

## Synthesis of a Flexible Ligand for Assembling Two Metal Ions in Close Proximity. Crystal Structures of Binuclear Nickel and Copper Complexes

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### Introduction

Binuclear metal complexes are successful devices for the recognition and assembly of external species. For this reason, the ligands obtained by forming binuclear complexes with various metal ions are of great interest. If the two metal ions coordinated present an unsaturated coordination environment, the binuclear complex can be used as receptor for a secondary species. In this way, binuclear complexes are able to mimic many biological sites, especially those where the two metals can cooperate to form an active center as, for example, in oxygen receptors, activators, and carriers.<sup>1</sup> The natures of the two metal ions, their coordination requirements, and the distance between them are the key elements in assembling host species, which are the targets of current research. Binuclear hosts are often obtained by using macrocyclic ligands with a high number of donor atoms, and usually, the transition metal ions guide the ligand arrangement fixed by the coordination requirements of the ions.<sup>2</sup>

We have synthesized the new noncyclic ligand 2,6-bis{[bis-(2-aminoethyl)amino]methyl}phenol, **L-OH** (Figure 1), with which it is possible to assemble two transition metal ions close to each other, forming simple and stable unsaturated binuclear complexes.

### Experimental Section

**Syntheses.** (a) **2,6-Bis{[bis(2-aminoethyl)amino]methyl}phenol (L-OH).** This ligand was obtained as its hydrobromide salt by reacting 2 equiv of *N,N'*-iminodiethylenebis(phthalimide)<sup>3</sup> (7.3 g, 0.02 mol) with 1 equivalent of 2,6-dibromoanisole<sup>4</sup> (2.9 g, 0.01 mol) in refluxing DMF (400 mL) in the presence of Na<sub>2</sub>CO<sub>3</sub> as base. The deprotection of the nitrogen atoms was carried out in aqueous 3 M HCl, and the

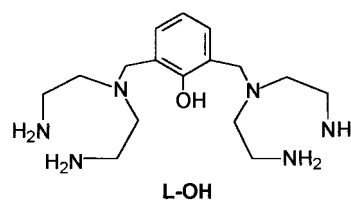


Figure 1. Structure of the ligand **L-OH**.

demethylation of the aromatic oxygen, in HBr/CH<sub>3</sub>COOH/phenol. Yield of **L-OH**·6HBr: 63%. <sup>1</sup>H NMR (D<sub>2</sub>O, pH 3, 25 °C): 3.19 (t, 8H), 3.27 (t, 8H), 4.17 (s, 4H), 6.94 (t, 1H), 7.29 (d, 2H) ppm. <sup>13</sup>C NMR: 36.1, 51.0, 55.0, 120.8, 122.4, 133.8, 156.4 ppm. MS (FAB): *m/z* 326 (M + H<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>38</sub>Br<sub>6</sub>N<sub>6</sub>O: C, 23.73; H, 4.73; N, 10.38. Found: C, 23.8; H, 4.9; N, 10.3.

(b) **[Cu<sub>2</sub>(L-O)(OH)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (1).** A sample of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (22.2 mg, 0.06 mmol) in water (10 mL) was slowly added to an aqueous solution (10 mL) of **L-OH** (9.7 mg, 0.03 mmol). The resulting solution was stirred for 10 min at room temperature, followed by evaporation of the solvent, which led to crystallization of the complex as blue crystals. Anal. Calcd for C<sub>16</sub>H<sub>34</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>11</sub>: C, 28.08; H, 5.01; N, 12.28. Found: C, 28.0; H, 4.9; N, 12.2.

(c) **[Ni<sub>2</sub>(L-O)Cl<sub>3</sub> (2).** A sample of NiCl<sub>2</sub>·6H<sub>2</sub>O (14.3 mg, 0.06 mmol) in water (10 mL) was slowly added to an aqueous solution (10 mL) of **L-OH** (9.7 mg, 0.03 mmol). The resulting solution was stirred for 10 min at room temperature, followed by evaporation of the solvent, which led to crystallization of the complex as green crystals. Anal. Calcd for C<sub>16</sub>H<sub>31</sub>Cl<sub>3</sub>N<sub>6</sub>Ni<sub>2</sub>O: C, 35.12; H, 5.71; N, 15.36. Found: C, 35.0; H, 5.7; N, 15.2.

**X-ray Crystallography.** The crystal structures of both **1** and **2** were solved by direct methods using the SIR-97 program<sup>5</sup> and subsequently refined by the full-matrix least-squares program SHELXL-97.<sup>6</sup> The intensity data were collected on a Siemens P4 diffractometer, in the ranges 5 < 2θ < 130° and 8 < 2θ < 130°, respectively, for **1** and **2**, using graphite-monochromated Cu Kα radiation and the θ–2θ technique. The intensities were corrected for Lorentz and polarization effects. After the structures were solved, an absorption correction was applied by using the DIFABS<sup>7</sup> program. Crystal data and structure determination parameters are reported in Table 1. Geometrical calculations were performed by PARST97,<sup>8</sup> and molecular plots were produced by the ORTEP program.<sup>9</sup>

**Emf Measurements.** Equilibrium constants for complexation reactions were determined by pH-metric measurements (pH = –log [H<sup>+</sup>]) in 0.15 mol/L Me<sub>4</sub>NCl at 298.1 ± 0.1 K, using the fully automatic equipment that has been already described;<sup>10</sup> the emf data were acquired with the PASAT computer program.<sup>11</sup> A combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO<sub>2</sub>-free Me<sub>4</sub>NOH solutions and determining the equivalent point by Gran's method,<sup>12</sup> which gives the standard potential *E*<sup>o</sup> and the ionic product of water (p*K*<sub>w</sub> = 13.73(1) at 298.1 K in 0.15 mol/L Me<sub>4</sub>NCl; *K*<sub>w</sub> = [H<sup>+</sup>][OH<sup>–</sup>]). Ligand and metal ion concentrations of 1 × 10<sup>–3</sup>–2 × 10<sup>–3</sup> M were employed for the potentiometric

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**Table 1.** Crystal Data and Structure Refinement Details for **1** and **2**

	<b>1</b>	<b>2</b>
empirical formula	C <sub>16</sub> H <sub>34</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>11</sub>	C <sub>16</sub> H <sub>31</sub> Cl <sub>3</sub> N <sub>6</sub> Ni <sub>2</sub> O
fw	684.47	547.24
temp (K)	293	293
$\lambda$ (Å)	1.541 80	1.541 '80
space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	14.368(1)	11.142(5)
<i>b</i> (Å)	14.099(1)	10.307(4)
<i>c</i> (Å)	26.116(3)	18.692(8)
$\beta$ (deg)	97.009(8)	91.15(3)
<i>V</i> (Å <sup>3</sup> )	5250.9(8)	2146(2)
<i>Z</i>	8	4
<i>d</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.732	1.694
abs coeff (mm <sup>-1</sup> )	4.458	5.785
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> ): <sup>a</sup> <i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub>	0.0550, 0.1505	0.0617, 0.1861
<i>R</i> indices (all data): <i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub>	0.0598, 0.1549	0.0735, 0.1974

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P$  is  $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$ .

measurements. At least three measurements were performed for each reaction in the pH range 2–11, and the HYPERQUAD computer program was used to process the potentiometric data.<sup>13</sup> All titrations were treated either as single sets or as separate entities, for each system, without significant variation in the values of the determined constants.

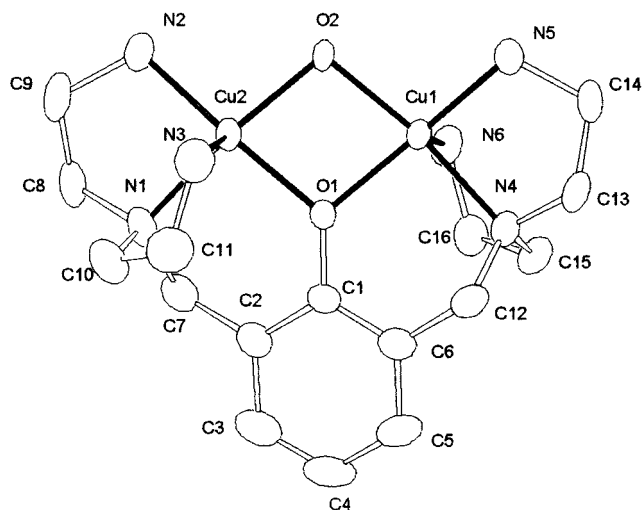
**NMR Spectroscopy.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC-200 instrument, operating at 200.13 and 50.33 MHz, respectively. <sup>1</sup>H NMR peak positions are reported with respect to HOD ( $\delta = 4.75$  ppm), and dioxane is the reference standard for the <sup>13</sup>C NMR measurements ( $\delta = 67.4$  ppm).

## Results and Discussion

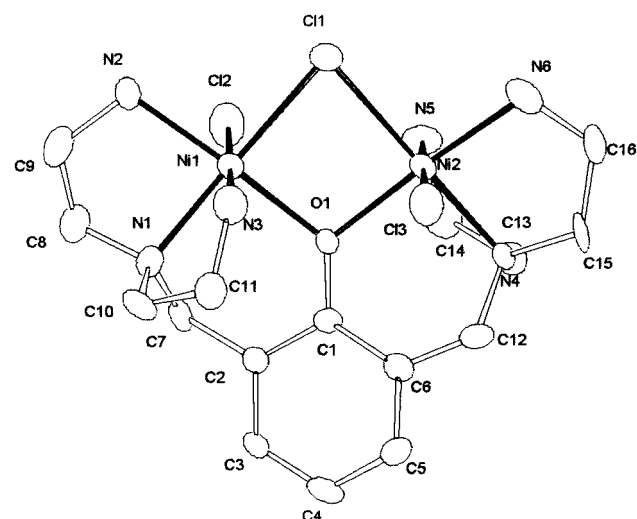
**Descriptions of the X-ray Crystal Structures of [Cu<sub>2</sub>-(L-O)(OH)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**1**) and Ni<sub>2</sub>(L-O)Cl<sub>3</sub> (**2**).** The asymmetric unit of **1** contains two independent complex cations, four perchlorate counteranions, and two molecules of water. The two independent complex cations are virtually identical, having an rms (root mean square) value of 0.146 (the rms value was determined using all the non-hydrogen atoms of the two complex cations). Each copper atom (Cu1, Cu2, Cu3, Cu4) is pentacoordinated by the three nitrogen atoms and the oxygen atom of the L-O ligand and by the oxygen atom of the hydroxide anion. The two copper atoms of each independent dimer are bridged by the two oxygen atoms (see Figure 2), and it is noteworthy that the complex cation has a noncrystallographic 2-fold axis, passing through the atoms C1, C4, O1, O2 [C17, C20, O3, O4].

The coordination geometry of each copper is an irregular square pyramid, with the four atoms of each base, (N1, N2, O1, O2) and (O1, O2, N4, N5) [(N7, N8, O3, O4) and (N10, N11, O3, O4)] well in a plane (the maximum deviations from the mean planes are 0.161(4), 0.040(4), 0.129(5), and 0.089(5) Å for N2, N5, N8, and N11, respectively). The copper atoms are 0.2043(7), 0.2188(7), 0.2246(7), and 0.2526(7) Å (Cu1, Cu2, Cu3, and Cu4, respectively) from the mean planes of the square bases and are shifted toward the atoms in the apical positions. The mean planes (N1, N2, O1, O2) and (N4, N5, O1, O2) [(N7, N8, O3, O4) and (N10, N11, O3, O4)] are almost coplanar, the angle between them being 6.4(1)° [6.8(1)°], and both form angles of 15.3(1)° [16.6(1), 13.4(1)°] with the aromatic ring.

The Cu···Cu, Cu···N, and Cu···O distances (see Figure 2) are in agreement with those found for analogue compounds (Cu···Cu distance average 3.004 Å for **1**) by an analysis carried out using the Cambridge Structural Database (CSD), V5.17.<sup>14</sup> A



**Figure 2.** ORTEP view of compound **1**. Relevant bond distances (Å): Cu1–Cu2 3.0107(8), Cu1–O1 1.965(3), Cu1–O2 1.956(3), Cu1–N4 2.045(4), Cu1–N5 1.991(4), Cu1–N6 2.285(4), Cu2–O1 1.981(3), Cu2–O2 1.963(3), Cu2–N1 2.039(4), Cu2–N2 2.002(3), Cu2–N3 2.217(4), Cu3–Cu4 2.998(1), Cu3–O3 1.961(3), Cu3–O4 1.956(3), Cu3–N10 2.053(4), Cu3–N11 2.000(5), Cu3–N12 2.259(5), Cu4–O3 1.994(3), Cu4–O4 1.949(3), Cu4–N7 2.046(4), Cu4–N8 1.998(4), Cu4–N9 2.242(5).



**Figure 3.** ORTEP view of compound **2**. Relevant bond distances: Ni1–Ni2 3.226(2), Ni1–C11 2.451(2), Ni1–C12 2.569(2), Ni1–O1 2.069(4), Ni1–N1 2.092(6), Ni1–N2 2.091(6), Ni1–N3 2.069(6), Ni2–C11 2.457(2), Ni2–C13 2.548(2), Ni2–O1 2.057(4), Ni2–N4 2.080(6), Ni2–N5 2.077(6), Ni2–N6 2.090(7).

network of hydrogen bonds involving the hydrogens bonded to the nitrogen atoms of the ligands and the oxygen atoms of the perchlorate counteranions is present, with distances of interaction in the range 2.030(4)–2.997(1) Å.

The asymmetric unit of **2** contains one complex molecule. The nickel atoms are hexacoordinated by the three nitrogens and the oxygen atom of the L-O ligand and by two chloride ions (see Figure 3). As in **1**, atoms C1, C4, O1, and C11 lie on a noncrystallographic 2-fold axis.

The coordination geometry for each nickel can be described as an octahedron in which atoms N1, N2, O1, and C11 [N4, N6, O1, and C11] are at the corners of the equatorial base and atoms N3 and C12 [N5 and C13] occupy the apical positions.

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**Table 2.** Logarithms of the Equilibrium Constants Determined in 0.15 mol/L NMe<sub>4</sub>Cl at 298.1 K for the Complexation Reactions of **L-OH** with Ni(II) and Cu(II) Ions

reaction	log <i>K</i> <sup>a</sup>	
	Ni(II)	Cu(II)
M <sup>2+</sup> + 3H <sup>+</sup> + <b>L-OH</b> = M( <b>L-OH</b> )H <sub>3</sub> <sup>5+</sup>		36.61(1)
M <sup>2+</sup> + 2H <sup>+</sup> + <b>L-OH</b> = MH <sub>2</sub> ( <b>L-OH</b> ) <sup>4+</sup>	28.64(1)	33.02(1)
M <sup>2+</sup> + H <sup>+</sup> + <b>L-OH</b> = MH( <b>L-OH</b> ) <sup>3+</sup>	23.96(1)	28.27(1)
M <sup>2+</sup> + <b>L-OH</b> = M( <b>L-OH</b> ) <sup>2+</sup>	15.13(2)	21.01(1)
M <sup>2+</sup> + <b>L-OH</b> + H <sub>2</sub> O = M( <b>L-O</b> ) <sup>+</sup> + H <sub>3</sub> O <sup>+</sup>	5.49(2)	11.60(1)
2M <sup>2+</sup> + <b>L-OH</b> = M <sub>2</sub> ( <b>L-OH</b> ) <sup>4+</sup>		30.27(1)
2M <sup>2+</sup> + <b>L-OH</b> + H <sub>2</sub> O = M <sub>2</sub> ( <b>L-O</b> ) <sup>3+</sup> + H <sub>3</sub> O <sup>+</sup>	15.94(1)	25.95(1)
M <sub>2</sub> ( <b>L-O</b> ) <sup>3+</sup> + OH <sup>-</sup> = M <sub>2</sub> ( <b>L-O</b> )OH <sup>2+</sup>	5.18(1)	7.65(1)

<sup>a</sup> Values in parentheses are the standard deviations in the least significant digits.

The maximum deviations from the mean square planes (N1, N2, O1, C11) and (N4, N6, O1, C11) are due to N2 and N6 [0.137(6) and 0.120 (7) Å, respectively], with the nickel ions Ni1 and Ni2 0.010(1) and 0.039(1) Å from the base, shifted toward the chloride ions Cl2 and Cl3, respectively. The angle between the mean plane formed by the four atoms defining the base of the octahedron and the vector Cl2–N3 [Cl4–N5] is 86.8(1)° [87.0(1)°]. The mean planes (N1, N2, O1, C11) and (N4, N6, O1, C11) are almost coplanar [the angle between them is 2.5(1)°] and form angles of 10.2(2) and 11.5(2)°, respectively, with the aromatic ring. The conformation assumed by the **L-O** ligand is similar to that shown by the same ligand in complex **1**; in fact, the rms factor is 0.252 (determined using all the non-hydrogen atoms of the ligand in the two complexes). An analysis carried out using the CSD revealed that the distances Ni···Ni, Ni···Cl, Ni···O, and Ni···N (see Figure 3) are comparable to those previously reported for nickel(II) in similar complexes.<sup>14</sup> No significant hydrogen bonds are present.

**Metal Ion Coordination in Aqueous Solution.** The great tendency of **L-OH** to assemble two metal ions is well illustrated by the stability constants determined in aqueous solution by potentiometric measurements and reported in Table 2. For the reaction 2M<sup>2+</sup> + **L-OH** + H<sub>2</sub>O = [M<sub>2</sub>(**L-O**)]<sup>3+</sup> + H<sub>3</sub>O<sup>+</sup>, the stability constant values are log *K* = 25.95 and log *K* = 15.94 for Cu(II) and Ni(II), respectively. As shown, the formation of the binuclear species involves the simultaneous deprotonation of the hydroxyl group of the phenol, which does not occur in the absence of the metal. Furthermore, the addition of one hydroxide ion to the [M<sub>2</sub>(**L-O**)]<sup>3+</sup> species to form the [M<sub>2</sub>(**L-O**)(OH)]<sup>2+</sup> species is very favorable (log *K* = 7.65 and 5.18 for the complexes of Cu(II) and Ni(II), respectively), suggesting

that the bridged disposition of the hydroxide group is also preserved in solution.

**Concluding Remarks.** **L-OH** contains two diethylenetriamine subunits linked at the central nitrogen atoms by 2,6-dimethylphenol. In this ligand, the two binding subunits are separate, each being able to bind one metal ion, and the phenol group in its deprotonated form has a strong tendency to bridge the two metal ions. For this reason, the two metal ions are forced to remain close to each other, and the phenolate group plays a key role in determining the molecular geometry of the binuclear species. Moreover, because of the number of binding sites, the ligand does not completely saturate the coordination sites of the metal ions and the complexes formed can be used to assemble at least one secondary ligand. This capability is well illustrated in the two crystal structures obtained here using two different dipositive metal ions, Cu(II) and Ni(II). In both cases, the very short distances between the two metal ions (3.0107(8) and 2.998(1) Å for Cu1–Cu2 and Cu3–Cu4, respectively, and 3.226(2) Å for the two Ni(II) ions) permit the binding of another species, with a preference for those that can bridge the two-metal center by the same donor atom. In the Cu(II) complex, this ligand is the hydroxide anion, while, in the Ni(II) complex, the bridging ligand is the chloride anion. The coordination around each Ni(II) ion is completed by binding one chlorine, thus forming an octahedral coordination sphere.

The studies in aqueous solution demonstrate the capability of **L-OH** to form binuclear species with the ions Cu(II) and Ni(II), giving high addition stability constant values for the binuclear species.

In summary, both solution- and solid-state studies revealed the tendency of binuclear species to saturate the coordination environment of the metal ions by adding a secondary ligand capable of bridging the two metal cations. For this reason, **L-OH** and its binuclear species having suitable metal ions can be utilized to investigate many supramolecular interactions and reactivities.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for the structure determinations of [Cu<sub>2</sub>(**L-O**)(OH)]-(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**1**) and Ni<sub>2</sub>(**L-O**)Cl<sub>3</sub> (**2**). This material is available free of charge via Internet at <http://pubs.acs.org>.

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