

A New Diaza-18-Crown-6 Ligand Containing Two Quinolin-8-ylmethyl Side Arms: Crystal Structures and Characterization of the Ligand, the Protonated Ligand and Its Mononuclear Barium(II) and Dinuclear Copper(II) Complexes

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A new 7,16-bis(quinolin-8-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane ligand, **L**, has been prepared and its crystal structure reported. In addition, the structure of the protonated ligand H_2L has been determined. H_2L is of interest because of interatomic interactions between the ligand and perchlorate ions. The mononuclear Ba(II) (BaL), and dinuclear Cu(II) (Cu_2L) complexes of **L** have been prepared and their crystal structures determined. Stability constants and other thermodynamic data valid in methanol at 23 or 25° for these and several other complexes of **L** have been obtained. Among the metal ions studied, **L** forms the most stable complex with Ba^{2+} . In addition, **L** selectively binds Cu^{2+} over Ni^{2+} by about 3 orders of magnitude. Some of the complexes have been studied using nmr and uv-vis spectroscopic techniques. Crystal data are given for **L**, space group, $P2_1/c$, $a = 8.8325(14) \text{ \AA}$, $b = 13.808(3) \text{ \AA}$, $c = 13.310(3) \text{ \AA}$; $\beta = 94.72(2)^\circ$; $Z = 2$, $R = 0.0727$; for H_2L , space group, $P2_1/c$, $a = 14.685(3) \text{ \AA}$, $b = 15.035(6) \text{ \AA}$, $c = 17.369(4) \text{ \AA}$, $\beta = 90.366(12)^\circ$, $Z = 4$, $R = 0.0781$; for BaL , space group, $Pbcn$, $a = 17.314(3) \text{ \AA}$, $b = 9.539(2) \text{ \AA}$, $c = 22.081(3) \text{ \AA}$, $Z = 4$, $R = 0.0354$; and for Cu_2L , space group, Cc , $a = 19.762(2) \text{ \AA}$, $b = 14.413(2) \text{ \AA}$, $c = 14.935(2) \text{ \AA}$, $\beta = 98.753(12)^\circ$, $Z = 4$, $R = 0.0564$. Cu^{2+} forms a hydroxo-bridged dinuclear complex with **L** while Ba^{2+} forms a mononuclear complex with **L** in which its two side arms are not involved in complexation.

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Introduction.

The synthesis and complexation properties of macrocyclic ligands containing two ligating side arms have attracted considerable attention in recent years [1-6]. Such ligands not only form mononuclear cryptates with metal ions [7,8], but also dinuclear pseudocryptates by inclusion of two metal ions into the cavity [9-11]. The general ideas underlying the design of such systems have been presented, and a number of dimetallic cryptates of different structural types have been reported [12-13]. Various types of dinuclear complexes have been obtained with macrocycles containing two chelating subunits such as saturated macrocycles [14-17] and macrocyclic Schiff-base ligands [18-21]. In these complexes, the metal cations are bound to the chelating units and held by the macrocyclic framework at a distance and in a coordination arrangement that may allow further binding of a bridging species in a "cascade"-type complexation process [9]. Dinuclear macrocyclic complexes containing imidazolato [22-24], azido [25-26], and hydroxo [25-29] bridges have been described. The interest of these types of complexes lies in their unusual physical and chemical properties. They can be used as models of biological dimetallic sites [12,30,31] and dinuclear catalysts possessing highly selective chemical reactivity.

Attachment of two side chains to a macrocyclic framework can also yield dinucleating ligands capable of binding metals both within the macrocyclic cavity and between the functionalized side arms. This may generate two types

of ligands: heterotopic ligands capable of simultaneously binding two different metals in proximity (Figure 1A) and homotopic ligands which may form homonuclear complexes of metal ions (Figure 1B) [32,33]. In this context, we have recently reported that *o*-aminophenol-substituted diaza-18-crown-6 ligands function as heterobinuclear receptors for Cu^{2+} and Na^+ as shown in Figure 1A [34].

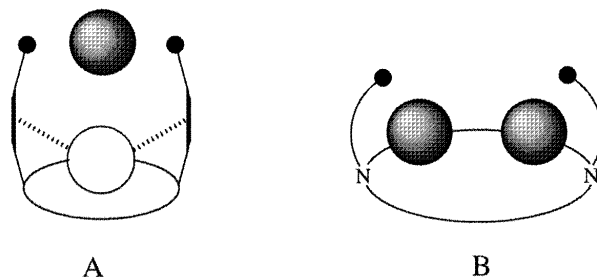


Figure 1. A. Heterotopic ligand capable of binding two different metal ions; B. Homotopic ligand capable of forming homonuclear complexes.

Herein, we report the synthesis and the solid state structure of a new diaza-18-crown-6 ligand (**L**) bearing two quinolin-8-ylmethyl groups as additional donor pendants, the structure of the protonated ligand with $HClO_4$, and the complexation properties of **L** with Na^+ , K^+ , Mg^{2+} , Ba^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , and Zn^{2+} . We also report the crystal structures of mononuclear $BaL(ClO_4)_2$, and dinuclear $[Cu_2L(\mu-OH)](ClO_4)_3$ complexes. In the $BaL(ClO_4)_2$ complex, six donor atoms (N_2O_4) of the diazacrown are

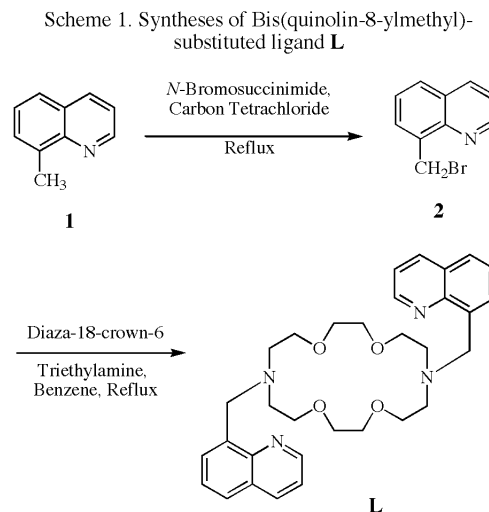
coordinated to barium as well as two bidentate perchlorates and a water molecule, however, the quinoline arms are not involved in the coordination. This is in contrast to the $\text{Cu}_2\text{L}(\mu\text{-OH})(\text{ClO}_4)_3$ complex in which three atoms from the diazacrown and a nitrogen atom from the pendant quinoline arms coordinate to each Cu^{2+} . Also coordinated to both copper ions is a hydroxide ion which forms a single bridge between the two Cu^{2+} .

Results and Discussion.

Synthesis.

The synthetic route to ligand 7,16-bis(quinolin-8-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane **L** is depicted in Scheme 1. Intermediate 8-bromomethylquinoline (**2**) was easily isolated as crystals from ethanol in an 88% yield after the reaction of 8-methylquinoline (**1**) with *N*-bromosuccinimide in the presence of benzoyl peroxide in refluxing carbon tetrachloride. The reaction of diaza-18-crown-6 with 8-bromomethylquinoline (**2**) in the presence of triethylamine as base in anhydrous benzene gave **L** in an 87% yield after purification by column chromatography on silica gel and recrystallization from methylene chloride/ethanol.

The barium (II) and dinuclear copper (II) complexes of ligand **L** were obtained by the reaction of ligand **L** with barium perchlorate trihydrate or cupric perchlorate hexahydrate in acetonitrile. We also tried to prepare the ferric complex of Ligand **L** by the reaction of **L** with ferric perchlorate perhydrate. The salt obtained from this reaction was $\text{L}(\text{HClO}_4)_2 \cdot 1.5 \text{H}_2\text{O}$.



Complexation Thermodynamics.

Interactions of **L** with sodium, potassium, magnesium, barium, cobalt, cupric, nickel, and zinc ions were evaluated by calorimetric and uv-visible spectrophotometric titrations [35-37] in an absolute methanol solution. The values of equilibrium constants ($\log K$) and enthalpy (ΔH) and entropy changes ($T\Delta S$) for these interactions are listed in Table 2. With the exception of nickel ions, ligand **L** forms stable complexes with the metal ions studied ($\log K > 3$). Among the metal ions studied, barium forms the most stable complex with **L**. **L** is selective for barium ions over the other cations studied by more than two orders of magnitude.

Table 1
Crystallographic Data for the Structural Studies

	L	H_2L	BaL	Cu_2L
Formula	$\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_4 \cdot \text{CH}_2\text{Cl}_2$	$\text{C}_{32}\text{H}_{42}\text{N}_4\text{O}_4(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$	$[\text{Ba}(\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_4)(\text{H}_2\text{O})](\text{ClO}_4)_2$	$\text{Cu}_2 \cdot \mu\text{OH}(\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_4)(\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN}$
Formula wt	629.61	786.65	898.42	1028.17
F(000)	668	1656	1824	2112
Crystal size, mm	0.3 x 0.25 x 0.25	0.4 x 0.3 x 0.08	0.34 x 0.30 x 0.25	0.5 x 0.5 x 0.3
μ , mm^{-1}	0.244	0.236	1.305	1.281
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	Pbcn	Cc
a, Å	8.8325(14)	14.685(3)	17.314(3)	19.762(2)
b, Å	13.808(3)	15.035(6)	9.539(2)	14.413(2)
c, Å	13.310(3)	17.369(4)	22.081(3)	14.935(2)
β , °	94.72(2)	90.366(12)	90.00	98.753(12)
Volume, Å ³	1617.8(5)	3835	3646.8	4204.2
Z	2	4	4	4
ρ calc, Mg/m^3	1.293	1.363	1.637	1.624
$2\theta_{\text{max}}$, °	50.00	45.00	50.00	55.00
Independent data	2378 ($R_{\text{int}} = 0.0509$)	5004 ($R_{\text{int}} = 0.0892$)	3217 ($R_{\text{int}} = 0.0263$)	4927 ($R_{\text{int}} = 0.0202$)
Data/restraints/parameters	2375/0/202	5003/0/479	3209/0/236	4922/2/501
Goodness-of-fit on F^2	1.046	1.044	1.048	1.044
Final R indices	$R1 = 0.0727$ $wR2 = 0.1727$	$R1 = 0.0781$ $wR2 = 0.1616$	$R1 = 0.0358$ $wR2 = 0.0890$	$R1 = 0.0564$ $wR2 = 0.1495$
Largest peak, Δ map, $\text{e}\text{\AA}^{-3}$	0.228	0.258	1.031	0.984
Largest hole, Δ map, $\text{e}\text{\AA}^{-3}$	-0.510	-0.256	-0.736	-0.482

Ligand **L** shows selectivity for cupric over nickel ions by about three orders of magnitude. We first intended to determine $\log K$ for the interaction of nickel ions with **L** by the calorimetric method. The very small heat of reaction suggested weak complexation for which the $\log K$ value could not be accurately calculated from the calorimetric data. Therefore, we used a spectroscopic method [37] to evaluate the interaction and obtained $\log K < 1.5$ which is consistent with the calorimetry study. The small $\log K$ value for nickel-**L** complexation is probably a result of the preorganization of the ligand. The nickel ion has a d^8 electronic configuration and is capable of forming square-planar, tetrahedral, or octahedral complexes. However, the preorganization of the ligand may place the donor atoms (especially the four nitrogens) in positions that cannot match the coordination requirement of Ni^{2+} no matter how the ligand adjusts its conformation during complexation. On the other hand, Jahn-Teller effects of the Cu^{2+} complexes may allow Cu^{2+} to bear a greater distortion resulting in a more stable Cu^{2+} -**L** complex compared to Ni^{2+} -**L**.

The calorimetric titration indicated that ligand **L** forms a binuclear complex with cupric ions. (Cu^{2+} :**L**) complexes of both 1:1 and 2:1 (cupric ion to **L**) are observed while all other cations studied form only 1:1 complexes. The data in Table 2 indicate that the thermodynamic quantities for formation of cupric ions-**L** from cupric ions and **L** and for formation of $(Cu^{2+})_2$ -**L** from cupric ions and Cu^{2+} -**L** are similar. Most binuclear copper (II) complexes reported are formed with all-nitrogen-containing macrocyclic ligands [38-42], including the binuclear cupric complex with a tetraazacrown ether containing two 8-hydroxyquinoline arms reported by our laboratory [43]. To the best of our knowledge, $(Cu^{2+})_2$ -**L** is the first binuclear copper(II) complex formed with a diaza-18-crown-6 ligand.

Table 2

Thermodynamic Quantities for the Interactions of Macrocyclic Ligand **L** with several Metal Ions in Methanol Solution [a]

Cation	$\log K$	ΔH	$T\Delta S$
Na^+	3.73 ± 0.02	-22.5 ± 0.3	-1.2
K^+	4.58 ± 0.03	-39.1 ± 0.3	-13.0
Mg^{2+}	4.02 ± 0.07	9.9 ± 0.6	32.8
Ba^{2+}	6.73 ± 0.08 [c]	-19.4 ± 0.4 [c]	19.0
Co^{2+}	3.21 ± 0.06	14.4 ± 0.8	32.7
$Cu^{2+}(1)$ [b]	4.43 ± 0.04	-35.7 ± 0.5	-10.4
$Cu^{2+}(2)$ [b]	4.15 ± 0.04	-32.8 ± 0.6	-9.11
Ni^{2+}	< 1.5		
Zn^{2+}	3.66 ± 0.08		

[a] Both ΔH and $T\Delta S$ values are in kJ/mol. Except for copper(II), all thermodynamic parameters are for 1:1 interactions. The $\log K$ values for nickel and zinc interactions were evaluated at 23° by uv-visible spectrophotometric titrations and other $\log K$ values were determined at 25° by calorimetric titrations. [b] Thermodynamic parameters for $Cu^{2+}(1)$ and $Cu^{2+}(2)$ refer to the formation of the 1:1 complex Cu^{2+} -**L** (from copper(II) and **L**) and the 2:1 complex $(Cu^{2+})_2$ -**L** (from copper(II) and Cu^{2+} -**L**), respectively. [c] Determined by a competitive calorimetric titration.

Entropy effects play a major role in the complexation of magnesium, barium, and cobalt ions (Table 2). The high stability constant of Ba^{2+} -**L** results from both enthalpy and entropy effects. On the other hand, the formation of magnesium and cobalt complexes is essentially entropy driven.

X-ray Crystal Structures.

Crystal structures of the ligand **L**, the protonated ligand H_2 **L** and the barium (Ba **L**) and copper (Cu_2 **L**) complexes of **L** are reported. In some respects, the structures of H_2 **L** and **BaL** reported are similar to those of two 5-chloro-8-hydroxyquinoline diaza-18-crown-6 ligands, **3** and **4** (Figure 2), and the Ba -**4** complex [7,8]. The three ligands have the same crown ring and have sidearms containing quinoline rings attached to the crown ether nitrogen atoms. However, the quinoline rings of **L** are attached at the carbon in the 8 position while the attachment in **3** and **4** are at the 7 and 2 positions, respectively. Also, the quinoline rings in **3** and **4** have a chloride attached at the 5 position and a hydroxy group at the 8 position while there is no substitution of the quinoline ring in **L**. The hydroxy group at the 8 position in **4** provides a good donor atom for complex formation because of its proximity to the nitrogen donor atom. The two donor atoms provide the possibility of bidentate sidearms. These structural differences suggest that the sidearms in **L** may not play the same role as they did in **4**.

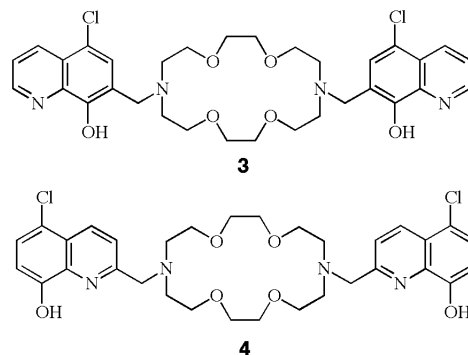
Figure 2. 5-Chloro-8-hydroxyquinoline-substituted ligands **3** and **4**.

Table 3

Hydrogen Bond and Short C-H...O Contact Data for H_2 **L**

D—H...	A	H...A(Å)	D...A(Å)	D C H...A(°)	Translation of A
N1 H1	N19	2.01	2.799	134	x, y, z
C9 H9A	O51	2.51	3.362	127	x, y, z
C9 H9A	O54	2.19	3.333	162	x, y, z
C3 H3A	O52	2.59	3.266	171	x+1, y, z
C10 H10B	O53	2.59	3.461	149	x+1, y, z
N21 H21	N39[a]	1.90	2.710	125	x, y, z
C8 H8A	O64[a]	2.43	3.394	171	x, y, z

[a] In molecule B

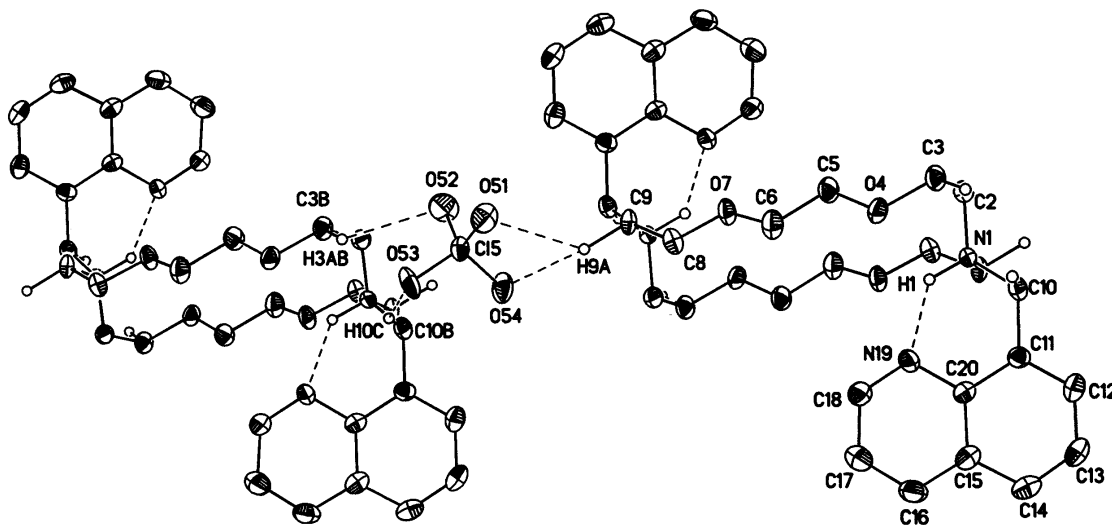


Figure 3. The perchlorate ion sandwiched between two A molecules in the structure of H_2L . The thermal ellipsoids were drawn at the 25% probability level.

Ligand **L** exists in a planar, extended conformation as there are no possible intramolecular interactions between the sidearms and the crown ring. This was not the case in either **3** or **4** where there are $O-H\cdots N$ ring hydrogen bonds, intramolecular for **3** and intermolecular for **4**, involving the hydroxy group on the sidearms and the crown ring nitrogen atoms [7,8].

In the protonated ligand H_2L there are intramolecular interactions involving the protonated nitrogen atoms of the crown ring and the quinoline nitrogen atoms. The H-bond data are listed in Table 3. H_2L is more compact than **L** as the side arms are located above and below the crown ether ring (Figure 3). In this respect, H_2L is similar to **3** and **4** [7]. The unit cell of H_2L contains two crystallographically different but chemically identical molecules. The molecule containing atoms N1 through C20 and their symmetry related

atoms is referred to as molecule A and the molecule containing atoms N21-C40 and symmetry related atoms is called molecule B. The unit cell also contains a CH_3CN molecule which does not interact with either H_2L molecule. Molecule A is interesting because it interacts with each of the oxygens of the ClO₄⁻ ion. This perchlorate ion is sandwiched between two molecule A ligands which are related by a translation of one unit cell in the x direction. The binding of the perchlorate ion is shown in Figure 3. The $C-H\cdots O$ interactions are also listed in Table 3. These data indicate that only one of the interactions, $C9-H9A\cdots O54$, is significant. However, the combination of the four interatomic interactions hold the ClO₄⁻ group in a stationary position. This is indicated by the relatively small values for the equivalent isotropic displacement parameters for the perchlorate oxygens O51-O54, the average of which are $0.081(7)\text{\AA}^2$. A comparison of this value with a similar value for the oxygen atoms in the Cl6 perchlorate ($0.187(46)\text{\AA}^2$), which interacts weakly with molecule A, shows the effect of these intramolecular and packing forces.

The structure of BaL is shown in Figure 4. This complex contains a crystallographic 2-fold axis with the barium ion and a water ligand lying on that axis. The barium ion has a coordination number of eleven, the same as that found for barium in the $Ba^{2+}\text{-4}$ complex [7,8]. A comparison of the types of donor atoms involved in the coordination in the two barium complexes shows similarities but also significant differences. The coordination of the barium by the crown ring is similar in both structures with all six donor atoms of the diaza-18-crown-6 ligand interacting with the cation. Also, a seventh site occupied by a water ligand is present in both complexes. However, in the $Ba^{2+}\text{-4}$ complex, the remaining four sites are occupied by donor atoms of the two bidentate sidearms and the result is a structure resembling a cryptand which results in a very stable complex with a $\log K$ of 12.2

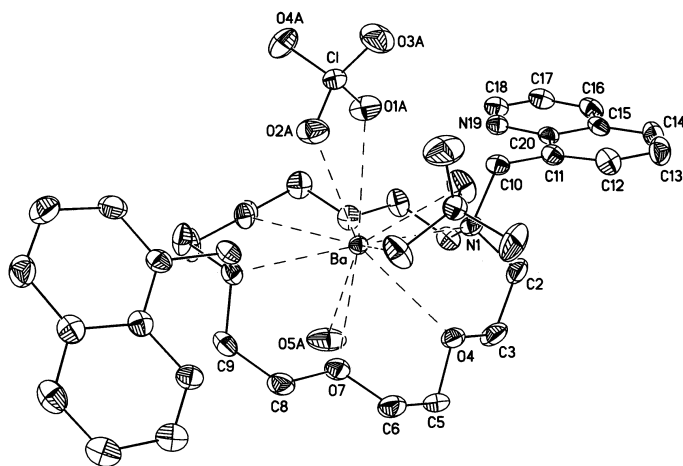


Figure 4. The crystal structure of BaL. Hydrogen atoms were omitted for clarity. The thermal ellipsoids were drawn at the 40% probability level.

[8]. This is in contrast to the BaL complex in which the sidearms are not involved in the complexation of the barium cation and instead the remaining four coordination sites are occupied by oxygens from two bidentate perchlorate ligands. The log *K* value for the formation of BaL is only 6.2, which is approximately the same as that for barium with diaza-18-crown-6 (6.12) [44]. A comparison of the geometry of the coordination spheres for the two barium complexes indicates that they are similar. The 18-crown-6 ring forms a nearly planar arrangement of donor atoms below the barium ion and the water ligand being considerably below the crown ring. The sidearm donor atoms in Ba²⁺-4 and the perchlorate oxygen atoms in BaL are above the barium ion. The interatomic distances (barium-donor atoms) of BaL are listed in Table 4.

Table 4
Interatomic distances (Å) involving barium in BaL

atoms	distances (Å)
Ba - N1 _{ring}	3.068(3)
Ba - O4 _{ring}	2.853(3)
Ba - O7 _{ring}	2.820(3)
Ba - O1AcIO ₄ ⁻	3.006(4)
Ba - O2AcIO ₄ ⁻	2.928(4)
Ba - O5AcIO ₄ ⁻	2.889(6)

The Cu₂L complex is of interest for a number of reasons but it is particularly interesting because the two copper(II) ions are bound by the 18-crown-6 and are linked by a hydroxy oxygen. The conformation of the crown ring in Cu₂L differs significantly from that of the crown ring in BaL. The conformation of the crown ring in BaL is similar to that found in other 18-crown-6 complexes in

which group I and group II cations lie in the cavity of the macrocycle and interact electrostatically with the donor atoms of the ring. The result is an arrangement of the ring in which the D-C-C-D (D = N or O donor atoms) torsion angles are approximately 60° while the C-C-D-C torsion angles are about 180°. However, when two transition metal ions are bound, the required geometry of the transition metal ions produces a large change in the conformation of the ligand. The three atoms, Cu-OH-Cu, are too large to lie inside the cavity so they sit above the cavity and the copper ions interact with the donor atoms of the ring and the sidearms as shown in Figure 5. Each copper(II) is coordinated by two nitrogen atoms (a ring and a quinoline nitrogen), two ring oxygen atoms and the linking hydroxy oxygen atom. Both copper ions have a square pyramidal coordination and in each case the base consists of two nitrogen atoms, one ring oxygen and the hydroxy oxygen atom. The apical sites are occupied by the second ring oxygen atoms, O4 for Cu1 and O13 for Cu2. The bond distances and angles for the coordination of the copper ions are listed in Table 5. The copper-O41 distances listed in Table 5 establish that the hydroxy oxygen is midway between the two copper atoms.

The geometry of the three-atom guest of Cu₂L is similar to that found in other dinuclear copper complexes. In the [Cu₂L(μ-OH)]³⁺ ion, the copper-oxygen-copper angle is 135.7° and the copper-copper interatomic distance is 3.527 Å, both of which are within the ranges reported in similar complexes. In previously reported copper-hydroxy-copper moieties the angles range from 100 to 146° and the copper-copper distances range from 2.972 to 3.663 Å [45-46].

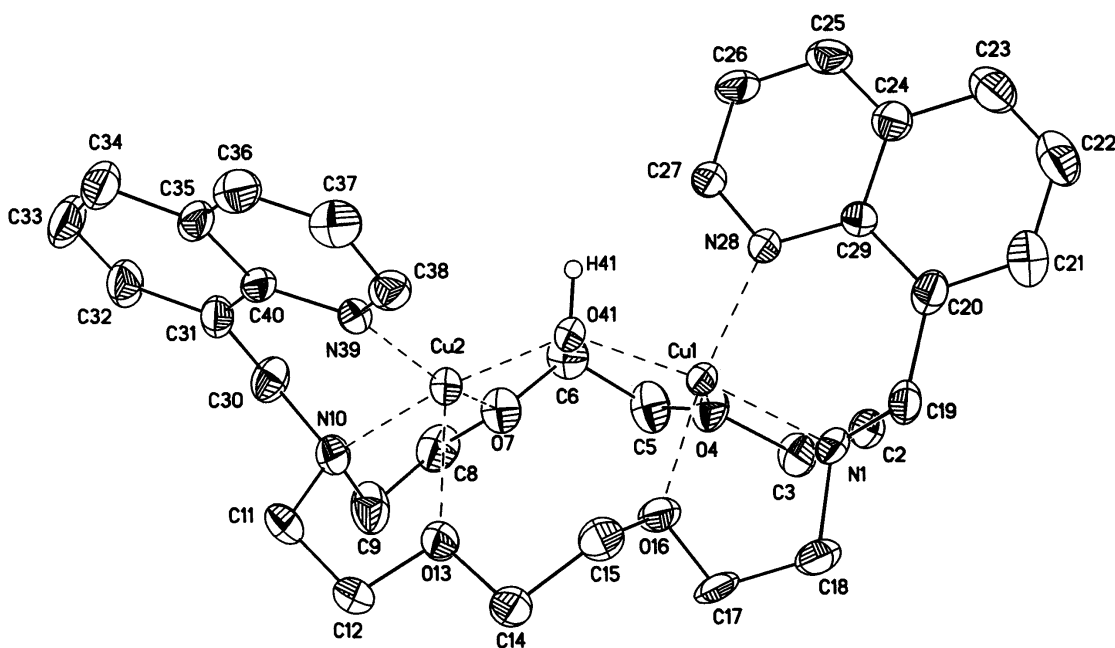


Figure 5. The crystal structure of Cu₂L. The perchlorate ions, the acetonitrile molecule, and the hydrogen atoms were omitted for clarity. The thermal ellipsoids were drawn at the 30% probability level.

Table 5
Selected Interatomic distances (Å) and angles (°) of Cu₂L

Cu1 - O41	1.903(5)	Cu2 - O41	1.904(5)
Cu1 - N1	1.996(6)	Cu2 - N10	2.000(7)
Cu1 - N28	2.017(6)	Cu2 - N39	2.020(6)
Cu1 - O16	2.010(6)	Cu2 - O7	2.069(6)
Cu1 - O4	2.347(6)	Cu2 - O13	2.368(6)
O41 - Cu1 - N1	171.4(3)	O41 - Cu2 - N10	171.3(3)
O41 - Cu1 - O16	89.0(2)	O41 - Cu2 - O7	91.1(2)
O41 - Cu1 - N28	97.4(2)	O41 - Cu2 - N39	98.0(2)
O41 - Cu1 - O4	101.3(2)	O41 - Cu2 - O13	100.2(2)
N1 - Cu1 - O16	82.7(3)	N10 - Cu2 - O7	82.8(3)
N1 - Cu1 - N28	91.2(3)	N10 - Cu2 - N39	90.1(3)
N1 - Cu1 - O47	8.3(3)	N10 - Cu2 - O13	76.2(3)
N28 - Cu1 - O16	164.0(3)	N39 - Cu2 - O7	154.9(3)
N28 - Cu1 - O4	91.3(3)	N39 - Cu2 - O13	91.8(2)
O16 - Cu1 - O4	101.9(3)	O7 - Cu2 - O13	109.7(2)

UV-Visible Spectra.

Selected uv-visible spectra of free and metal-ion complexed ligand **L** in methanol are shown in Figure 6. Ligand **L** exhibits two absorption bands originating from the quinoline groups, one at 227 nm ($\epsilon = 7.38 \times 10^4 M^{-1}cm^{-1}$) and the other at 284 nm ($\epsilon = 9.51 \times 10^3 M^{-1}cm^{-1}$). Upon addition of metal ions (10 times the ligand concentration) to the ligand solution, changes in the ligand spectrum are observed. Among the metal ions studied (magnesium, barium, copper(II), cobalt, nickel, and zinc) copper(II) causes the most significant changes and barium the least changes in the ligand spectrum. In the presence of copper(II), the intensity of the absorption bands is increased significantly and the absorption maxima of the ligand at 227 and 284 nm are shifted to 234 and 279 nm, respectively. These results suggest a different type of binding for copper(II) from that of the other cations, probably due to the binuclear complex. The very small change in the uv spectrum of the ligand produced by barium was surprising since barium formed a very stable complex with the ligand. A possible reason for this is that the two quinoline groups do not

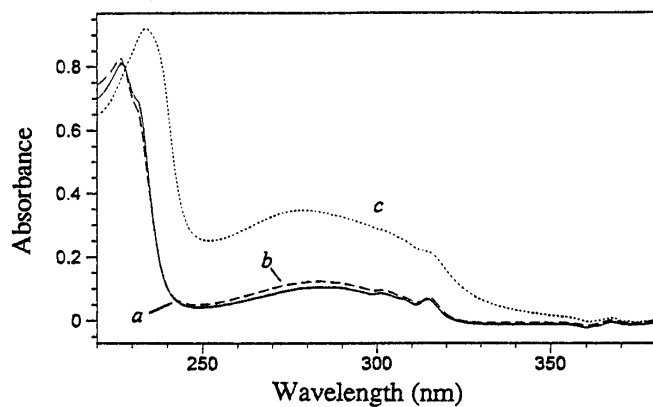


Figure 6. Uv-visible spectra of **L** (a) and its Ba²⁺ (b) and Cu²⁺ (c) complexes in methanol.

interact with the barium ion, which was supported by nmr and X-ray crystal structural studies.

¹H nmr Spectra.

¹H nmr spectra of free and complexed **L** in perdeuterated methanol are shown in Figure 7. The presence of barium does not result in a significant change in quinoline proton signals ($\delta = 7.5 - 9.0$ ppm), indicating that the quinoline rings of the ligand are not involved in the binding in the solution structure as well as in the solid state structure. On the other hand, large changes in the ¹H nmr spectra of macrocyclic methylenes ($\delta = 3.0 - 4.5$ ppm) indicate a strong interaction of the macroring donor atoms of the ligand with magnesium and barium ions.

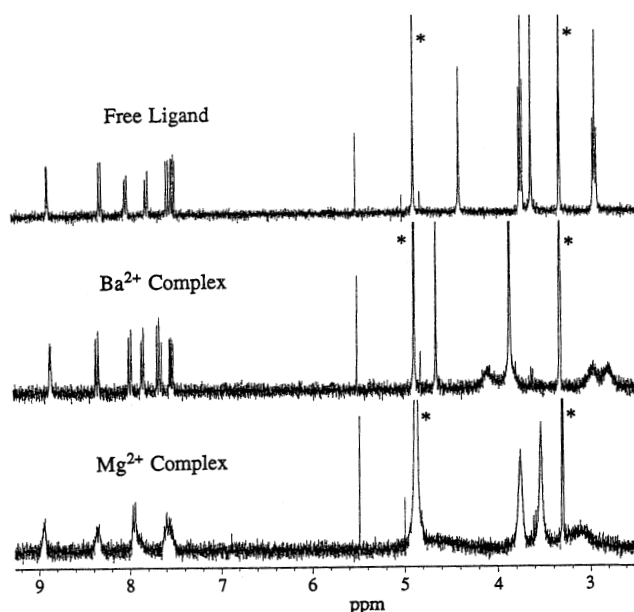


Figure 7. ¹H nmr spectra of free ligand **L** and its Ba²⁺ and Mg²⁺ complexes in perdeuteromethanol.

Magnetic Properties of Copper(II) Complexes.

Dinuclear complexes of copper(II) have been studied extensively due to their interesting magnetic properties [47]. The copper ions in dinuclear copper compounds can be coupled antiferromagnetically or ferromagnetically. Hydroxide bridged dinuclear copper complexes are often antiferromagnetically coupled [45,46]. The room temperature solution (acetonitrile and dimethyl sulfoxide) magnetic moment ($\mu_{\text{eff}}/\text{Cu}$) of 1.28 BM for Cu₂L(μ -OH)³⁺ indicates antiferromagnetic coupling between the copper ions and gives an average spin of 0.62 for each copper. These data indicate that the hydroxo bridged complex is present in the solution as well as the solid state. Due to this coupling, ¹H nmr signals for Cu₂L(μ -OH)³⁺ can be observed [48]. If the

solution structure of $\text{Cu}_2\text{L}(\mu\text{-OH})^{3+}$ is the same as the solid state structure, then half of the protons on the diazacrown will be nonequivalent while the protons on the quinoline side arms will be equivalent and a total of 20 different ^1H nmr signals are expected. Eleven isotropically shifted ^1H nmr signals are observed for $\text{Cu}_2\text{L}(\mu\text{-OH})^{3+}$: five of which are sharp ($\delta = 16.8, 14.7, 12.7, 8.0,$ and 7.3 ppm), four of which are broad ($\delta = 17.0, 14.2, 6.6,$ and 6.3 ppm), and two of which are very broad ($\delta = 41$ and 66 ppm). The nine most upfield signals are narrow enough to be integrated and all integrate to one with respect to each other. Thus, either several protons are broadened to the extent that they are not observed or the structure of the molecule is different in solution than in the solid state.

EXPERIMENTAL

The ^1H and ^{13}C nmr spectra were recorded at 300 MHz in deuterochloroform. Hrms were obtained using the fast atom bombardment (fab) technique. All solvents were purified by standard procedures. Starting materials were commercial reagents and were used without further purification. Reagent grade inorganic chemicals were obtained from the indicated sources and used without further purification: sodium bromide (Baker), cupric chloride (Wasatch), magnesium perchlorate (Allied), barium bromide (Johnson-Matthey), cobalt chloride hexahydrate (Fisher), cupric chloride (Aldrich), nickel nitrate hexahydrate (Baker), and zinc chloride (Mallinckrodt AR).

Preparation of 8-Bromomethylquinoline (**2**) (Scheme 1).

8-Bromomethylquinoline was prepared in a manner similar to that described by Kimura *et al.* [49]. A solution of 8-methylquinoline (**1**) (12.6 g, 88 mmoles) in 400 ml of carbon tetrachloride was refluxed with *N*-bromosuccinimide (16.0 g, 90 mmoles) in the presence of benzoyl peroxide (0.7 g) for 12 hours. The hot solution was filtered and the brown filtrate was evaporated under reduced pressure. The residue was dissolved in 50 ml of chloroform, and the solution was washed twice with saturated aqueous sodium carbonate and once with water. The organic phase was dried over anhydrous sodium sulfate and evaporated. The residue was recrystallized from ethanol to give 17.2 g (88%) of **2** as white crystals. The mp and nmr spectral data were identical to those reported [49].

7,16-Bis(quinolin-8-ylmethyl)-1,4,10,13-tetroxa-7,16-diazacyclooctadecane (**L**) (Scheme 1).

A solution of **2** (2.0 g, 9.0 mmoles) in 50 ml of benzene was added dropwise to a solution of diaza-18-crown-6 (1.0 g, 3.8 mmoles) and triethylamine (1.6 g, 15.8 mmoles) in 50 ml of benzene under nitrogen. The mixture was stirred at room temperature for 20 hours and then refluxed for 2 hours. The solvent was evaporated under reduced pressure. The residue was treated with a mixture of water and chloroform (1:2). The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. After evaporation, the residue was purified by column chromatography on silica gel with acetone as eluent. The product was recrystallized from methylene chloride/ethanol to give 1.81 g (87%) of **L** as yellow crystals, mp 95-96°; ^1H nmr: δ 2.93. (t, 8H), 3.66 (m, 16H), 4.43 (s, 4H), 7.36 (dd, 2H), 7.52 (d, 2H),

7.65 (dd, 2H), 8.02 (d, 2H), 8.11 (dd, 2H), 8.90 (dd, 2H); ^{13}C nmr: δ 54.78, 54.86, 70.33, 71.00, 120.95, 126.53, 126.74, 128.36, 129.20, 136.54, 138.23, 147.02, 149.42; hrms: *m/z* calcd. for $\text{C}_{32}\text{H}_{41}\text{O}_4\text{N}_4$ ($\text{M}+\text{H}$) $^+$: 545.3130, found: 545.3132. Crystals of this compound suitable for X-ray analysis were grown by slow evaporation of a dilute solution with a mixed methylene chloride:methanol solvent (1:2) at room temperature.

Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_4\cdot\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$: C, 61.20; H, 6.85. Found: C, 61.24; H, 6.62.

Preparation of $[\text{Ba}(\text{L})](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$.

To **L** (13.6 mg, 0.025 mmole) dissolved in 1 ml of acetonitrile was added barium perchlorate trihydrate (9.75 mg, 0.025 mmole) dissolved in 1 ml of acetonitrile at room temperature. Crystals of the complex suitable for X-ray analyses were obtained by slow evaporation of this solution at room temperature to give 18.7 mg (85%).

Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_{12}\cdot\text{Cl}_2\text{Ba}$: C, 43.63; H, 4.58. Found: C, 43.58; H, 4.72.

Preparation of $[\text{Cu}_2(\text{L})(\text{OH})](\text{ClO}_4)_3\cdot\text{CH}_3\text{CN}$.

This dark blue complex was obtained in a similar fashion as for the above complex except that 2 equivalents of cupric perchlorate hexahydrate were used instead of the barium salt to give 23.1 mg (90%) of the complex.

Anal. Calcd for $\text{C}_{32}\text{H}_{41}\text{O}_{17}\text{Cl}_3\text{Cu}_2\cdot\text{CH}_3\text{CN}$: C, 39.72; H, 4.32. Found: C, 40.10; H, 4.65.

Preparation of $\text{L}(\text{HClO}_4)_2\cdot 1.5 \text{H}_2\text{O}$.

In an attempt to prepare the ferric complex of **L**, 13.6 mg (0.025 mmole) of **L** was dissolved in 1 ml of acetonitrile and 8.86 mg (0.025 mmole) of ferric perchlorate perhydrate dissolved in 1 ml of acetonitrile was added at room temperature. Crystals of the salt $\text{L}(\text{HClO}_4)_2\cdot\text{CH}_3\text{CN}$ suitable for X-ray analysis were obtained by slow evaporation of this solution at room temperature. *Caution!* The perchlorate salts must be handled with care as they are potential explosives.

Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_4\cdot 2 \text{HClO}_4\cdot 1.5 \text{H}_2\text{O}$: C, 49.74; H, 5.87. Found: C, 49.65; H, 5.69.

Preparation of Mg-L.

The Mg-L complex was formed by mixing magnesium perchlorate with **L** in perdeuterated methanol in an nmr tube.

Calorimetric Measurements.

Values of $\log K$, ΔH , and $T\Delta S$ for the interactions of metal ions (except nickel and zinc ions) with **L** were determined as described earlier [35] in absolute methanol solutions at $25.0 \pm 0.1^\circ$ by titration calorimetry using a Tronac Model 450 calorimeter equipped with a 20 ml reaction vessel. The metal ion solutions were titrated into the macrocyclic ligand solutions and the titrations were carried out to a 2-fold excess of metal ions. In general, concentrations of the ligands were $2.2 - 3.2 \times 10^{-3} \text{ M}$ and those of the metal ions $7.5 \times 10^{-2} \text{ M} - 0.1 \text{ M}$. In the case of cupric ion, the concentration of the ligand was $1.5 \times 10^{-3} \text{ M}$ and that of cupric ion, $5.1 \times 10^{-2} \text{ M}$. After a 2:1 (cupric ion:L) complex was observed, the cupric ion concentration was increased to 0.11 M. The method used to process the calorimetric data and to calculate the $\log K$ and ΔH values has been described [36]. Calorimetric titrations showed no detectable heat for the nickel ion-L interaction and a white precipitate was observed when the ligand ($1.5 - 2.1 \times 10^{-3} \text{ M}$) was titrated with zinc ion. Therefore, $\log K$ values for nickel and zinc

ion interactions were evaluated by a uv-visible spectrophotometric method.

Uv-Visible Spectral Measurements.

Uv-visible spectra were recorded at $23 \pm 1^\circ$ in a 1-cm quartz cell by using a Hewlett-Packard 8453 spectrophotometer. Absolute methanol was used as the solvent. For the determination of stability constants, a $5.0 \times 10^{-5} M$ **L** solution (2.50 mL) was titrated by nickel or zinc ion solutions and the uv-visible spectra were recorded after each titration. The method described by Bourson and Valeur [37] was employed to calculate log *K* values. Absorbance data at 280 and 284 nm were used to make the calculations for **L**-zinc and **L**-nickel interactions, respectively. Since nickel nitrate showed a weak absorption at 284 nm in methanol solution ($\epsilon = 10.9 M^{-1}cm^{-1}$), the values of ligand absorbance were corrected by subtracting the nickel absorption.

¹H nmr Spectral Measurements.

¹H nmr spectra of free and complexed **L** were recorded using a Varian Unity INOVA 300 (300 MHz) spectrometer at 25° in perdeuterated methanol. Tetramethylsilane (TMS) was used as the internal standard. The concentration of **L** was $5 \times 10^{-3} M$ and those of the metal ions were 6 times that of the ligand. ¹H nmr measurements of Cu₂**L**(μ-OH)(ClO₄)₃ were recorded in acetonitrile-*d*₃ and referenced to residual solvent ($\delta = 1.98$ ppm). Solution magnetic susceptibility measurements were done with the Evans susceptibility method [50,51].

X-ray Structure Determinations.

The crystal data and some experimental details for **L**·CH₂Cl₂ (**L**), H₂**L**(ClO₄)₂·CH₃CN (H₂**L**), [Ba**L**(H₂O)(ClO₄)₂] (Ba**L**), and Cu₂(μ-OH)**L**·CH₃CN (Cu₂**L**) are listed in Table 1. The intensity data for the four structures were collected using a Bruker P4 automated diffractometer which utilized MoK α radiation ($\lambda = 0.71073$ Å). Additional crystal data and experimental details are contained in the supplementary material. The four structures were solved using direct methods followed by Fourier methods to complete the structures. The ligand **L** in both **L** and H₂**L** lies about a center of inversion. In the protonated ligand there are two crystallographically independent molecules in the unit cell so its asymmetric unit consists of two half molecules. The barium complex contains a crystallographic two-fold axis with the barium ion and water ligand and oxygen atom (O5A) lying on the axis. The copper complex does not contain crystallographic symmetry though it does contain a pseudo two-fold axis. There is disorder in the copper complex involving atoms in the region of C17 but it was only possible to resolve the disorder for C17.

All nonhydrogen atoms in the four structures except the perchlorate oxygen atoms of the copper complex were refined anisotropically. These oxygen atoms were disordered as indicated by their large isotropic thermal parameters. The carbon atom of the methylene chloride in **L** was disordered across a center of inversion but it was possible to refine the two partial atoms anisotropically. Positions for all hydrogen atoms were calculated with the exception of the hydrogen atoms bonded to C9 in **L**, H₂**L**, and Ba**L**, the hydrogen atoms of the acetonitrile ligands in H₂**L** and Cu₂**L**, the water hydrogens in the barium complex and the hydroxy hydrogen and the hydrogens bonded to C17, C17' and C18 of the copper complex. It was possible to obtain positions for all of these hydrogen atoms using difference maps with the exception of the hydrogen atoms of the acetonitrile ligands in

the H₂**L** and Cu₂**L** compounds and the hydrogen atoms bonded to C17 and C17' and to the neighboring carbon C18 in the copper complex. The riding model was used for the refinement of all hydrogen atoms. All programs used in the solution, refinement and display of these structures are contained in the SHELXTL PC [52] program package.

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Supplementary Material.

Atomic coordinates, displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Centre.

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