a 6- versus a 7-membered chelate ring in the EM3 and EM4 complexes respectively as Cu_2L^{4+} species are formed. The hydrolysis of Cu_2L^{4+} also presents an anomaly. The K_a of Cu_2L^{4+} in forming Cu_2LOH^{3+} is smaller than the K_a of Cu_2LOH^{3+}. This indicates that $Cu_2L(OH)_2^{2+}$ is more stable than Cu_2LOH^{3+} and probably consists of a dimeric structure with bridging hydroxy groups similar to many binuclear Cu(II) complexes.[25]

The distribution of species from the calculated equilibrium constants indicate that in solutions containing equimolar ratios of Cu(II) and L (pH < 3.3 for EM3 and pH < 4.4 for EM4) a greater proportion of Cu(II) is bound as Cu_2L^{4+} than CuL^{2+}. In 2:1 Cu(II):L solutions in the pH range 4−5.5 approximately 10% of the ligand is bound as $Cu(EM3)^{2+}$. For EM4 at similar conditions of concentration and pH less than 1% of $Cu(EM4)^{2+}$ is present.

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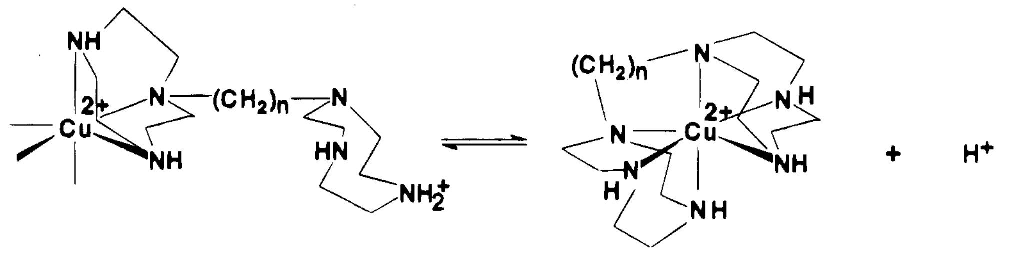
Scheme 1



CuHL^{3+}

CuL^{2+}

Table 7. Atomic coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Cu_2(EM4)Cl_4]$[a]

	x	*y*	*z*	*U*, Å^3
Cu	7058(1)	733(1)	1449(1)	21(1)
Cl(1)	6605(1)	424(2)	−557(1)	33(1)
Cl(2)	7707(1)	3235(1)	1391(1)	42(1)
N(1)	8470(3)	−1103(4)	1863(3)	18(1)
N(2)	7274(3)	911(4)	3233(3)	22(1)
N(3)	6061(3)	−1169(4)	1745(3)	21(1)
C(1)	9090(4)	−444(6)	2968(4)	27(1)
C(2)	8272(4)	−5(7)	3829(4)	27(1)
C(3)	6169(4)	384(6)	3560(4)	26(2)
C(4)	5804(4)	−1178(5)	2967(4)	27(2)
C(5)	6669(4)	−2614(6)	1445(4)	28(2)
C(6)	7894(4)	−2610(5)	2047(4)	24(1)
C(7)	9200(4)	−1329(6)	945(4)	27(2)
C(8)	9742(4)	148(6)	551(4)	29(2)

[a] Estimated standard deviations are given in parentheses. Equivalent isotropic *U* is defined as one-third of thetrace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

There are few equilibrium studies reported for series of ligands capable of forming binuclear metal complexes. One series that has been studied by Paoletti, Micheloni and coworkers are very large polyazacycloalkanes ([3k]aneN$_k$, k = 8 - 12).[26] Aqueous equilibrium studies of these ligands with Cu(II) all show extremely large formation constants for Cu_2L^{4+} (log β_{Cu_2L} = 36.3, 36.0, 37.8, 38.8, 39.3 for *k* = 8−12 respectively). The formation constants for these dicopper(II) species are much larger than those determined here for the dicopper(II) bis(triazacycloalkanes). X-ray diffraction studies show that several of these complexes contain four nitrogen atoms bonded to each Cu(II). Spectroscopic evidence showing similar solution and solid state absorbance maxima indicates that at least four nitrogen atoms remain coordinated in solution. The dicopper(II) bis(triazacycloalkanes) have only three nitrogen atoms bonded per metal.

In the same series of ligands both CuL^{2+} and Cu_2L^{4+} species are formed by [21]aneN$_7$. The formation constant of Cu([21]-aneN$_7$), log β_{CuL} = 19.48 (μ = 0.15 (NaClO$_4$), 25 °C),[27] is several orders of magnitude smaller than the corresponding ones for Cu(EM3)$^{2+}$ and Cu(EM4)$^{2+}$ (Table 2). This might be due to the large size and flexibility of [21]aneN$_7$ when compared to the bis(triazacyclononane) ligands that contain [9]aneN$_3$ groups with relatively fixed N-donor stereochemistry. In contrast, the equilibrium constant for the reaction $Cu^{2+} + CuL^{2+} \rightharpoonup Cu_2L^{4+}$ with [21]aneN$_7$, log K_2 = 11.01 (μ = 0.15 (NaClO$_4$), 25 °C),[27] is several orders of magnitude greater than those of the bis(triazacyclononanes) (K_2, Table 3). One possible reason is that several Cu−N bonds of the CuL^{2+} complexes of the bis(triazacyclononanes) must be broken in order to form Cu_2L^{4+}. This is not the case for Cu([21]aneN$_7$)$^{2+}$ where several of the potential N-donor atoms remain noncoordinated. Thus, in the above reaction complexation of the second Cu(II) by [21]aneN$_7$ might be expected to have a greater enthalpic contribution to the free energy.

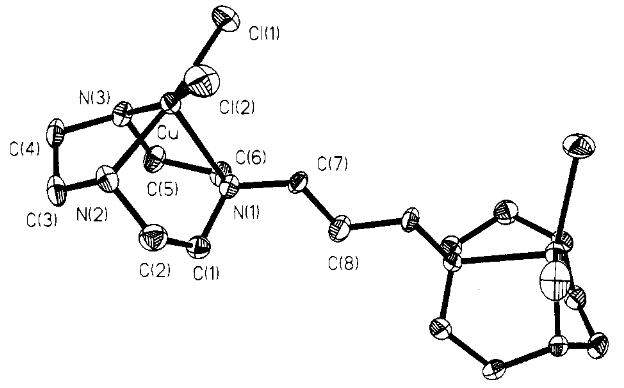


Figure 1. Thermal ellipsoid plot showing the structure of $[Cu_2(EM3)Cl_4]$ in $[Cu_2(EM3)Cl_4]\cdot 2H_2O$. Thermal ellipsoids are at the 50% probability level. Hydrogen and oxygen atoms are omitted.

The UV−vis spectra of 1:1 and 2:1 Cu(II)−L aqueous solutions were measured at pH values where equilibrium calculations showed that CuL^{2+} or Cu_2L^{4+}predominate as complex species. Spectra of CuL^{2+} and Cu_2L^{4+} show similar features: an absorbance maxima near 15 400 cm^{-1} and less intense peak 9430 cm^{-1} (Table 4). The aqueous solution spectrum of Cu[9]aneN$_3^{2+}$ is, not surprisingly, quite similar.[20a] Although differences in absorption maxima are small, Cu(EM3)$^{2+}$ absorbs at slightly higher energy than Cu(EM4)$^{2+}$ (Δ = 210 cm^{-1}). The complexes Cu$_2$(EM3)$^{2+}$ and Cu$_2$(EM4)$^{2+}$ absorb at nearly identical energy with nearly twice the molar absorbtivity of the 1:1 complexes. This suggests that in solution a slightly different coordinative environment exists for the 1:1 complexes, while the 2:1 complexes have similar environments.

The structure of the complexes $Cu_2(EM3)Cl_4\cdot 2H_2O$ and $Cu_2(EM4)Cl_4$ are shown in Figures 1 and 2 respectively. Bond lengths and angles are given in Tables 8 and 9. The major distinction between the structures is that the Cl$^-$ are approximately *syn* in $Cu_2(EM3)Cl_4\cdot 2H_2O$ and *anti* for $Cu_2(EM4)Cl_4$. In both complexes the stereochemistry about Cu(II) is 5-coordinate with the two Cl$^-$ and two secondary amine N atoms occupying positions at the base of a square pyramid capped by the tertiary amine N atom. The mean deviation of atoms from the plane is 0.08 Å for $Cu_2(EM3)Cl_4\cdot 2H_2O$ and 0.12 Å for $Cu(EM4)Cl_4$ with the Cu(II) displaced 0.18 and 0.20 Å, respectively, from the plane in the direction of N1. The Cu−N1 bond distances, where the N1 atoms are the tertiary amine atoms,

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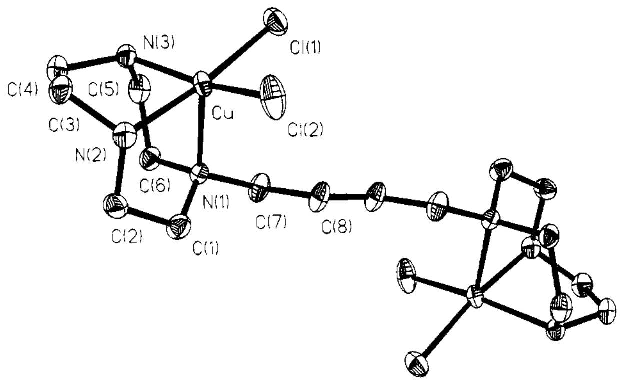

Figure 2. Thermal ellipsoid plot showing the structure of [Cu_2(EM4)-Cl_4]. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $Cu_2(EM3)Cl_4 \cdot 2H_2O$

Distances			
Cu−Cl(1)	2.284(2)	Cu−Cl(2)	2.303(2)
Cu−N(1)	2.251(4)	Cu−N(2)	2.052(4)
Cu−N(3)	2.023(4)	N(1)−C(1)	1.473(7)
N(1)−C(6)	1.476(7)	N(1)−C(7)	1.484(6)
N(2)−C(2)	1.487(7)	N(2)−C(3)	1.474(7)
N(3)−C(4)	1.483(7)	N(3)−C(5)	1.496(7)
C(1)−C(2)	1.542(8)	C(3)−C(4)	1.520(8)
C(5)−C(6)	1.531(7)	C(7)−C(8)	1.525(6)
C(8)−C(7a)	1.525(6)		
Angles			
Cl(1)−Cu−Cl(2)	95.4(1)	Cl(1)−Cu−N(1)	101.6(1)
Cl(2)−Cu−N(1)	108.8(1)	Cl(1)−Cu−N(2)	172.5(1)
Cl(2)−Cu−N(2)	89.2(1)	N(1)−Cu−N(2)	82.4(2)
Cl(1)−Cu−N(3)	91.0(1)	Cl(2)−Cu−N(3)	164.1(1)
N(1)−Cu−N(3)	84.0(1)	N(2)−Cu−N(3)	83.1(1)

average 0.22 Å longer than the in-plane Cu−N distances in both compounds. The structure of two 5-coordinate Cu(II)-[9]aneN_3 complexes, Cu([9]aneN_3)Br_2[28] and Cu([9]aneN_3)Cl_2,[29] have been reported. Both complexes show similar square pyramidal stereochemistry about Cu(II). $Cu_2(EM3)Cl_4 \cdot 2H_2O$ and Cu_2(EM4)Cl_4 have Cu − N and Cu − Cl bond distances that fall into the normal range for Cu(II) complexes with these donor atoms.[29] The N−Cu−N bond angles average 82.8(7)° and are typical for [9]aneN_3 complexes, illustrating the inflexibility of the 9-membered triaza ring in forming three fused 5-membered chelate rings.[3,4] The Cu−Cu distances in $Cu_2(EM3)Cl_4 \cdot 2H_2O$ and $Cu_2(EM4)Cl_4$ are 8.6 and 8.3 Å respectively. It is interesting that in these particular structures the compound with the longer bridging chain has the shorter intramolecular metal−metal distance.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for $Cu_2(EM4)Cl_4$[a]

Distamces			
Cu−Cl(1)	2.301(1)	Cu−Cl(2)	2.260(1)
Cu−N(1)	2.285(3)	Cu−N(2)	2.034(4)
Cu−N(3)	2.061(4)	N(1)−C(1)	1.477(6)
N(1)−C(6)	1.481(6)	N(1)−C(7)	1.483(7)
N(2)−C(2)	1.494(6)	N(1)−C(3)	1.494(6)
N(3)−C(4)	1.486(7)	N(3)−C(5)	1.491(6)
C(1)−C(2)	1.540(7)	C(3)−C(4)	1.520(7)
C(5)−C(6)	1.514(7)	C(7)−C(8)	1.509(7)
C(8)−C(8a)	1.514(11)		
Angles			
Cl(1)−Cu−Cl(2)	96.0(1)	Cl(1)−Cu−N(1)	100.4(1)
Cl(2)−Cu−N(1)	113.5(1)	Cl(1)−Cu−N(2)	173.3(1)
Cl(2)−Cu−N(2)	88.3(1)	N(1)−Cu−N(2)	82.4(1)
Cl(1)−Cu−N(3)	91.5(1)	Cl(2)−Cu−N(3)	161.1(1)
N(1)−Cu−N(3)	81.9(1)	N(2)−Cu−N(3)	82.9(1)

[a] Estimated standard deviations are given in parentheses.

Conclusions

It has been shown that bis(triazacycloalkanes) are excellent ligands for forming binuclear metal complexes. With Cu(II), and quite likely with many other metal ions, the binuclear nature of the complexes extends from the solid state to aqueous solution. This family of ligands allows construction of binuclear complexes where metal−metal distances can be varied. Of course, insertion of a more rigid bridging group would allow more certainty in predicting these distances. An advantage of these ligands in studying reactivity of bimetal centers over bis(macrocyclic) type ligands is the general availability of more coordination sites for interactions with other ligands (substrate). Further, because of the kinetic inertness of many triazacycloalkane complexes it should be possible to make bis(triazacycloalkane) complexes, containing two different metals.

It has been determined that the 1:1 Cu(II) complexes of these ligands are stable in solution. Although we have isolated solids containing equimolar ratios of Cu(II) and ligand we have not been successful in obtaining satisfactory crystals for X-ray study. The structures of [Fe(EM2)]$Br_3 \cdot 4H_2O$[30] and [Cu(EM2)]$SO_4 \cdot 6H_2O$[31] are monomeric. However, it is likely that many of the 1:1 metal complexes will be dimeric[10] or oligomeric,[9] and the structures may or may not contain bridging groups. This will almost certainly be the case as the number of atoms in the bridging group is extended.

Supplementary Material Available: Tables of bond lengths and angles, complete atomic coordinates, anisotropic thermal parameters, and H-atom coordinates for $Cu_2(EM3)Cl_4 \cdot 2H_2O$ and $Cu_2(EM4)Cl_4$. (8 pages). Ordering information is given on any current masthead page.

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(31) Zompa, L. Unpublished results. Like [Fe(EM2)]$Br_3 \cdot 4H_2O$,[30] all six nitrogens are coordinated to Cu(II).