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Synthesis and crystal structure of copper complex of 7,16-bis(2-hydroxy-5-methyl-3-nitrobenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

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Abstract

A lariat crown ether compound 7,16-bis(2-hydroxy-5-methylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane has been prepared via one-pot Mannich reaction. A copper(II) complex with the ligand 7,16-bis(2-hydroxy-5-methyl-3-nitrobenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane was unexpectedly synthesized and characterized by elemental analysis, IR and UV spectra. The crystal structure of the complex has been determined by X-ray diffraction. Both crystal structure analysis and spectroscopy study indicated that the side-arm phenols of lariat crown ether are nitrated while complexing with $Cu(NO_3)_2$. Structure shows that the copper(II) ion is coordinated to two nitrogen and four oxygen atoms, two from the crown ether and other two from the deprotonated phenolate groups. The coordination polyhedron is a distorted octahedron.

Keywords: *N*,*N'*-Disubstituted diaza-18-crown-6; Copper complex; Crystal structure

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1. Introduction

Macrocycles functionalized with coordinating pendent arms have received much attention recently as a result of their enhanced coordinating ability and their favourable kinetics for the overall formation process of complexes [1]. Many azacrown macrocycles functionalized with chromophoric groups were found to be efficient photometric agents [2,3]. Their complexes with particular cations exhibit specific UV or fluorescence response and can be used for the quantitative determination of those cations [4]. Side-armed crown ethers have proved to be efficient carriers for liquid membranes [5,6], and pH switching complexing agents [7]. Some of the azacrown ethers with two ionizable arms exhibit favourable complexing abilities toward many divalent metal ions [8].

Moore and coworkers [9] have reported the first ligand which contains phenolic pendent arms and prepared its Gd^{3+} complex. Some lariat crown ethers containing hydroxyl functional groups, such as 2-hydroxybenzyl, 3-*tert*-butyl-2-hydroxy benzyl [10], attached to the secondary amine nitrogen on triaza macrocycles, were also reported. The crystal structures of their copper complexes showed that the Cu^{2+} center is in a square-based-pyramidal environment of

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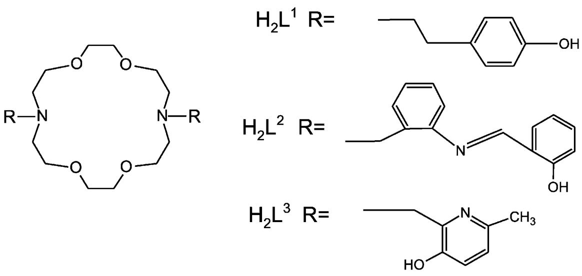
three nitrogen donors and of two phenolate oxygen atoms. In 1999, Dewall and co-workers [11] prepared a ligand, H_2L^1 and found this receptor complexes K^+ by using the phenolic sidearms as π-donor groups but not when the macrocycle-bound cation is Na^+. Recently, four 8-hydroxyquinoline-containing tetraaza crown ethers were studied for their potential application as highly selective Cu^{2+} receptors [12]. Among Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}, the most stable complexes were formed with Cu^{2+}. In the other example [13], the X-ray crystal structure of $[Cu_2(L^2)](ClO_4)_2$ had confirmed the binuclear nature of the compound with both metal ions identical coordination environment and each one placed out of the crown hole but efficiently encapsulated by the corresponding pendent arm. Our very recent paper reported the synthesis of a new sidearm diaza-18-crown-6 ligand, H_2L^3, and its copper nitrate complex. The crystal structure of the complex showed that the two unionized phenolic groups are coordinated to the central Cu^{2+} from above and below the ring plane [14].



Many of the double-armed crown ethers were obtainable by treatment *N*,*N*′-bis(methoxymethyl)-4,13-diaza-18-crown-6 with appropriate substituted phenols [15–17] until Ki-Whan Chi and co-workers [18] reported a new convenient one-pot Mannich reaction method. Since then, a wide variety of lariat crown ethers containing different pendent arms have been prepared and their properties have been studied [19,20]. The 7,16-bis(2-hydroxy-5-methylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane was synthesized in 1995 for the first time [16], but its complex has not been synthesized and studied yet. In this paper, we report the synthesis and structure of a new copper complex in which the ligand was not the original lariat crown ether but its nitro derivative.

2. Experimental

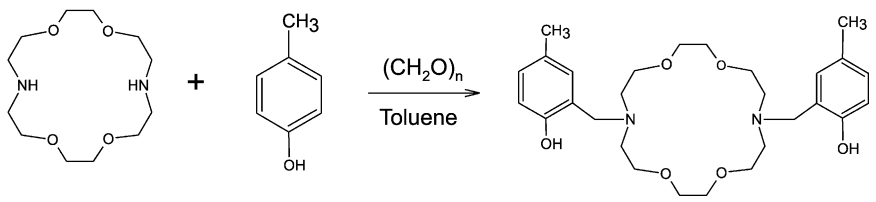
2.1. Materials and methods

Diaza-18-crown-6 was prepared according to the literature method [21]. All commercially available chemicals were of reagent grade and were used without further purification except toluene which was dried with sodium.

C, H and N were determined using an Elementar Vario EL elemental analyzer. UV spectra were measured using a WFZ-900-D4 spectrophotometer in methanol solution. The IR spectra were recorded on a NEXUS670 FTIR spectrometer using KBr pellets in the 400–4000 cm^{-1} region.

2.2. Preparation of the lariat crown ether

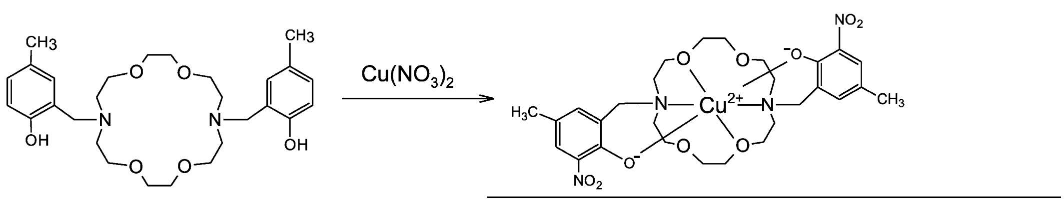
The crown ether was prepared as follows.



An anhydrous toluene solution (45 ml) containing 4,13-diaza-18-crown-6 (0.262 g, 1.00 mmol), paraformaldehyde (0.074 g, 2.45 mmol), and 4-methylphenol (0.259 g, 2.40 mmol) was refluxed at 110 °C for 24 h. The solvent was evaporated by rotatory evaporation, and a small amount of MeOH was added. The mixture was ultrasonicated for 20 min.

The resulting solid was collected by filtration and dried. Mp 104–106 °C. Elemental analysis and spectroscopy study showed a good agreement with that reported [18].

2.3. Preparation of the complex



$Cu(NO_3)_2 \cdot 3H_2O$ (0.180 g, 0.60 mmol) in 6 ml acetone and 2 ml acetonitrile mixture solution was added dropwise to the solution of 7,16-bis(2-hydroxy-5-methylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (0.100 g, 0.20 mmol) in 6 ml acetone. The colour of the reaction solution changed to dark brown and some brown powder precipitated from the solution. It was refluxed with stirring 4 h. The precipitate was collected by filtration. The mother liquor was stored at room temperature for several days and some dark yellow crystals were obtained from the mother liquor. Anal. calcd for $C_{28}H_{38}CuN_4O_{10}$ ($M_r = 654.16$) (%): C, 51.36; H, 5.81; N, 8.56; found (%): C, 51.43; H, 4.90; N, 8.63. To our surprise, the analytical result does not fit the formula $C_{28}H_{42}N_2O_6 \cdot Cu(NO_3)_2$ which corresponds to the complex copper nitrate with original lariat crown ether but fits the formula $C_{28}H_{38}CuN_4O_{10}$, which indicated a copper complex with the lariat crown ether nitro derivative. Single crystal analysis showed the original pendent side-arm crown ether has been converted to its nitro derivative (see below). The spectroscopy measurements also support this suggestion. According to the experimental results, we suppose 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 Cu^{2+} ion.

2.4. X-ray crystallography

A crystal with dimensions 0.30 × 0.25 × 0.20 mm^3 was selected for X-ray diffraction experiment. The measurements were performed on a CCD area detector diffractometer at 293 K with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs [22]. All nonhydrogen atoms were refined anisotropically. A summary of the crystallographic data and details of the structure refinements are listed in Table 1.

3. Results and discussion

3.1. IR and UV spectra

For the original free ligand 7,16-bis(2-hydroxy-5-methylbenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, the multiple bands at 1143–1112 cm^{-1} assigned to ν (C–O–C) and ν (C–N–C) are shifted to 1137–1083 cm^{-1}, indicating the complexation of

Table 1
Summary of data collection and crystal parameters

Empirical formula	$C_{28}H_{38}CuN_4O_{10}$
Formula weight	654.16
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 8.571(4)$ Å, $\alpha = 102.073(9)°$ $b = 8.784(4)$ Å, $\beta = 100.994(8)°$ $c = 11.582(6)$ Å, $\gamma = 115.197(8)°$
Volume	732.1(6) Å^3
Z, calculated density	2, 1.484 Mg/m^3
Absorption coefficient	0.810 mm^{-1}
F(000)	343
Crystal size	0.30 × 0.25 × 0.20 mm^3
Θ range for data collection	1.90–25.02°
Limiting indices	$-10 \le h \le 8$, $-4 \le k \le 10$, $-13 \le l \le 12$
Reflections collected/unique	3064/2578 [R(int) = 0.0248]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.984
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0419$, $wR2 = 0.0848$

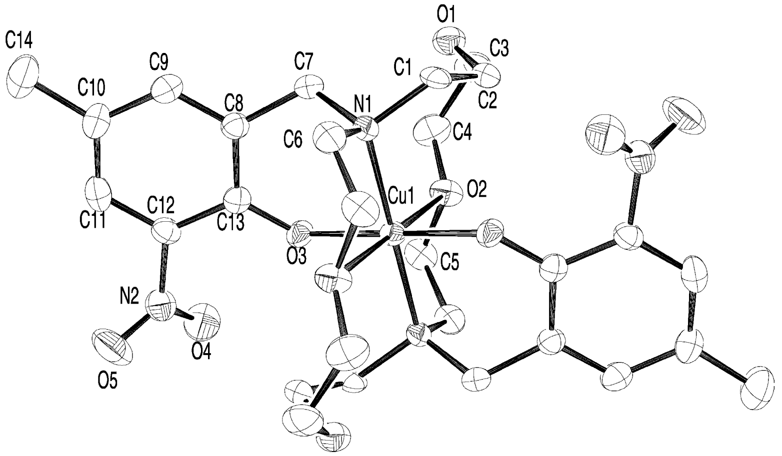


Fig. 1. An ORTEP-3 [23] drawing of the complex with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

the ether oxygen and the secondary amine nitrogen atoms to Cu^{2+} ion. In the complex we found two new intense bands at 1471 and 1350 cm^{-1} which can be assigned to the asymmetric and symmetric $-NO_2$ stretching vibrations, indicating the side-arm phenols of the original lariat crown ether being nitrated while complexing with Cu^{2+}. No bands for the free nitrate or coordinated nitrate have been observed in the complex. This also verified the nitration of the side-arm phenols. The band at 3428 cm^{-1} assigned to the side-arm phenolic hydroxyl in free lariat crown ether disappeared in complex indicating the deprotonation of the phenols on coordinating to Cu^{2+}. The aromatic ring vibration at 1498 cm^{-1} in the original free ligand was shifted to a higher frequency 1513 cm^{-1} also showing the coordination of side-arm phenols to Cu^{2+}.

The UV spectra of the original ligand in methanol solution exhibit two intense absorption bands at 226 and 284 nm, corresponding to $\pi-\pi^*$ transitions of the aromatic ring. In the spectra of the complex, these two bands were expectedly shifted to higher wavelengths at 231 and 303 nm. The deprotonated phenolate ions 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 [17]. The two less intense shoulders at 210 and 270 nm, which are assigned to the $n-\pi^*$ transitions of the NO_2 groups, were obscured by the very intense $\pi-\pi^*$ transition of the aromatic ring at 231 nm.

3.2. Crystal structure

Fig. 1 shows the molecular structure of the complex. Fig. 2 shows the molecular packing arrangement in the unit cell viewed along the *b*-axis. The selected bond lengths and angles are given in Table 2.

The molecular structure of the complex comprises a centrosymmetric Cu^{2+} ion, and the central Cu^{2+} ion is six-coordinated to four oxygen atoms (two, O(3) and O(3A), from two side-arm phenolate groups, and the other two, O(2) and O(2A), from the crown ether ring) and two tertiary amine nitrogen atoms N(1) and N(1A).The long distance (3.832(2) Å) of Cu–O(1) and Cu–O(1A) shows that these two ether oxygen atoms O(1) and O(1A) were not coordinated to the

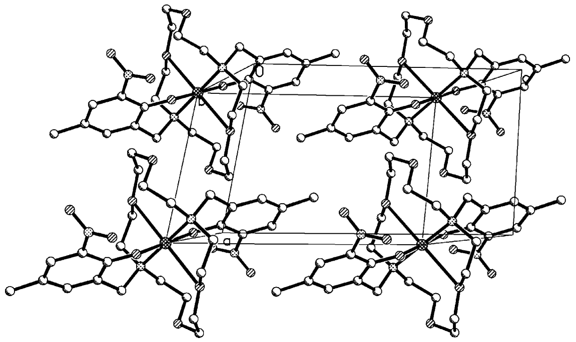


Fig. 2. Molecular packing arrangement in the unit cell viewed along the *b*-axis.

Table 2
The selected bond lengths (Å) and angles (°) for the complex

Bond lengths			
Cu(1)–O(3)	1.932(2)	Cu(1)–O(3A)	1.932(2)
Cu(1)–N(1)	2.092(2)	Cu(1)–N(1A)	2.092(2)
Cu(1)–O(2)	2.647(3)	Cu(1)–O(2A)	2.647(3)
O(4)–N(2)	1.224(4)	O(5)–N(2)	1.227(4)
C(12)–N(2)	1.461(4)	O(3)–C(13)	1.306(3)
Bond angles			
O(3A)–Cu(1)–O(3)	180.000(1)	N(1A)–Cu(1)–N(1)	180.000(1)
O(3A)–Cu(1)–N(1A)	91.70(9)	O(3)–Cu(1)–N(1)	91.70(9)
O(3)–Cu(1)–N(1A)	88.30(9)	O(3A)–Cu(1)–N(1)	88.30(9)
C(1)–N(1)–Cu(1)	111.69(18)	C(6)–N(1)–Cu(1)	111.27(18)
C(7)–N(1)–Cu(1)	110.76(17)	C(13)–O(3)–Cu(1)	127.93(18)
C(11)–C(12)–N(2)	116.3(3)	C(13)–C(12)–N(2)	119.9(3)
O(4)–N(2)–O(5)	122.9(3)	O(4)–N(2)–C(12)	119.4(3)
O(5)–N(2)–C(12)	117.7(3)		

Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, $-z+2$.

Cu^{2+} ion. The crown ether ring is twisted to meet the requirement of the coordination geometry.

In bibrachial lariat ether complexes, generally, when two side arms are attached to a macroring, complexation may be augmented by ligation from the same or opposite sides of the macroring. When complexation occurs from the same side (*syn* fashion), the complexes are expected to resemble cryptate complexes [24,25]. The two sidearms were found to arrange in a *syn* fashion in the sodium complexes of some lariat ethers based on the 4,13-diaza-18-crown-6 system [24–26]. However, the sidearms being in *anti* fashion may keep less conformational strain in the ligand, thus binding metal ion such as potassium cation more strongly than *syn* fashion. In our present copper complex of the bibrachial lariat ether, the side arms are arranged in a *anti* fashion as in the potassium iodide complex of *N*,*N*′-bis(3-oxabutyl)-1,10-diaza-18-crown-6 [24]. This may be attributed to the octahedral geometry request of the copper complex and the steric hindrance between the two phenolate groups in the ligand. Fig. 3 shows the skeletal drawing of its donor atoms and the metal ion. The donor atoms N(1), N(1A), O(2) and O(2A) of the crown ether ring are coplanar, and the centrosymmetric Cu^{2+} ion resides in the N_2O_2 plane of the four donor atoms, and the oxygen atoms of the two sidearms, O(3) and O(3A), are located above and below the plane of the ring. The bond angles of 91.90(7) and 88.30(9)° for O(3)–Cu(1)–N(1) and O(3A)–Cu(1)–N(1) indicate that the line connecting the two oxygen atoms, O(3) and O(3A), is nearly vertical to the above plane.

The crystal structure shows no NO_3^- existing in the complex, and the two pendent arms of ligand existing in deprotonated phenolate forms. The bond lengths of N(2)–O(4) (1.224(4) Å) and N(2)–O(5) (1.227(4) Å) showed the existence of NO_2 group and verified that the two side-arm phenols of the lariat crown ether were nitrated while complexing with Cu^{2+}. It is also worthy of note that the nuclear distances of Cu(1)–O(3) (1.932(2) Å) and

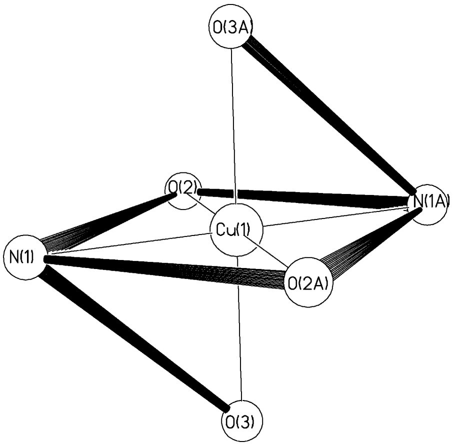


Fig. 3. Skeletal drawing of the copper complex.

Cu(1)–O(3A) (1.932(2) Å) are significantly shorter than that of Cu(1)–O(2) (2.647(3) Å), Cu(1)–O(2A) (2.647(3) Å), Cu(1)–N(1) (2.092(2) Å) and Cu(1)–N(1A) (2.092(2) Å). This is probably due to the fact that O(3) and O(3A) have a favourable geometry for coordination compared to the donors on the ring. The latter donors have to overcome a larger strain coming from the ring twisting distortion. The coordination polyhedron could be described as a distorted octahedron. This special coordination geometry of the complex may be due to the flexibility of the ligand and the John–Teller effect of $Cu^{2+}(d^9)$ ion.

Acknowledgements

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References

[1] F. Mclaren, P. Moore, A.M. Wynn, J. Chem. Soc., Chem. Commun. (1989) 798.
[2] Y. Sakai, N. Kawan, H. Nakamura, M. Takagi, Talantam 33 (1986) 407.
[3] 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.
[4] Y. Katayama, R. Fukuda, I. Iwasaki, K. Nita, M. Takagi, Anal. Chim. Acta 204 (1988) 113.
[5] B.P. Czech, A. Czech, B. Son, H.K. Lee, R.A. Bartsch, J. Heterocycl. Chem. 23 (1986) 465.
[6] H. Tsukube, K. Yamashita, T. Iwachido, M. Zenki, Tetrahedron Lett. 30 (1989) 3983.
[7] J. Strezbicki, W.A. Charewicz, R.A. Bartsch, J. Inclusion Phenom. 6 (1988) 57.
[8] M. Hiraoka, Crown Ethers and Analogous Compounds, Elsevier, Amsterdam, 1992, p. 126.
[9] D.A. Moore, P.E. Franwick, M.J. Welch, Inorg. Chem. 28 (1989) 1504.
[10] U. Auerbach, U. Eckert, K. Wieghardt, B. Nuber, J. Weiss, Inorg. Chem. 29 (1990) 938.
[11] S.L. Dewall, L.J. Brbour, G.W. Gokel, J. Am. Chem. Soc. 121 (1999) 8405.
[12] S.C. Lee, R.M. Izatt, X.X. Zhang, E.G. Nelson, J.D. Lamb, P.B. Savage, J.S. Bradshaw, Inorg. Chim. Acta 317 (2001) 174.
[13] C. Rodriguez-Infante, D. Esteban, F. Avecilla, A. de Blas, T. Rodríguez-Blas, J. Mahia, AL. Macedo, C.F.G.C. Geraldes, Inorg. Chim. Acta 317 (2001) 190.
[14] X. Jia, W. Zhu, Y. Zhang, X. Yan, J. Mol. Struct. 604 (2002) 159.
[15] N.G. Lukyanenko, V.N. Pastushok, A.V. Bordunov, Synthesis (1991) 241.
[16] A.V. Bordunov, N.G. Lukyanenko, V.N. Pastushok, K.E. Krakowiak, J.S. Bradshaw, X. Kou, J. Org. Chem. 60 (1995) 4912.
[17] X.X. Zhang, A.V. Bordunov, J.S. Bradshaw, N.K. Dalley, X. Kou, R.M. Izatt, J. Am. Chem. Soc. 117 (1995) 11507.
[18] K.W. Chi, H.C. Wei, T. Kottke, R.J. Lagow, J. Org. Chem. 61 (1996) 5684.
[19] N. Su, J.S. Bradshaw, X.X. Zhang, P.B. Savage, K.E. Krakowiak, R.M. Izatt, J. Org. Chem. 64 (1999) 3825.
[20] N. Su, J.S. Bradshaw, P.B. Savage, K.E. Krakowiak, R.M. Izatt, S.L. Dewall, G.W. Gokel, Tetrahedron 55 (1999) 9737.
[21] S. Kulstad, L.A. Malmaston, Acta Chem. Scand. B 33 (1979) 469.
[22] G.M. Sheldrick, SHELXS-97 and SHELEXL-97, University of Gottingen, Germany, 1997.
[23] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[24] E.D. Gandour, F.R. Fronczek, V.J. Gatto, C. Minganti, R.A. Schultz, B.D. White, K.A. Arnold, D. Mazzocchi, S.R. Miller, G.W. Gokel, J. Am. Chem. Soc. 108 (1986) 4078.
[25] K.A. Arnold, L. Echegoyen, F.R. Fronczek, R.D. Gandour, V.J. Gatto, B.D. White, G.W. Gokel, J. Am. Chem. Soc. 109 (1987) 3716.
[26] Z. Kilic, M. Yildiz, T. Hokelek, B. Erdogan, J. Chem. Soc., Dalton Trans. (1998) 3635.