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Synthesis and Structure of a *Trans*-oxpn-bridged Binuclear Copper(II) Complex

NAI-LIANG HU*, JIAN-HONG BI †, ZI-XIANG HUANG‡ and YU-HUA SHEN
Department of Chemistry, Anhui University, Hefei-230 039, PR China
E-mail: bijianhong@ahieedu.net.cn

A novel complex $[(CuL)_2(trans\text{-oxpn})](ClO_4)_2{\cdot}2DMF$, where oxpn is the dianion of N,N′-bis-(3-aminopropyl)oxamide and L = 1,10-N,N-fluorenone, was synthesized by the reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with Cu(oxpn) and L in the mixed solvent and characterized by IR spectra and elemental analysis. A single-crystal X-ray study shows that the complex is a four coordinated copper(II) with a plane square environment compound. The crystal is triclinic, space group p-1, with unit cell parameters: a = 9.03960(10) Å, b = 11.0938(3) Å, c = 11.3864(3) Å, $\alpha = 106.97(10)^\circ$, $\beta = 97.8450(10)^\circ$, $\gamma = 90.1180(10)^\circ$, V = 1080.87(4) $Å^3$, Z = 1, Mr = 1036.78, Dc = 1.593 Mg/m^3, $\mu = 1.185\ mm^{-1}$, F(000) = 532, T = 293(2) K, R = 0.0548, wR = 0.1323 for 3707 reflections with $I > 2\sigma(I)$.

Key Words: Crystal Structure, Copper(II) complex, 1,10-N,N-Fluorenone, N,N′-Bis-(3-3-aminopropyl)oxamide.

INTRODUCTION

Interests in the design, synthesis and study of binuclear copper complexes have expanded considerably over the last decades with different bridged-ligands[1–11], because they can be used as models for a number of important biological systems containing a coupled binuclear copper active site[12, 13]. The focus of much of this work has been on magnetic exchange interactions between the two copper ions[14], which may be diagnostic for the nature and geometry of the ligand-bridged binuclear centre, is very important for inorganic chemists to design new molecular materials with unusual magnetic and electrical properties[3, 5]. As one sort of these important ligands, oxamidates have played a key role in the design of polymetallic systemd owing to their ability to facilitate strong exchange interactions[4]. One of the most important properties of these ligands is very easy *cis-trans* conformational change affording symmetric and asymmetric oxamidato bridges[6–11]. The

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†Department of Chemistry, Anhui Institute of Education, Hefei-230 061, PR China
‡Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China.

different magnetic and electrical properties between *cis*- and *trans*-binuclear copper complexes have seldom been reported in view of the stereochemical factors. In this communication, the synthesis and the structure of a new complex $[Cu_2(trans\text{-}oxpn)L_2](ClO_4)_2$ were reported.

EXPERIMENTAL

[Cu(oxpn)] was synthesized by the reported method[8] and 1,10-N,N-fluorenone was synthesized using the method with the same principle as described elsewhere[15]. $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared by our laboratory. All solvents were commercially available and mostly of analytical grade. IR spectra were recorded on a Nicolet 170sx spectrophotometer, elemental analyses were performed on a Perkin-Elmer 240 analyzer.

Synthesis

To a 25 mL methanol solution of [Cu(oxpn)] (1 mmol) was added a 20 mL mixed solvent (methanol : DMF = 9 : 1) of 1, 10–N,N-fluorenone (L) (2 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) with stirring, the mixture was refluxed for 1 h to obtain a clear blue solution and after standing at room temperature for three weeks, well-shaped black-blue single crystals were obtained by slow evaporation. Elemental analyses for $Cu_2C_{36}H_{42}C_{12}N_{10}O_{14}$: Calcd.: C, 41.46; H, 4.05; N, 13.50%; Found: C. 41.37; H, 4.63; N, 13.60%.

Crystal structure determination

A deep blue crystal having approximate dimensions of 0.52 × 0.28 × 0.24 mm was selected and mounted on a glass fibre in a random orientation for X-ray diffraction study. Diffraction experiments were performed on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) at temperature 293(2) K, ω scan technique, $1.93° \leq \theta \leq 25.09°$. A total of 5513 reflections were collected, of which 3707 reflections were unique with $R_{int} = 0.0202$. Lp effects and empirical absorption were applied in data corrections. The structure was solved by direct methods and expanded using Fourier techniques, and SHELXS-97 program system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 289 variable parameters for 3707 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.0548 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.1323 \quad (2)$$

where $w = 1/[\sigma 2(F_0^2) + (0.00984P)^2 + 1.7425P]$ and $P = (F_0^2 + 2F_c^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.909 and –0.288e/$Å^3$, respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are given in Table-1 while the selected bond lengths and bond angles are listed in Table-2. The molecular structure of $[(CuL)_2(oxpn)](ClO_4)_2{\cdot}2DMF$ is shown in Fig. 1 with the hydrogen atoms omitted for clarity. Molecular packing arrangement in the unit cell is shown in Fig. 2. The molecule is symmetric and consists of $[(CuL)_2(\textit{trans}\text{-oxpn})]^{2+}$ cations with two DMF molecules and ClO_4^- ions to each copper atom on the same side. Each copper atom has the same coordination environment in a slightly distorted square plane so as to only lay out coordination environment of Cu atom. Cu is displaced by *ca.* 0.0483 Å out of the square plane defined by N(3) of L, N(1), N(2) and O(1A) of oxpn. In addition, atoms N(1), N(2), N(3), CuO(1A), C(4), C(4A), Cu(A), O(1), N(1A), N(2A), N(3A) are nearly coplanar. This mean plane deviation is *ca.* 0.0457 Å and the dihedral angle between the plane and L plane is 75°. Two L cycles are parallel. The Cu . . . Cu (A) distance of 5.23 Å is nearly same as that found in $[Cu_2(Him)(\textit{trans}\text{-oxpn})(NO_3)_2]$ (5.24 Å)[7]. The three atoms around N(2) lie in a plane with the sum of bond angles being 360°. This fact, together with the bond distances involved and the planarity of the oxamidato ligand, reveals that N(2) atoms and the π-carbonyl electrons are delocalized to form a conjugated system. The C(4)–C(4A) bond distance of 1.500 Å suggests a single bond, very close to those observed in other oxamidato-bridged copper(II) complexes. The distances between N(1) and O(12), N(1) and O(14), C(22) and

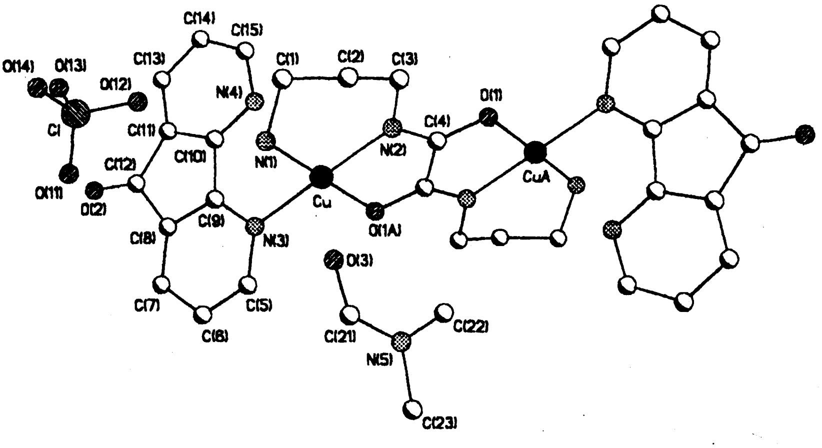

Fig. 1. Molecular structure of $[(CuL)_2(\textit{trans}\text{-oxpn})](ClO_4)_2{\cdot}2DMF$, omitted one ion and a DMF molecule on the side of Cu(A); hydrogen atoms are not shown

O(3), C(14) and O(12) of 2.945, 3.134, 3.445, 2.816, 3.445 Å, respectively, suggest hydrogen bonding interactions.

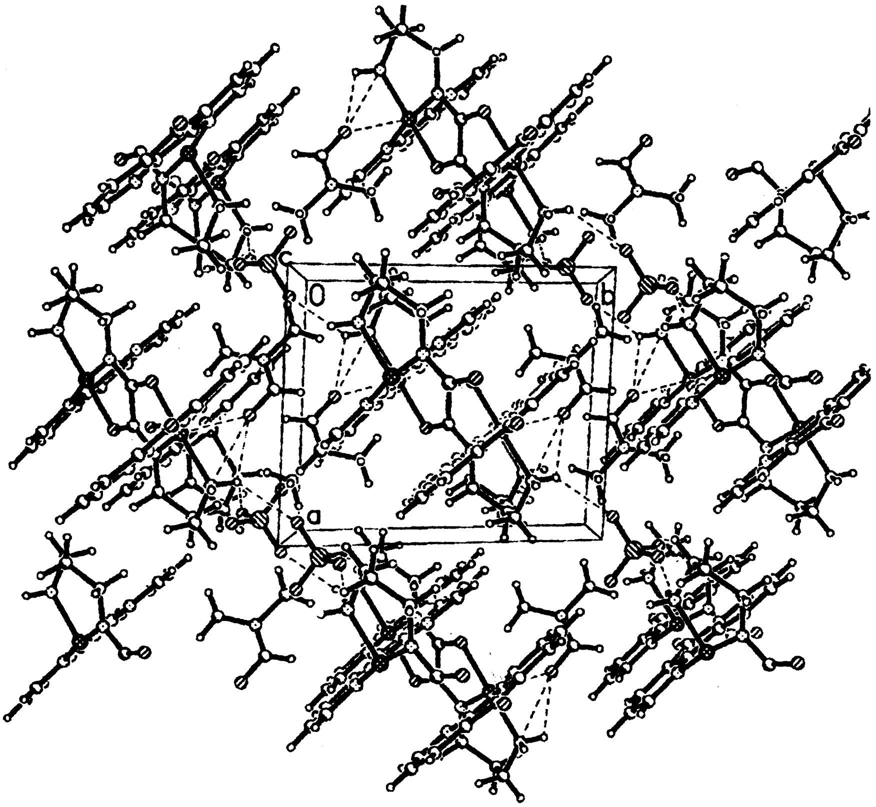

Fig. 2. Molecular packing arrangement in the unit cell

The IR spectrum of title complex has an absorption at 1591 cm^{-1} (amide I band) and a medium-intensity peak at 1320, 725 cm^{-1} ν(NCO stretch) as well as a triplet nearly at 3284 cm^{-1} ν(NH_2 stretches)[8]. Bands at 1079 (sharp) and 622 (sharp) cm^{-1} are diagnostic of perchlorate ions[13]. A sharp band centred at 1683 cm^{-1} and bands at 1572, 1561 cm^{-1} can be assigned to the CO and cycle stretches of 1,10-N,N-fluorenone. A sharp band at 1729 cm^{-1} is attributed to ν(NCO) of DMF.

Safety Note

Perchlorate salts of metal complexes with organic ligands are potentially explosive. In the synthesis described here, only small amounts of material were carried out at the millimole scale. The dilute solutions were handled with great caution and evaporated slowly at room temperature.

TABLE-1

ATOMIC COORDINATES (× 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($A^2 \times 10^3$)

Atom	X	Y	Z	U(EQ)
Cu	4013(1)	3278(1)	2915(1)	48(1)
O(1)	4108(3)	5724(3)	6298(3)	51(1)
O(2)	4341(6)	2941(5)	–2746(4)	96(1)
N(1)	2126(4)	2241(4)	2177(3)	53(1)
N(2)	3262(4)	4198(4)	4455(3)	50(1)
N(3)	4959(4)	2549(3)	1343(3)	49(1)
N(4)	2806(5)	4619(4)	1224(4)	59(1)
C(1)	753(6)	2732(6)	2670(5)	70(1)
C(2)	889(6)	2942(6)	4032(5)	74(2)
C(3)	1802(6)	4104(6)	4808(5)	76(2)
C(4)	4261(5)	4984(4)	5226(4)	45(1)
C(5)	6005(6)	1678(5)	1195(5)	59(1)
C(6)	6582(6)	1183(5)	118(5)	66(1)
C(7)	6062(6)	1569(5)	–920(5)	67(1)
C(8)	5003(5)	2456(5)	–795(4)	56(1)
C(9)	4502(5)	2938(4)	353(4)	50(1)
C(10)	3455(5)	3935(4)	291(4)	52(1)
C(11)	3315(6)	4070(5)	–899(4)	58(1)
C(12)	4239(7)	3134(5)	–1657(5)	69(1)
C(13)	2410(7)	4999(6)	–1149(6)	75(2)
C(14)	1701(7)	5711(6)	–214(6)	74(2)
C(15)	1928(6)	5502(5)	934(6)	70(1)
CL	535(1)	1177(1)	–1626(1)	64(1)
O(11)	1723(10)	480(12)	–1863(11)	246(6)
O(12)	715(11)	1859(8)	–402(6)	192(4)
O(13)	447(7)	2040(5)	–2332(6)	127(2)
O(14)	–752(7)	434(6)	–1924(6)	140(2)
N(5)	6719(5)	947(5)	4719(4)	68(1)
C(21)	5600(9)	549(7)	3830(6)	94(2)
C(22)	7024(12)	2202(9)	5430(10)	135(3)
C(23)	7831(11)	38(10)	4961(9)	135(3)
O(3)	4651(4)	1244(4)	3493(4)	79(1)

TABLE-2
THE SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Bond	Bond length	Angle	(°)
Cu-N(2)	1.964(3)	O(1)1-Cu-N(3)	89.19(13)
Cu-O(1)	1.978(3)	N(1)-Cu-N(3)	92.01(15)
Cu-N(1)	1.993(4)	C(4)-O(1)-Cu	110.5(3)
Cu-N(3)	2.042(4)	C(1)-N(1)-Cu	116.9(3)
O(1)-C(4)	1.282(5)	C(4)-N(2)-C(3)	118.5(4)
O(1)-Cu	1.978(3)	C(4)-N(2)-Cu	112.5(3)
N(1)-C(1)	1.473(7)	C(3)-N(2)-Cu	129.0(3)
N(2)-C(4)	1.297(5)	C(9)-N(3)-Cu	118.6(3)
N(2)-C(3)	1.443(6)	C(5)-N(3)-Cu	125.7(3)
C(4)-C(4)	1.500(9)	N(2)-C(3)-C(2)	113.8(4)
N(2)-Cu-O(1)	84.28(13)	O(1)-C(4)-N(2)	127.2(4)
N(2)-Cu-N(1)	94.68(15)	O(1)-C(4)-C(4)	118.2(5)
O(1)-Cu-N(1)	177.76(15)	N(2)-C(4)-C(4)	114.5(4)
N(2)-Cu-N(3)	172.00(15)		

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Supplementary Material

Crytallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-236006.

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