

# Synthesis and Crystal Structure of the Copper Complex of 7,16-Bis(2-hydroxy-5-methylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

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A lariat crown ether ligand 7,16-bis (2-hydroxy-5-methylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**L1**) has been prepared via one-pot Mannich reaction. Its copper(II) complex Cu-**L1** was synthesized and characterized by elemental analysis, IR and UV-visible spectroscopy. The crystal structure of the complex has been determined by X-ray diffraction analysis. The result shows that the copper(II) ion is six-coordinated by two nitrogen and four oxygen atoms, two from the crown ether and the other two from the deprotonated phenolate anions, forming an elongated octahedral complex. Electrochemical study indicates that the complex undergoes reversible reduction in DMF solution.

**Keywords**    *N,N'*-disubstituted diaza-18-crown-6, copper(II) complex, crystal structure, cyclic voltammetry

## Introduction

Many azacrown macrocycles functionalized with chromophoric groups were found to be efficient photometric agents.<sup>1,2</sup> Their complexes with particular cations exhibit specific UV or fluorescence response and can be used for the quantitative determination of those cations.<sup>3</sup> Side-armed crown ethers have proved to be efficient carriers for liquid membranes<sup>4,5</sup> and pH switching complexing agents.<sup>6</sup> Some of the azacrown ethers with two ionizable arms exhibit favorable complexing abilities toward many divalent metal ions.<sup>7</sup> Some Cu(II) complexes with lariat crown ethers containing phenolic groups have been reported, in which the pendant phenolic groups are all deprotonated on complexation to Cu<sup>2+</sup>.<sup>8-10</sup>

7,16-Bis(2-hydroxy-5-methylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**L1**) is a potential N<sub>2</sub>O<sub>6</sub> macrocyclic receptor which possesses two phenolic groups that can be deprotonated to form an di-anionic ligand. Its crystal structure reveals that the hydroxyl groups of both side-arms pointed to the center of azacrown ring from opposite sides.<sup>11</sup> Its preferred conformation may be ideal for axial complexation with a central guest cation. The study of the stability constants of this ligand with divalent metal ions showed that they were in accordance with the order of Williams-Irving series.<sup>12</sup> But the structures of these complexes have not been established yet. Here, the synthesis and structure of its copper complex are reported.

## Experimental

Diaza-18-crown-6 **1** was prepared according to the reported method.<sup>13</sup> All commercially available chemicals were of analytical grade and used without further purification except toluene, which was dried with metal sodium.

Elemental analysis for carbon, hydrogen and nitrogen was conducted using an Elementar vario EL elemental analyzer. UV spectra were measured using a GBC Cintra 10e UV-visible spectrophotometer in methanol solution. The IR spectra were recorded in the range of 400—4000 cm<sup>-1</sup> on a Nicolet-AVATAR 360 FT-IR spectrometer using KBr pellets. Cyclic voltammetry measurements were carried out on a CH Instrument model 705A electrochemical analyzer. All measurements were performed under a dry nitrogen atmosphere in DMF solution using 0.1 mol/L Et<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. A three-electrode assembly comprising a platinum-working electrode, a platinum auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode was used.

### Preparation of lariat crown ether

The crown ether was prepared following Scheme 1. An anhydrous toluene solution (45 mL) containing 4,13-diaza-18-crown-6 **1** (0.26 g, 1 mmol), paraformaldehyde (0.07 g, 2.45 mmol), and 4-methylphenol (0.26 g, 2.4 mmol) was refluxed at 110 °C for 24 h. The solvent was evaporated by rotatory evaporation followed by the addition of a small amount of MeOH. The mix-

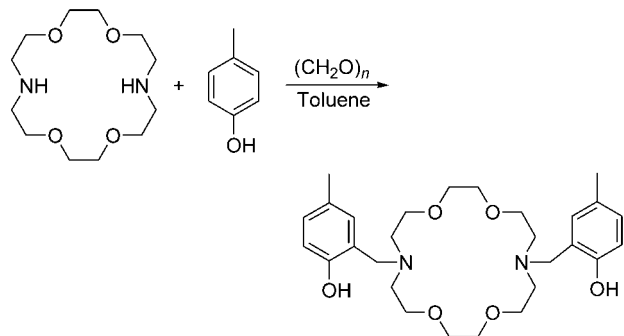
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ture was then ultrasonicated for 20 min. The solid product was collected by filtration and dried. m.p. 114—116 °C (114—115 °C in lit.<sup>11</sup>). Elemental analysis and spectroscopy study showed a good agreement with that reported.<sup>11</sup>

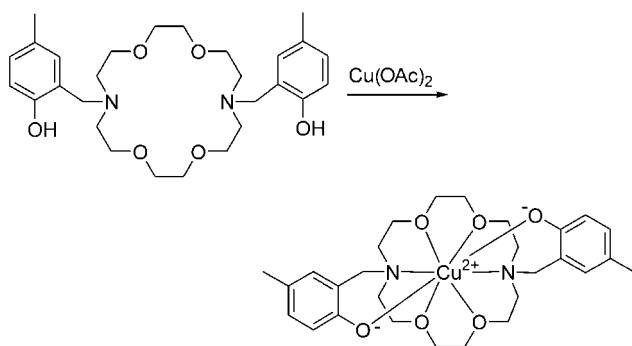
### Scheme 1



### Preparation of complex Cu-L1

A solution of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.04 g, 0.2 mmol) in MeCN (10 mL) was added dropwise to a suspension of the ligand (0.10 g, 0.2 mmol) in 5 mL MeCN (Scheme 2). The colour of the reaction mixture changed to dark brown suddenly and the powder of the ligand was dissolved. The mixture was then refluxed with stirring for 4 h. The mother liquor was stored at room temperature for several hours to yield some dark yellow crystals of complex Cu-L1. Anal. calcd for  $\text{C}_{28}\text{H}_{40}\text{CuN}_2\text{O}_6$  ( $M_r = 564.16$ ): C 59.56, H 7.09, N 4.96; found C 59.31, H 6.73, N 4.96.

### Scheme 2



## Results and discussion

### Crystal structure

A crystal with dimensions 0.30 mm × 0.25 mm × 0.20 mm was selected for X-ray diffraction experiment. The measurements were performed on a SMART 1000 CCD diffractometer at 293 K with graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.071073$  nm). The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXS-97 and SHELXL-97 program packages. All non-hydrogen atoms were refined anisotropically.

A summary of the crystallographic data and details of the structure refinements are listed in Table 1.

**Table 1** Summary of data collection and crystal parameters of complex Cu-L1

Empirical formula	$\text{C}_{28}\text{H}_{40}\text{CuN}_2\text{O}_6$
Formula weight	564.16
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system	Triclinic
Space group	$P-1$
Crystal size	0.30 mm × 0.25 mm × 0.20 mm
Unit cell dimension	$a = 0.8789(7)$ nm, $b = 0.9327(7)$ nm, $c = 0.9456(7)$ nm, $\alpha = 90.72(1)^\circ$ , $\beta = 108.43(1)^\circ$ , $\gamma = 112.05(1)^\circ$
Volume	$0.6740(9)$ nm <sup>3</sup>
Z	1
Calculated density	$1.390$ Mg · m <sup>-3</sup>
Absorption coefficient	$0.855$ mm <sup>-1</sup>
$\theta$ range for data collection	$2.30^\circ$ — $25.00^\circ$
Limiting indices	$-10 \leq h \leq 9$ , $-11 \leq k \leq 10$ , $-9 \leq l \leq 10$
Reflections collected/unique	2843/2204 ( $R_{\text{int}} = 0.0249$ )
Goodness-of-fit on $F^2$	1.002
Final R indices [ $I > 2\sigma(I)$ ]	$R_1^a = 0.0458$ , $wR_2^a = 0.0913$
R indices (all data)	$R_1^a = 0.0647$ , $wR_2^a = 0.0972$

<sup>a</sup>

$$R_1 = \frac{\sum \|F_o| - |F_c|\|}{\sum |F_o|} \quad wR_2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum w(F_o^2)^2}}$$

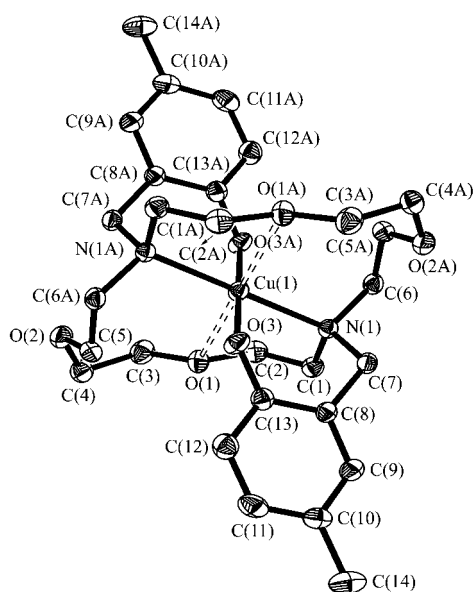
Selected bond lengths and angles are given in Table 2. The molecular structure of complex Cu-L1 and the coordination polyhedron of  $\text{Cu}^{2+}$  in the complex are showed in Figures 1 and 2, respectively.

**Table 2** Selected bond lengths (nm) and angles (°) for complex Cu-L1

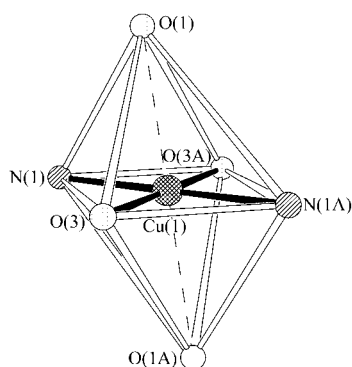
Cu(1)—O(3)	0.1895(3)	Cu(1)—O(3A)	0.1895(3)
Cu(1)—N(1)	0.2130(3)	Cu(1)—N(1A)	0.2130(3)
Cu(1)—O(1)	0.2736(3)	Cu(1)—O(1A)	0.2736(3)
O(1)—C(2)	0.1425(4)	O(1)—C(3)	0.1426(4)
O(2)—C(4)	0.1435(4)	O(2)—C(5)	0.1429(6)
O(3)—C(13)	0.1332(4)	N(1)—C(1)	0.1495(4)
N(1)—C(6)	0.1496(4)	N(1)—C(7)	0.1503(4)
O(3A)—Cu(1)—O(3)	180.00(15)	N(1A)—Cu(1)—N(1)	180.00(14)
O(3A)—Cu(1)—N(1A)	91.94(10)	O(3)—Cu(1)—N(1)	91.94(10)
O(3)—Cu(1)—N(1A)	88.06(10)	O(3A)—Cu(1)—N(1)	88.06(10)
C(1)—N(1)—Cu(1)	112.04(18)	C(6)—N(1)—Cu(1)	110.28(19)
C(7)—N(1)—Cu(1)	111.15(19)	C(13)—O(3)—Cu(1)	126.6(2)

Symmetry transformations used to generate equivalent atoms:

#1  $-x+1, -y, -z$ .



**Figure 1** Molecular structure of the complex Cu-L1.



**Figure 2** Coordination polyhedron of  $\text{Cu}^{2+}$  ion in complex Cu-L1.

The crystal structure shows that there is no  $\text{CH}_3\text{COO}^-$  existing in the complex, and the two pendant arms of the ligand exist in deprotonated phenolate forms. The molecular structure of the complex comprises a centrosymmetric  $\text{Cu}^{2+}$ , which is six-coordinated by four oxygen atoms [two, O(3) and O(3A), from two sidearm phenolate groups, and the other two, O(1) and O(1A), from the crown ether ring] and two tertiary amine nitrogen atoms N(1) and N(1A). The calculated result of the least squares plane shows that Cu(1), N(1), N(1A), O(3) and O(3A) are coplanar. The apical Cu—O distances [0.274 nm for Cu(1)—O(1) and Cu(1)—O(1A)] are longer than those of equatorial Cu—O and Cu—N bonds, giving an elongated octahedral geometry (Figure 2). The six-coordinated geometry is very similar to that of our previous copper complex.<sup>16</sup> This coordination geometry of the complex can be attributed to the flexibility of the ligand and the Jahn-Teller effect of  $\text{Cu}^{2+}$  ( $d^9$ ) ion.

The crown ether ring is twisted to meet the requirement of the coordination geometry. The six donors of the crown ring are not coplanar and adopt a chair con-

formation. The deviations from the least-squares plane for O(1), O(2), N(1), O(1A), O(2A) and N(1A) are  $-0.01370$ ,  $0.01178$ ,  $0.01709$ ,  $0.01369$ ,  $-0.01178$  and  $-0.01709$  nm, respectively. The O(2) and O(2A) atoms reside slightly above and below the  $\text{N}_2\text{O}_2$  [N(1), N(1A), O(1) and O(1A)] plane-1 respectively and are far from the center copper(II) ion (0.3810 nm). The dihedral angle between the aromatic ring plane and the above plane-1 is  $70.2(2)^\circ$ . The central  $\text{Cu}^{2+}$  ion is encapsulated by the crown ether ring and the two side-arms.

Compared to the octahedral copper(II) complex of 1,8-dicarboxymethyl derivative of cyclam,<sup>17</sup> in which the two additional anionic donors occupy the elongated sites, the Cu—O distances of the pendant arms in our complex, however, are shorter than Cu—O and Cu—N distances of the crown ether ring. This may be attributed to the formation of the stable six-membered chelating rings.

According to the crystal data of the ligand L1,<sup>18</sup> the average distances of C—N and C—O in the crown ether ring are 0.1461 and 0.1419 nm, respectively, and the C—O distance in the phenolic groups is 0.1367 nm. However, in complex Cu-L1, those of C—N and C—O in the crown ether ring are 0.1496 and 0.1429 nm, respectively, and the C—O distance in the phenolate groups is 0.1332 nm. For the crown ether ring, the C—N and C—O bonds lengthen on complexation to  $\text{Cu}^{2+}$ . This is probably due to the fact that the coordination of  $\text{Cu}^{2+}$  to the donor atoms weakens C—N and C—O bonds. The larger difference of C—N distances (0.0035 nm) than that of C—O (0.0010 nm) between the free ligand and the copper complex illustrates that Cu—N bond is stronger than Cu—O bond, which is in accordance with the soft-hard acid-base theory. The shorter distance of C—O bonds for phenolate groups in the complex may be attributed to its deprotonation, causing an increment in electron density between oxygen and carbon atoms and results in a stronger C—O bond.

### IR and UV-vis spectra

The vibration band at  $3208\text{ cm}^{-1}$  assigned to the side-arm phenolic hydroxyl in free ligand disappears in the complex. The multiple bands at  $1143\text{--}1112\text{ cm}^{-1}$  assigned to  $\nu(\text{C—N—C})$  and  $\nu(\text{C—O—C})$  are shifted to  $1133\text{--}1083\text{ cm}^{-1}$ , indicating the complexation of the ether oxygen and the tertiary amine nitrogen atoms to  $\text{Cu}^{2+}$ . No band of  $\text{—COO}^-$  was observed in the complex. The disappearance of  $\nu(\text{O—H})$  and the absence of the acetate indicate that the phenols are deprotonated when coordinated to  $\text{Cu}^{2+}$ . The shift of  $\nu(\text{C—O})$  of phenolic groups from  $1255\text{ cm}^{-1}$  in the free ligand to higher frequency of  $1293\text{ cm}^{-1}$  in the complex may be attributed to an increment in electron density between C and O atoms, *i.e.* an enhancement of the C—O bond.

The UV-vis spectrum of the free ligand in methanol solution exhibits two very intense absorption bands at 226 and 284 nm, corresponding to  $\pi\text{--}\pi^*$  transitions of the aromatic ring. In the spectrum of the complex, these two bands shifted to higher wavelengths, *i.e.*, 244 and

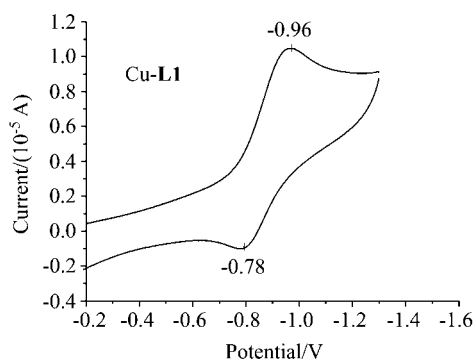
291 nm, respectively, with an increment in intensity. A new intense band at 219 nm was observed. The absorption peak of phenols in the vicinity of 286 nm may be used as a criterion for the complex formation.<sup>14</sup> The strong complexation usually results in a large change for this band in both absorption position and intensity. The complex exhibits both increased absorption intensity at 291 nm and a bathochromic shift of the band (from 284 to 291 nm). Moreover, the deprotonated phenolate ions cause an increase in electron density of the aromatic rings, resulting in large bathochromic shifts of the UV bands and an enhancement in absorption intensity.<sup>15</sup> The moderate absorption at 457 nm corresponds to a charge-transfer transition which involves the Cu(II) ion and phenolate groups of the macrocyclic receptor.<sup>9,10</sup>

**Table 3** Absorption spectral data of the ligand **L1** and complex Cu-**L1** (in methanol)

Compound	$\lambda_{\max}/\text{nm}$ ( $\epsilon_{\max}$ )			
<b>L1</b>	226 (12440)	284 (5300)		
Cu- <b>L1</b>	219 (9180)	241 (10480)	291 (6980)	457 (1880)

### Cyclic voltammetry

Cyclic voltammogram of complex Cu-**L1** was measured in DMF with a platinum electrode (Figure 3). The complex shows one redox wave at  $-0.96$  V, corresponding to the reduction of  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$ . One oxidation wave at  $-0.78$  V, corresponding to the oxidation of  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^{\text{II}}$ , is also observed. The result shows that the redox process of the complex is reversible. Compared with the copper(II) complex of other diazamacrocyclic ligand,<sup>19</sup> the redox process in the present complex shifted towards more cathodic potential. The coordination of the metal ion with the electron rich phenolate oxygen atoms results in the increase in the electron density, thus leading to the stabilization of copper(II) state of our complex.



**Figure 3** Cyclic voltammogram of complex Cu-**L1** in DMF solution, using a platinum electrode at a scan rate of  $0.1 \text{ V} \cdot \text{s}^{-1}$ .

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