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Synthesis and Structural Characterization of Copper(II) Complex with Asymmetrical Salen-Type Bisoxime Ligand

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A new mononuclear Cu(II) complex, [CuL], has been synthesized by the reaction of copper(II) acetate tetrahydrate with H_2L (H_2L = 4-bromo-6'-methoxy-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol). X-Ray crystallographic analysis reveals that the complex crystallizes in the monoclinic system, space group P2(1) and the unit cell contains two crystallographically independent but chemically identical molecules which interlink each other into a 1D infinite chain through four strong intermolecular O12-H12C···O4, O12-H12D···O5, O11-H11C···O9 and O11-H11D···O10 hydrogen bonds.

Key Words: Copper(II) complex, Asymmetrical bisoxime ligand, Synthesis, Crystal structure.

INTRODUCTION

Salen-type ligand and its derivatives which contain N_2O_2 site are easily coordinated to *d*-block transition metals in a tetradentate fashion to afford stable mononuclear complexes[1,2]. Consequently, increasing interest has been focused on their potential applications, such as near infrared chiroptical sensors[3], single-source precursors for metal-organic chemical vapor deposition (MOCVD)[4], metallomesogens[5], interesting magnetic properties[6-8] and so forth. Further, synthesizing unsymmetrical salen derivatives, which consist of two different salicylideneimine moieties, is much more difficult because a statistical mixture of three possible condensation products is usually obtained[9]. However, our team has synthesized several refined chiral unsymmetrical salen-type bisoxime ligands and obtained their copper(II) complexes. Herein, we report the synthesis and crystal structure of a copper(II) complex with an asymmetrical bisoxime ligand [H_2L], 4-bromo-6-methoxy-2,2'-[ethylenediyldioxy*bis*(nitrilomethylidyne)] diphenol.

EXPERIMENTAL

5-Bromosalicylaldehyde and 2-hydroxy-3-methoxybenzaldehyde from Aldrich were used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

Preparation of H_2L: 1,2-*Bis*(aminooxy)ethane was synthesized by a similar method[10]. Yield, 52.7 %. Anal. calcd. (%) for $C_2H_8N_2O_2$: C, 26.08; H, 8.76; N, 30.42. Found (%): C, 25.92; H, 8.87; N, 30.39.

4-Bromo-6-methoxy-2,2'-[ethylenediyldioxy*bis* (nitrilomethylidyne)]diphenol (H_2L) was synthesized as follows: Firstly, synthesis for mono-oxime, a solution of 1,2-*bis*(aminooxy)-ethane (1749 mg, 19 mmol) in ethanol (70 mL) was added to a solution of 2-hydroxy-3-methoxybenzaldehyde (1489 mg, 10 mmol) in ethanol (40 mL) and the mixture was stirred at 326-328 K for 4 h. The solution was concentrated *in vacuo* and the residue was purified by column chromatography (SiO_2, chloroform/ethyl acetate, 20:1) to afford 941 mg colourless crystals of monooxime compound. Yield, 52.0 %, m.p 367-368 K. Analysis for $C_{10}H_{14}N_2O_4$ (226.23): calcd. (%) C, 53.09; H, 6.24; N, 12.38. Found (%): C, 52.94; H, 6.31; N, 12.32.

Then, a solution of the obtained monooxime (430 mg, 1.9 mmol) in ethanol (30 mL) was added to a solution of 5-bromosalicylaldehyde (385 mg, 1.9 mmol) in ethanol (20 mL) and the mixture was stirred at 328-333 K for 6 h. The formed precipitate was separated by filtration and washed successively with ethanol and *n*-hexane. The product was dried under vacuum to yield 0.6253 g of the H_2L yield, 80.38 %, mp. 381-382 K. Anal. calcd. (%) for $C_{17}H_{17}N_2O_5Br$: C, 49.89; H, 4.19; N, 6.85. Found (%): C, 49.92; H, 21; N 6.77.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE COMPLEX

Empirical formula	$C_{17}H_{17}BrCuN_2O_6$
Formula weight	488.78
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)
Cell dimensions, (Å, º)	a = 13.9529(14), b = 7.6135(7), c = 18.5996(17), β = 109.716(2)
Volume ($Å^3$)	1860.0(3)
Z	4
Density (calculated) (mg/m^3)	1.745
Absorption coefficient (mm^{-1})	3.359
$F_{(000)}$	980
Index ranges	$-16 \le h \le 16$, $-8 \le k \le 9$, $-22 \le l \le 13$
Reflections collected	8122/5636 [$R_{(int)}$ = 0.0913]
Independent reflections	2253
Data/restraints/parameters	5636/0/490
Goodness of fit indicator	1.196
R [I > 2σ(I)]	R_1 = 0.0585, wR_2 = 0.0950
Largest diff. peak and hole (e $Å^{-3}$)	0.816 and -0.869

Synthesis of Cu(II) complex: A solution of copper(II) acetate hydrate (2.1 mg, 0.11 mmol) in ethanol (2 mL) was added dropwise to a solution of H_2L (5.3 mg, 0.13 mmol) in ethanol (2 mL) at room temperature. The colour of the mixing solution turned to brown immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for about three weeks. The solvent was partially evaporated and several pale-brown needle-like single crystals suitable for X-ray crystallographic analysis were obtained.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.46 mm × 0.30 mm × 0.07 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 896948.

RESULTS AND DISCUSSION

X-Ray crystallographic analysis revealed the crystal structure of the Cu(II) complex. And the structure is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. The complex crystallizes in the monoclinic system, space group P(2)1 and the unit cell contains two crystallographically independent but chemically identical molecules (molecules A and B, Fig. 1). And the dihedral angle of the two benzene rings (C4-C9 and C12-C17) in the molecule A is 51.76(3)º, while it is 55.34(3)º (C21-C26 and C29-C34) in the molecule B.

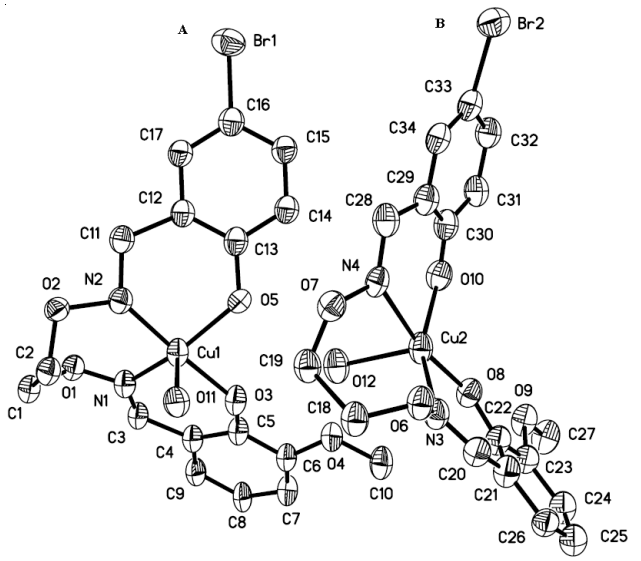

Fig. 1. Molecule structure of the complex with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º) FOR THE COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu(1)-N(2)	1.88(3)	Br(2)-C(33)	1.90(4)	O(3)-C(5)	1.32(4)
Cu(1)-O(3)	1.93(3)	N(1)-C(3)	1.25(4)	O(4)-C(6)	1.38(4)
Cu(1)-O(5)	1.93(2)	N(1)-O(1)	1.32(4)	O(4)-C(10)	1.41(4)
Cu(1)-N(1)	2.00(3)	N(2)-C(11)	1.41(4)	O(5)-C(13)	1.39(4)
Cu(1)-O(11)	2.23(2)	N(2)-O(2)	1.48(4)	O(6)-C(18)	1.41(5)
Cu(2)-O(8)	1.91(2)	N(3)-C(20)	1.21(4)	O(7)-C(19)	1.40(4)
Cu(2)-N(3)	2.07(3)	N(3)-O(6)	1.32(4)	O(8)-C(22)	1.26(4)
Cu(2)-O(10)	2.09(3)	N(4)-C(28)	1.34(5)	O(9)-C(27)	1.32(4)
Cu(2)-N(4)	2.17(3)	N(4)-O(7)	1.43(4)	O(9)-C(23)	1.52(4)
Cu(2)-O(12)	2.25(2)	O(1)-C(1)	1.45(5)	O(10)-C(30)	1.22(4)
Br(1)-C(16)	1.89(4)	O(2)-C(2)	1.42(4)	–	–
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
N(2)-Cu(1)-O(3)	176.6(13)	O(3)-Cu(1)-O(11)	91.9(10)	N(3)-Cu(2)-N(4)	94.5(11)
N(2)-Cu(1)-O(5)	92.0(11)	O(5)-Cu(1)-O(11)	94.6(9)	O(10)-Cu(2)-N(4)	84.9(11)
O(3)-Cu(1)-O(5)	86.0(10)	N(1)-Cu(1)-O(11)	113.4(11)	O(8)-Cu(2)-O(12)	96.2(10)
N(2)-Cu(1)-N(1)	91.4(12)	O(8)-Cu(2)-N(3)	88.6(11)	N(3)-Cu(2)-O(12)	110.5(11)
O(3)-Cu(1)-N(1)	89.1(11)	O(8)-Cu(2)-O(10)	88.0(10)	O(10)-Cu(2)-O(12)	93.1(10)
O(5)-Cu(1)-N(1)	151.7(11)	N(3)-Cu(2)-O(10)	156.3(11)	N(4)-Cu(2)-O(12)	92.6(10)
N(2)-Cu(1)-O(11)	91.0(10)	O(8)-Cu(2)-N(4)	169.0(12)	C(5)-O(3)-Cu(1)	122.4(5)

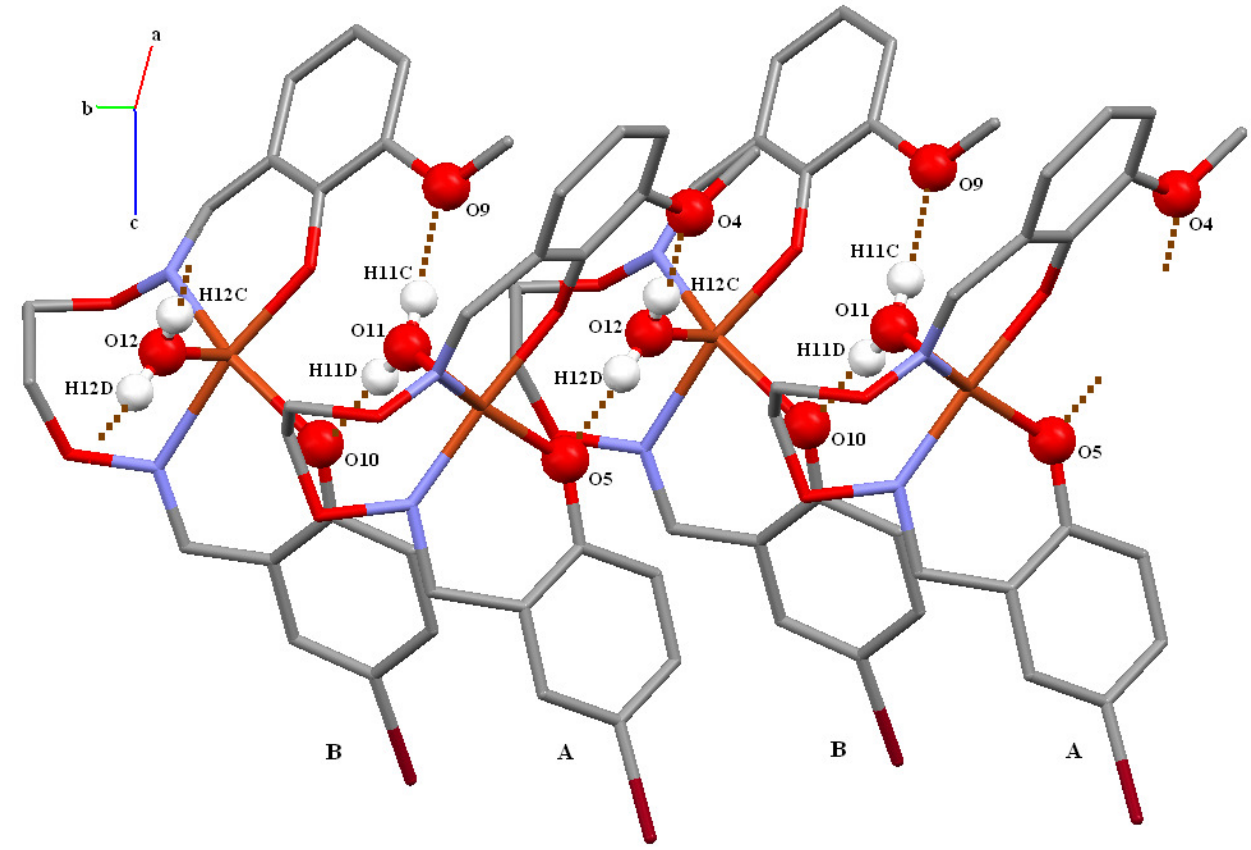

Fig. 2. Part of the infinite 1D chain motif of the complex. (Hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity

In the crystal structure, molecule A and molecules B interlink each other into a 1D infinite chain (Fig. 2) through four strong intermolecular O12-H12C···O4, O12-H12D···O5, O11-H11C···O9 and O11-H11D···O10 hydrogen bonds (Table-3). The packing diagram of the complex also shows an infinite regular network structure along the a axis and form a centro-symmetric rectangle-like large cave structure *via* carbon, oxygen, bromine and copper atoms along the a axis of the unit cell[11-13].

TABLE-3
HYDROGEN BONDS [Å, °] FOR THE COMPLEX

D-H···A	d(D-H)	d(H···A)	∠DHA	d(D···A)
O11-H11C···O9	0.85	1.95	179	2.801(4)
O11-H11D···O10	0.85	1.93	179	2.782(4)
O12-H12C···O4	0.85	2.02	177	2.872(4)
O12-H12D···O5	0.85	1.87	174	2.714(4)

REFERENCES

1. W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).
2. W.K. Dong, X.N. He, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao and X.L. Tang, *Polyhedron*, **28**, 1419 (2009).
3. M.A. Subhan, T. Suzuki and S. Kaizaki, *J. Chem. Soc.*, 1416 (2002).
4. W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009).
5. W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012).
6. A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, **107**, 8128 (1985).
7. W.K. Dong and J.G. Duan, *J. Coord. Chem.*, **61**, 781 (2007).
8. M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai and H. Okawa, *J. Chem. Soc.*, 259 (2000).
9. I. Sasaki, D. Pujol and A. Gaudemer, *Inorg. Chim. Acta*, **134**, 53 (1987).
10. W.K. Dong, J.F. Tong, Y.X. Sun, S.S. Gong and L. Li, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **41**, 155 (2011).
11. H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu and Y. Bai, *Z. Naturforsch.*, **66b**, 1049 (2011).
12. W.K. Dong, G. Wang, S.S. Gong, J.F. Tong, Y.X. Sun and X.H. Gao, *Transition Met. Chem.*, **37**, 271 (2012).
13. W.K. Dong, X.N. He, C.M. Dong, L. Wang, J.K. Zhong, X. Chen and T.Z. Yu, *Z. Kristallogr. New Cryst. Struct.*, **222**, 289 (2007).