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Syntheses and crystal structures of copper complexes of 7,16-bis (5-*t*-butyl-2-hydroxybenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

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Abstract

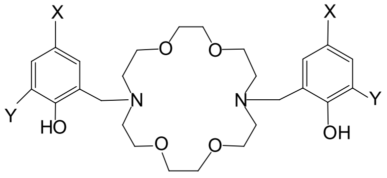
Reaction of the crown ether ligand H_2L (H_2L = 7,16-bis (5-*t*-butyl-2-hydroxybenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) with $Cu(Ac)_2$ and $Cu(NO_3)_2$ affords complexes **1** and **2**, respectively, which are characterized by elemental analysis, IR and UV–Visible spectroscopy and X-ray diffraction. Both crystal structure analysis and spectroscopy study unexpectedly showed that the two side-arm *p-tert*-butylphenols of the original crown ether are converted to nitro *p-tert*-butylphenols in complex **2**. In each complex the copper (II) ion is coordinated to two nitrogen and four oxygen atoms, two from the crown ether ring and other two from the deprotonated phenolate groups, which define an elongated octahedron. Electrochemical studies indicate that the two complexes undergo irreversible reduction in DMF solution.

Keywords: *N*,*N*′-disubstituted diaza-18-crown-6; Copper complex; Crystal structure

1. Introduction

Double-armed crown ethers and related macrocycles represent a new class of synthetic cation-binders, which are characterized by a parent macrocyclic ligand and a cation-ligating functionalized arm [1,2]. Many azacrown macrocycles functionalized with chromophoric groups were found to be efficient photometric agents [3,4]. Their complexes with particular cations exhibit specific UV or fluorescence response and can be used for the quantitative determination of those cations [5]. Some of the azacrown ethers with two ionizable arms exhibit favourable complexing abilities toward many divalent metal ions [6]. For example, the chromogenic crown ether **1** is known to be a good selective reagent for the determination of calcium ion concentration in blood serum [7].

Many of the double-armed crown ethers were obtainable by treatment of *N*,*N*′-bis (methoxymethyl)-4,13-diaza-18-crown-6 with appropriate substituted phenols [8–10] until Chi et al. [11] reported a new convenient one-pot Mannich reaction method. The azacrown ether **2** was synthesized by this method with good yield, but the yield of **1** was low due to the poor solubility of *p*-nitrophenol in benzene as well as the relatively weak nucleophilicity of *p*-nitrophenol and its anion [11]. The azacrown ether **3** containing two *o*-nitrophenol side-arms was synthesized by Su et al. [12] with only moderate yield. However, no complex of them has been synthesized and studied yet. In this paper, we report the synthesis and structures of the copper acetate complex of **2** and the copper nitrate complex in which the ligand was not the original ligand **2** but its nitro derivative **4**.



1 X = NO_2 Y = H
2 X = $C(CH_3)_3$ Y = H
3 X = CH_3 Y = NO_2
4 X = $C(CH_3)_3$ Y = NO_2

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2. Experimental

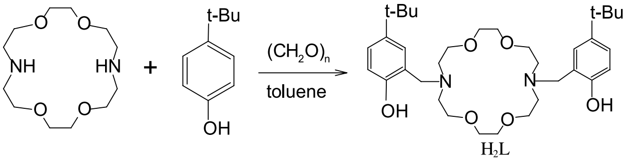
2.1. Materials and methods

Diaza-18-crown-6 was prepared according to the literature method [13]. All commercially available chemicals were of reagent grade and used without further purification except toluene, which was dried with sodium.

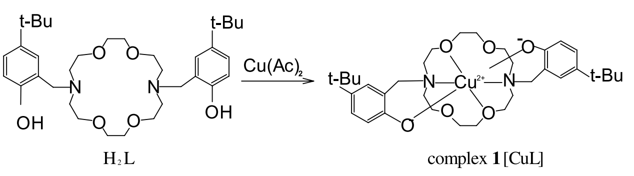
CHN Analyses were determined using an Elementar Vario EL elemental analyzer. UV spectra were measured using a GBC Cintra 10e UV–Visible spectrophotometer in CH_2Cl_2 solution. The IR spectra were recorded on a Nicolet-AVATAR 360 FT-IR spectrometer using KBr pellets in the 400–4000 cm^{-1} region. Cyclic voltammetry measurements were carried out on a CH Instruments model 705A electrochemical analyzer. All measurements were performed under a dry nitrogen atmosphere in DMF solution using 0.1 M Et_4NClO_4 as the supporting electrolyte. A three-electrode assembly comprising a platinum-working electrode, a platinum auxiliary electrode and a saturated calomel electrode (SCE) reference electrode were used.

2.2. Synthesis of the ligand H_2L

The crown ether 7,16-bis(5-*t*-butyl-2-hydroxybenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (H_2L) was prepared according to the literature [11] following the scheme below:

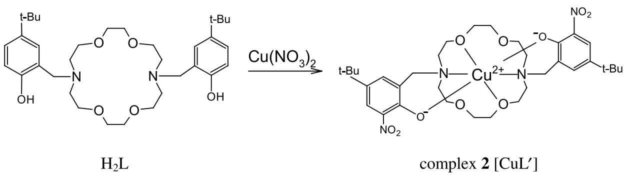


2.3. Synthesis of the complex **1**: $[CuL]\cdot 2CH_3CN$



When 5 ml acetonitrile solution of $Cu(Ac)_2\cdot H_2O$ (0.020 g, 0.1 mmol) was added dropwise to a solution of the ligand H_2L (0.059 g, 0.1 mmol) in 5 ml CH_2Cl_2, the colour of the reacting solution changed to dark brown suddenly. After refluxing with stirring for 4 h, the mother liquor was stored at room temperature for several days and some dark yellow crystals were deposited. The crystals cracked easily when removed from the mother liquor and the crystal structure analysis showed that the complex contains two solvated CH_3CN molecules. Elemental analysis was performed for the de-solvated sample. *Anal.* Calc. for $C_{34}H_{52}CuN_2O_6$ ($M_r = 647.5$): C, 63.01; H, 8.03; N, 4.32. Found: C, 63.20; H, 7.74; N, 4.64%.

2.4. Synthesis of the complex (**2**): $[CuL']$



$Cu(NO_3)_2\cdot 3H_2O$ (0.024 g, 0.1 mmol) and the ligand H_2L (0.059 g, 0.10 mmol) were dissolved in acetone-acetonitrile solvent mixture (10 ml/5 ml). The color of the reacting solution changed to dark brown, and it was refluxed with stirring for 4 h. The mother liquor was stored at room temperature for several days and some yellow crystals were obtained. To our surprise, the analytical result fits $C_{34}H_{50}CuN_4O_{10}$, which indicates that the lariat azacrown ether was nitrated by HNO_3 (NO_3^- from $Cu(NO_3)_2$, and H^+ from phenolic hydroxyl) while coordinated to the Cu^{2+} ion. *Anal.* Calc. for $C_{34}H_{50}CuN_4O_{10}$ ($M_r = 738.32$): C, 55.26; H, 6.78; N, 7.59. Found: C, 54.90; H, 6.56; N, 6.95%.

2.5. X-ray crystallography

The diffraction measurements were performed on a SMART 1000 CCD diffractometer at 293 K with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS 97 and SHELXL 97 programs [14]. All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and details of the structure refinements for complexes **1** and **2** are listed in Table 1.

3. Results and discussion

3.1. IR and UV–Visible spectra

For the original free ligand, H_2L, the multiple bands at 1142–1108 cm^{-1} assigned to v(C–N–C) and v(C–O–C) are shifted to 1138–1085 and 1117–1074 cm^{-1} in complexes **1** and **2**, respectively, indicating the complexation of the ether oxygen and the tertiary amine nitrogen atoms to the Cu^{2+} ion. The aromatic ring vibration at 1504 cm^{-1} in the free ligand was shifted to 1497 and 1512 cm^{-1} for complexes **1** and **2**, respectively, showing the coordination of side-arm phenols to Cu^{2+}. In complex **2**, we found

Table 1
Summary of data collection and crystal parameters for complexes **1** and **2**

	Complex **1**	Complex **2**
Empirical formula	$C_{38}H_{58}CuN_4O_6$	$C_{34}H_{50}CuN_4O_{10}$
Formula weight	730.42	738.32
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Crystal size (mm)	0.30 × 0.25 × 0.20	0.14 × 0.10 × 0.04
Unit cell dimensions		
a (Å)	9.016(4)	13.875(5)
b (Å)	22.595(10)	10.350(4)
c (Å)	9.849(5)	12.579(5)
β (°)	103.610(8)	100.002(7)
Volume (Å^3)	1590(2)	1779(1)
Z	2	2
Calculated density (Mg/m^3)	1.244	1.378
Absorption coefficient (mm^{-1})	0.608	0.675
Θ range for data collection (°)	1.80–25.03	2.47–25.02
Limiting indices	$-8 \leqslant h \leqslant 10$, $-23 \leqslant k \leqslant 26$, $-11 \leqslant l \leqslant 11$	$-16 \leqslant h \leqslant 16$, $-5 \leqslant k \leqslant 12$, $-14 \leqslant l \leqslant 14$
Reflections collected/unique	8034/3445	6297/2801
Goodness-of-fit on F^2	1.084	0.969
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0654$, $wR_2 = 0.1543$	$R_1 = 0.0848$, $wR_2 = 0.1949$

two new intense bands at 1463 and 1352 cm^{-1}, which can be assigned to the asymmetric and symmetric $-NO_2$ stretching vibrations. The band at 3426 cm^{-1} assigned to the side-arm phenolic hydroxyl in free lariat crown ether disappeared in both complexes. All these indicate the deprotonation of the phenols on coordinating to Cu^{2+}.

The UV spectra of the original ligand in CH_2Cl_2 solution exhibit one intense absorption band at 280 nm, corresponding to π–π^* transitions of the aromatic ring. In the spectra of the complexes, the band was expectedly shifted to higher wavelengths at 287 and 288 nm in complexes **1** and **2**, respectively. The absorption peak of phenols in the vicinity of 286 nm may be used as a criterion for complex formation [15]. Strong complexation usually results in a large change for this band in both absorption position and intensity. The two complexes exhibit both increased absorption intensity and bathochromic shift of the band. Moreover, the deprotonated phenolate anions cause an increase in electron density of the aromatic rings, which results in the large bathochromic shifts of the UV bands and an enhancement in absorption intensity [10]. There were two less intense shoulders in complex **2** assigned to the n–π^* transitions of the NO_2 groups. The visible spectra showed moderately intense absorption bands at 446 and 422 nm in complexes **1** and **2**, respectively, which were assigned to a phenolate-to-copper(II) transition [16,17].

3.2. Crystal structures

The molecular structures of complexes **1** and **2** are shown in Figs. 1 and 2. Selected bond lengths and angles for the complexes are collected in Table 2.

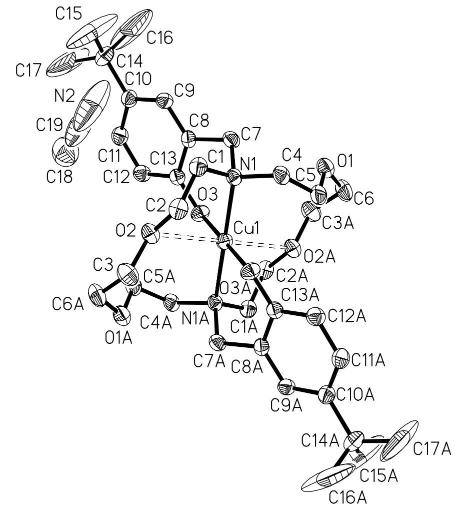


Fig. 1. Molecular structure of complex **1** showing the atomic numbering scheme.

In the centrosymmetric molecular structure of complex **1,** the central Cu^{2+} ion is six-coordinated to four oxygen atoms (from two side-arm phenolate groups and the crown ether ring), and two tertiary amine nitrogen atoms (Fig. 1). The apical Cu–O(crown) distance of 2.784 Å for Cu1–O2 is considerably longer than that of equatorial Cu–O(phenol) (1.896(3) Å for Cu1–O3) and that of Cu–N(crown) (2.141(3) Å for Cu1–N1) bonds, giving an elongated octahedral geometry. The dihedral angle between an aromatic ring and the mean plane of the crown ether donor atoms is 69.4(2) Å.

The coordination geometry of complex **2** is very similar to that of complex **1**. However, two-fold

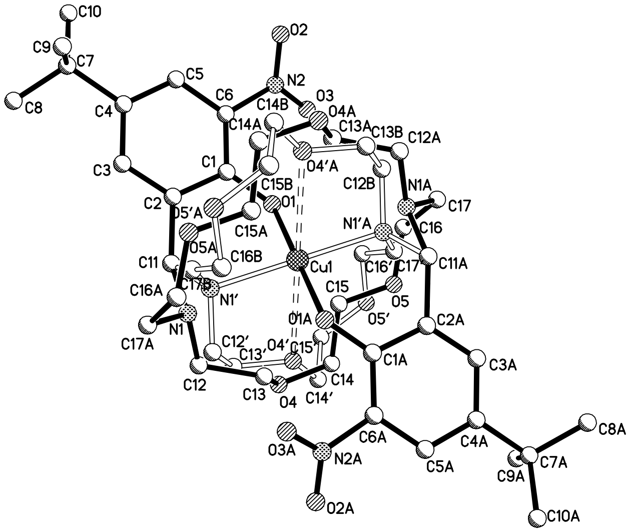


Fig. 2. Molecular structure of complex **2** showing the atomic numbering scheme.

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**		Complex **2**	
Bond lengths			
Cu(1)–O(2)	2.784(3)	Cu(1)–O(1)	1.951(5)
Cu(1)–O(3)	1.896(3)	Cu(1)–O(4′)	2.818(6)
Cu(1)–N(1)	2.141(3)	Cu(1)–N(1′)	2.087(6)
		O(2)–N(2)	1.220(9)
		O(3)–N(2)	1.194(9)
Bond angles			
O(3)–Cu(1)–N(1)	91.47(12)	O(1)–Cu(1)–N(1′)	91.6(2)
C(13)–O(3)–Cu(1)	126.1(2)	C(1)–O(1)–Cu(1)	119.7(4)
C(1)–N(1)–Cu(1)	112.3(2)	C(11)–N(1′)–Cu(1)	112.6(4)
C(4)–N(1)–Cu(1)	109.3(2)	C(12′)–N(1)–Cu(1)	105.2(6)
C(7)–N(1)–Cu(1)	111.5(2)	C(17′A)–N(1′)–Cu(1)	105.4(6)

Symmetry transformations used to generate equivalent atoms: $-x, -y+1, -z$ (complex **1**); $-x, -y, -z$ (complex **2**).

orientational disorder of the crown ether ring was found in the crystal. The site occupation factors for the two sets of disordered atoms were refined to 64.1 (labelled with ′) and 35.9%. The inter-nuclear distance of 1.951(5) Å for Cu1–O1 is significantly shorter than that of 2.087(6) Å for Cu1–N1′ and that of 2.818(6) Å for Cu1–O4′, which is similar to complex **1**. This is probably due to the low strain of the six-membered chelate rings. The elongated octahedral geometry of the complex may be due to the flexibility of the ligand and the Jahn–Teller effect of the $Cu^{2+}(d^9)$ ion.

3.3. Cyclic voltammetry

Cyclic voltammograms of the copper (II) complexes **1** and **2** were measured in DMF solution with a platinum electrode. Complex **1** showed two redox waves at −1.01 and −1.13 V, corresponding to the reduction of Cu^{II} to Cu^{I} and Cu^{I} to Cu^{0}, respectively. However, only one oxidation wave at −0.80 V was observed. For complex **2**, only one redox wave was observed at −1.00 V corresponding to the reduction of Cu^{II} to Cu^{I} and there is no evidence of the oxidation wave over the range investigated. The results showed that the redox processes in both complexes were irreversible (see Fig. 3).

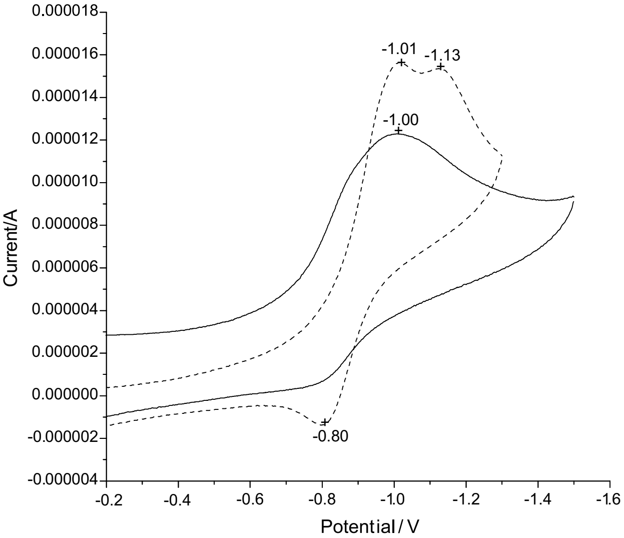


Fig. 3. Cyclic voltammograms in DMF solution of complexes **1** (- - -) and **2** (—) using a platinum electrode at a scan rate of 100 mV s^{-1} with Et_4NClO_4 as supporting electrolyte.

4. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 205995 (complex **1**) and 205996 (complex **2**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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References

[1] H. Tsukube, J. Coord. Chem. B-16 (1987) 101.
[2] R.M. Izatt, K. Pawlak, J.S. Bradshaw, Chem. Rev. 95 (1995) 2529.

[3] Y. Sakai, N. Kawan, H. Nakamura, M. Takagi, Talanta 33 (1986) 407.

[4] E. Chapoteau, B.P. Czech, C.R. Gebauer, A. Kumar, K. Leong, D.T. Mytych, W. Zazulak, D.H. Desai, E. Luboch, J. Krzykawski, R.A. Bartsch, J. Org. Chem. 56 (1991) 2575.

[5] Y. Katayama, R. Fukuda, I. Iwasaki, K. Nita, M. Takagi, Anal. Chim. Acta 204 (1988) 113.

[6] M. Hiraoka, Crown Ethers and Analogous Compounds, Elsevier, Amsterdam, 1992, p. 126.

[7] H. Nishida, M. Tazaki, M. Takagi, K. Ueno, Mikrochim. Acta (1981) 281.

[8] N.G. Lukyanenko, V.N. Pastushok, A.V. Bordunov, Synthesis (1991) 241.

[9] A.V. Bordunov, N.G. Lukyanenko, V.N. Pastushok, K.E. Krakowiak, J.S. Bradshaw, X. Kou, J. Org. Chem. 60 (1995) 4912.

[10] X.X. Zhang, A.V. Bordunov, J.S. Bradshaw, N.K. Dalley, X. Kou, R.M. Izatt, J. Am. Chem. Soc. 117 (1995) 11507.

[11] K.W. Chi, H.C. Wei, T. Kottke, R.J. Lagow, J. Org. Chem. 61 (1996) 5684.

[12] N. Su, J.S. Bradshaw, X.X. Zhang, P.B. Savage, K.E. Krakowiak, R.M. Izatt, J. Org. Chem. 64 (1999) 3825.

[13] S. Kulstad, L.A. Malmaston, Acta Chem. Scand. B 33 (1979) 469.

[14] G.M. Sheldrick, SHELXS 97 and SHELEXL 97, University of Gottingen, Germany, 1997.

[15] E. Kimura, Y. Kimura, T. Yastsunami, M. Shionoya, T. Koike, J. Am. Chem. Soc. 109 (1987) 6212.

[16] U. Auerbach, U. Eckert, K. Wieghardt, B. Nuber, J. Weiss, Inorg. Chem. 29 (1990) 938.

[17] X.H. Bu, M. Du, L. Zhang, Z.L. Shang, R.H. Zhang, M. Shionoya, J. Chem. Soc., Dalton Trans. (2001) 190.