

烷氧桥联混合配位的双核铜配合物的合成、结构及量子化学计算

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Alkoxo-bridged Dinuclear Copper(II) Complex with Mixed Ligands: Synthesis, X-ray Crystal Structure and Theoretical Investigation

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Abstract: The synthesis, structural characterization and theoretical investigation of a novel alkoxo-bridged dinuclear copper(II) compound has been described. The title compound has the formula $C_{22}H_{28}Cl_2Cu_2N_8O_{11}$. It consists of dinuclear units with bridging methoxo groups. The ligands 2-amino-pyridine and 2-amino-6-hydroxyl-pyridine are linked to each copper via the pyridine N atoms respectively, providing a square planar CuN_2O_2 unit. The ClO_4^- anions in the title compound are semi-coordinated to copper ion at the distance of 0.265 83(4) nm (Cu-O (ClO_4^-)). The Cu-Cu distances within the dinuclear units are 0.299 79(9) nm with Cu-O-Cu angles of 102.27(9)°. The structures are stabilized by intramolecular H-bonds between the amino hydrogen atoms and oxygen atoms. Based on crystal data, quantum chemistry calculation on DFT/B3LPY level was used to reveal the electronic structure of the title compound. CCDC: 270807.

Key words: copper(II) complex; mixed ligands complex; alkoxo-bridged; quantum chemistry calculation

0 Introduction

There has been intensive interests in the past few years for planar Cu-(μ -OR)-Cu dinuclear systems in which μ -OR=OH⁻, MeO⁻, EtO⁻ [1-5], especially for the magnetic behavior of planar [N₂Cu(μ -OH)] systems

and the magneto-structural correlation between the angle Cu-O-Cu and the magnetical exchange parameter J [6,7]. Some hydroxo-bridged Cu(II) compounds also have catalytic activity [8]. In addition, low-molecular-weight Cu(II) coordination compounds with nitrogen-containing donors have frequently been used to model

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the active site in copper proteins^[9,10], with the aim to obtain insight into the correlation between structure and the spectroscopic and magnetic behavior. In earlier investigations of copper(II) dinuclear units containing hydroxo or alkoxo bridges, the crystal structures and the spectroscopic parameters have been studied^[11–15].

To explore the steric hinderance of the amino group and other groups we used the 2-amino-pyridine as ligand, and then investigated the structural and electronic states of their Cu(II) complexes. These ligands have an additional potential donor and/or H-bonding group. Furthermore, such a study can give insight into the influence of variable amino substitution to the geometry around the Cu(II) atom or even to the packing of the molecules. In the study we describe the synthesis and characterization of an alkoxo-bridged dinuclear copper(II) complex $[\text{Cu}(\mu\text{-OCH}_3)(2\text{-amino-pyridine})(2\text{-amino-6-hydroxyl-pyridine})_2](\text{ClO}_4)_2$ with mixed ligands.

1 Experimental

1.1 Materials and instrumentation

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. IR spectra were carried out on a Nicolet Co. Magna-IR 750 spectrometer with KBr pellets in the 4 000~400 cm^{-1} regions. UV-Vis spectrum was recorded on a Perkin-Elmer lambda900 ultraviolet spectrograph. Thermal analysis was recorded on a Perkin-Elmer TGA7 thermal analysis system. Quantum chemistry calculation was carried on a Pentium IV computer with G03 program.

1.2 Preparation of the title compound

The title compound $[\text{Cu}(\mu\text{-OCH}_3)(2\text{-amino-pyridine})(2\text{-amino-6-hydroxyl-pyridine})_2](\text{ClO}_4)_2$ was prepared by direct reaction of $\text{Cu}(\text{ClO}_4)_2$, $\text{NaN}(\text{CN})_2$ and 2-amino-pyridine in methanol solvent. We have expected that $\text{NaN}(\text{CN})_2$ and 2-amino-pyridine could react to yield an organic ligand, which could coordinate to copper ions to form a multi-nuclear copper compound. But out of expectation, 2-amino-pyridine was oxidized to yield 2-amino-6-hydroxyl-pyridine. The detailed mechanism will be discussed in section 2.1.

2-amino-pyridine (0.197 6 g, 2.1 mmol) was dissolved in 10 mL methanol, and then $\text{NaN}(\text{CN})_2$ (0.186 9 g, 2.1 mmol) was added into the above solution. The mixture was stirred for about 30 minutes at the temperature of 70 °C. And then $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.128 g, 4.3 mmol) was added and the system was kept stirred for about two hours, and then filtered. The resulting solution was kept at room temperature for three days to obtain blue block single crystals (0.552 3 g, yield: 33.6%). The IR spectra were recorded in the 4 000~400 cm^{-1} region by using KBr pellets and Nicolet Co. Magna-IR 750 spectrometer. 2-amino-pyridine and ClO_4^- (cm^{-1}): $\nu_{\text{N-H}}$: 3 435(m), 3 348(s); $\nu_{\text{C=C}}$, $\nu_{\text{C=N}}$: 3 221(m), 2 752(m), 1 668(s), 1 462(s), 1 339(m); $\nu_{\text{C=O}}$: 1 650; $\nu_{\text{Ar-H}}$: 3 058(m); $\gamma_{\text{C-H}}$: 780(5), 689(m); $\nu_{\text{Cl-O}}$: 1 247(w), 1 091(s).

1.3 Data collection, structure solution and refinement

A blue block single crystal with dimensions of 0.30 mm \times 0.20 mm \times 0.12 mm was selected and the measurement of the crystal was carried out on SMART APEX II CCD diffractometer with Mo $K\alpha$ ($\lambda=0.071\ 073$ nm) for the data collection. A total of 26 322 reflections were collected in the range of $2.21^\circ < \theta < 28.26^\circ$ at 293(2) K, of which 3 729 ($R(\text{int})=0.023\ 0$) are independent and 3 134 are observed ones with $I > 2.000\sigma(I)$. The corrections of Lp factor and Multi-scan absorption correction were applied. All the collected reflections were used in the structure analysis. Heavy atoms were obtained by direct method, and other non-hydrogen atoms were determined with successive difference Fourier syntheses. Part hydrogen atoms were determined with successive difference Fourier syntheses and the rest were located at the calculated positions. With anisotropic thermal parameters all non-hydrogen atoms were refined by full-matrix least-squares on F^2 for 253 parameters. All calculations were performed on a computer with SHELX-97 program package^[16,17]. Crystallographic data and other relevant information are listed in Table 1. The relevant bond lengths and bond angles are given in Table 2.

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Table 1 Crystal data and structure refinement parameters for the title compound

Formula	C ₂₂ H ₂₈ Cl ₂ Cu ₂ N ₈ O ₁₁	<i>F</i> (000)	792
Molecular weight	778.52	θ range / (°)	2.21 to 28.26
Crystal size / mm	0.20 × 0.12 × 0.10	Index ranges	-10 ≤ <i>h</i> ≤ 11, -24 ≤ <i>k</i> ≤ 24, -13 ≤ <i>l</i> ≤ 13
Crystal system	Monoclinic	Reflections collected: total	26 322
Space group	<i>P</i> 2 ₁ / <i>n</i>	Independent reflections	3729
<i>a</i> / nm	0.828 47(17)	Reflections observed (>2σ)	3 134
<i>b</i> / nm	1.842 1(4)	<i>R</i> _{int}	0.023 0
<i>c</i> / nm	1.049 2(2)	Data / restraints / parameters	3 729 / 2 / 253
β / (°)	108.97(3)	Goodness-of-fit <i>S</i> on <i>F</i> ²	1.077
<i>V</i> / nm ³	1.514 3(6)	Final <i>R</i> ₁ <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.048 7, 0.156 2
<i>Z</i>	2	All data	0.055 7, 0.162 6
<i>D</i> _c / (g·cm ⁻³)	1.707	Largest peak and hole / (e·nm ⁻³)	923, -111 9
μ / mm ⁻¹	1.651		

Table 2 Selected bond lengths (nm) and bond angles (°)

Cu(1)-O(5) ^a	0.192 3(2)	Cu(1)-O(5)	0.192 8(2)	Cu(1)-N(2)	0.200 5(3)
Cu(1)-N(1)	0.201 3(3)	Cu(1)-O(1)	0.265 83(4)	Cu(1)-Cu(1) ^a	0.299 79(9)
Cl(1)-O(1)	0.140 7(3)	Cl(1)-O(2)	0.137 0(4)	Cl(1)-O(4A)	0.137 7(6)
Cl(1)-O(3)	0.152 7(5)	O(5)-C(11)	0.142 2(4)	O(6)-C(1)	0.121 6(9)
N(1)-C(5)	0.132 0(5)	N(1)-C(1)	0.133 8(6)	N(2)-C(10)	0.133 9(4)
N(2)-C(6)	0.134 6(5)	N(3)-C(10)	0.135 6(5)	N(4)-C(5)	0.124 6(8)
C(1)-C(2)	0.138 1(7)	C(2)-C(3)	0.129 0(17)	C(3)-C(4)	0.138 4(18)
C(4)-C(5)	0.136 5(11)	C(6)-C(7)	0.137 0(6)	C(7)-C(8)	0.138 3(7)
C(8)-C(9)	0.135 5(6)	C(9)-C(10)	0.142 0(5)		
O(5) ^a -Cu(1)-O(5)	77.73(9)	O(5) ^a -Cu(1)-N(2)	171.90(10)	O(5)-Cu(1)-N(2)	94.42(10)
O(5) ^a -Cu(1)-N(1)	96.10(11)	O(5)-Cu(1)-N(1)	170.73(11)	N(2)-Cu(1)-N(1)	91.45(12)
O(5) ^a -Cu(1)-Cu(1) ^a	38.92(6)	O(5)-Cu(1)-Cu(1) ^a	38.80(6)	N(2)-Cu(1)-Cu(1) ^a	133.19(8)
N(1)-Cu(1)-Cu(1) ^a	134.65(9)	O(2)-Cl(1)-O(4A)	122.5(4)	O(2)-Cl(1)-O(1)	114.0(3)
O(4A)-Cl(1)-O(1)	115.0(4)	O(2)-Cl(1)-O(4B)	89.9(15)	O(2)-Cl(1)-O(3)	100.7(4)
O(1)-Cl(1)-O(4B)	102.5(12)	O(1)-Cl(1)-O(3)	101.5(3)	O(4A)-Cl(1)-O(3)	97.3(4)
C(11)-O(5)-Cu(1) ^a	125.8(2)	C(11)-O(5)-Cu(1)	125.0(2)	Cu(1) ^a -O(5)-Cu(1)	102.27(9)
C(5)-N(1)-C(1)	114.7(4)	C(5)-N(1)-Cu(1)	121.8(3)	C(1)-N(1)-Cu(1)	122.2(3)
C(10)-N(2)-C(6)	119.1(3)	C(10)-N(2)-Cu(1)	122.7(2)	C(6)-N(2)-Cu(1)	117.8(2)

Symmetry transformations used to generate equivalent atoms: ^a -*x*, -*y*, -*z*.

2 Results and discussion

2.1 Crystal structure

The structure of title compound contains a dinuclear Cu unit and two anions (perchlorate anion). Dinuclear Cu unit has a center of symmetry located between two copper ions as illustrated in Fig.1. 2-amino-pyridine and 2-amino-6-hydroxyl-pyridine ligands act as monodentate molecule with N(1) and N(2) as coordinating atoms respectively.

The copper atoms are both square-planar coordinated with the basal plane formed by two nitrogen atoms from mixed ligands (with Cu-N distances which vary from 0.200 5(3) to 0.201 3(3) nm) and two oxygens of two methoxo ligands (with Cu-O distances varying from 0.192 3(2) to 0.192 8(2) nm). The O-Cu-N angles of basal plane are 170.73(11)° and 171.90(10)°, respectively, deviating 8° to 10° from linearity. The angle of Cu-O-Cu bridge is 102.27(9)°. The dihedral angle formed by two pyridine rings is 117.16°, indicat-

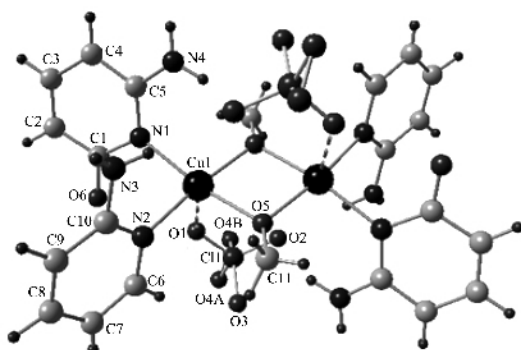


Fig.1 Structure of $[\text{Cu}(\mu\text{-OCH}_3)(2\text{-amino-pyridine})_2(\text{ClO}_4)_2]$ (O(4) is disordered)

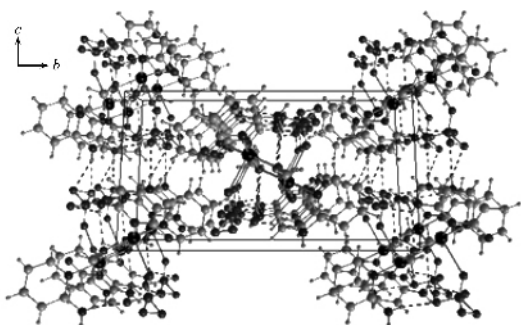
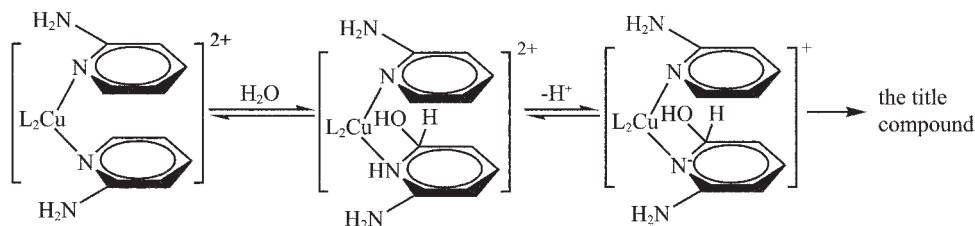


Fig.2 Crystal packing of the title compound

ing no existence of π - π stacking. The Cu-Cu distance within the dinuclear unit is 0.299 79(9) nm.

The perchlorate anion in the title compound is bridging at semi-coordination distance (Cu(1)-O(1)) 0.265 83(4) nm), which is much longer than normal



In addition, the whole structure is stabilized by intramolecular hydrogen bonds between the hydrogen atoms of the amino-nitrogen and the methoxo group and the oxygen atoms of the perchlorate group ($\text{N-H} \cdots \text{O}_{\text{perchlorate}}$ 0.292 2~0.310 2 nm). Details of the hydrogen bonds are listed in Table 3.

The dinuclear complex provides a new model for research of complexes with Cu_2O_2 in biological relevance and magnetic property. Further research will be

Cu-O distances. The copper ion is 0.003 92 nm above the equatorial plane (defined by N(1)-N(3)-O(5)-O(5)^a, a: $-x, -y, -z$) towards perchlorate oxygen.

The Cu-N and Cu-O distances are comparable with distances in the literature for similar compounds^[11~15]. The Cu-Cu distances and the Cu-O-Cu angles are in the range for comparable dinuclear square planar compounds from the literature in which Cu-Cu distance lies between 0.297 4 and 0.303 4 nm and Cu-O-Cu angles between 101.7° and 103.978°^[11~15,18].

It must be mentioned that because of oxidation of the 6-position in 2-amino-pyridine, the bond distance of C(5)-N(4) is shorten (0.124 6(8) nm) compared with C(10)-N(3) (0.135 6(5) nm) of 2-amino-pyridine. This phenomenon could be explained with Gillard mechanism^[19]: the coordination of pyridine-like ligand with metal ion could generate the effect similar to quaternization of pyridine, which will activate the carbon atom locating at nitrogen ortho-position. As a result, this carbon atom is apt to be attacked by nucleophilic reagent (such as OH^-). The reaction of OH^- attacking position-6 in 2-amino-pyridine is an nucleophilic mode, leading to increasing of electron cloud density on pyridine ring, and ultimately, strengthening C(5)-N(4). The mechanism could be presented as follows:

devoted to the affects of different mixed ligands on its properties.

2.2 Thermal analysis of the title compound

The title compound has two weight-loss stages. The first stage occurred at about 100~200 °C with the weight-loss of 3.145%, which could be attributed to the loss of absorption water on complex surface. The second one occurred at about 200~250 °C with weight-loss of 57.69%, which could be explained as the loss of two

Table 3 Hydrogen bonds in the title compound

D-H \cdots A	<i>d</i> (D-H) / nm	<i>d</i> (H \cdots A) / nm	\angle DHA / (°)	<i>d</i> (D \cdots A) / nm
N(3)-H(31) \cdots O(2) ^a	0.082(5)	0.212(5)	166.37	0.293 1(6)
N(3)-H(32) \cdots O(4A) ^b	0.083(4)	0.232(5)	156.61	0.310 0(7)
N(4)-H(4A) \cdots O(2) ^a	0.086	0.253	125.2	0.310 2(10)
N(4)-H(4A) \cdots O(3) ^a	0.086	0.242	125.2	0.299 8(10)
N(4)-H(4A) \cdots O(5) ^a	0.086	0.237	134.8	0.303 8(7)

Symmetry transformations used to generate equivalent atoms: ^a -*x*, -*y*, -*z*; ^b *x*, *y*, *z*+1.

organic ligands and methanol (the calculated value is 58.83%).

2.3 Electronic structure study of title compound

We adopt Gaussian03 program and B3LYP method^[20,21] which was brought forward by Becke to investigate the electronic structure of the title compound. Cep-4g basis sets is used for Cu atoms. 6-31g (d) basis sets was applied in C, O, N, Cl atoms and BNO method is used. 686 basis functions, 1 416 primitive gaussians, 178 alpha electrons and 178 beta electrons is involved in the calculation. The Mulliken atomic charges and natural electron configuration of compound is shown in Table 4. FMO of title compound are shown in Fig.3.

The energy of title compound is -3 489.400 90 a.u. after 33 cycles of calculation. HOMO (Fig.3) energy of crystal orbit is -0.247 12 a.u., and LUMO (Fig.3) energy is -0.216 62 a.u., the band gap is 0.030 5 a.u. (0.829 9 eV). Dipole moment of compound is 0.863 0 Debye, indicating the compound is center-containing.

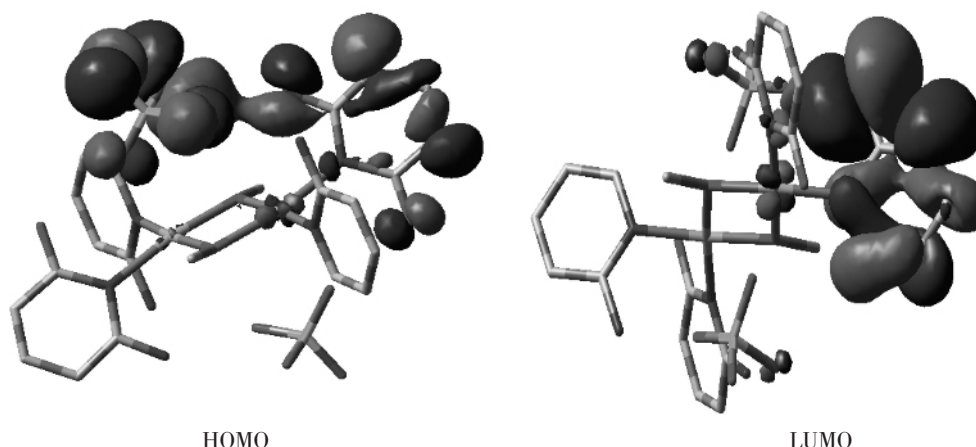
Table 3 shows that the net charges of Cu are 0.419 157 and 0.427 342, deviating greatly from +2. The total charge of 2-amino-pyridine and 2-amino-6-

Table 4 Mulliken atomic charges and natural electron configuration of part atoms

Atoms	Net charge	Electron configuration
Cu(1)	0.419 157	[core]4s ^{0.28} 3d ^{9.62} 4p ^{0.02} 4d ^{0.01} 5p ^{0.01} 6p ^{0.01}
Cu(1) ^a	0.427 342	[core]4s ^{0.28} 3d ^{9.62} 4p ^{0.02} 4d ^{0.01} 5p ^{0.01} 6p ^{0.01}
O(5)	-0.446 446	[core]2s ^{1.83} 2p ^{4.97} 3p ^{0.01}
O(5) ^a	-0.445 361	[core]2s ^{1.83} 2p ^{4.97} 3p ^{0.01}
N(1)	-0.519 867	[core]2s ^{1.35} 2p ^{4.31} 3p ^{0.02}
N(1) ^a	-0.526 104	[core]2s ^{1.35} 2p ^{4.32} 3p ^{0.02}
N(2)	-0.450 197	[core]2s ^{1.36} 2p ^{4.25} 3p ^{0.02}
N(2) ^a	-0.405 261	[core]2s ^{1.38} 2p ^{4.17} 3p ^{0.02}
O(1)	-0.507 972	[core]2s ^{1.83} 2p ^{5.02} 3d ^{0.02}
O(1) ^a	-0.507 523	[core]2s ^{1.83} 2p ^{5.01} 3d ^{0.02}
O(6)	-0.379 235	[core]2s ^{1.69} 2p ^{4.76} 3d ^{0.01}
O(6) ^a	-0.381 418	[core]2s ^{1.69} 2p ^{4.77} 3d ^{0.01}

Symmetry transformations used to generate equivalent atoms: ^a -*x*, -*y*, -*z*.

hydroxyl-pyridine are +0.066 453 and +0.097. So conclusion could be drawn that that part electrons have transferred from conjugation rings to Cu central atoms and come into being coordinate bonds. As shown in Table 4, the electron number of Cu 3d orbit and 4s orbit are 9.62 and 0.28 respectively (4p, 4d, 5p and 6p electron are so small that could be omitted). From

**Fig.3** FMOs of title compound

the above we can conclude that the Cu atom form coordinate bond with N and O atoms with $4s$ and $3d_{x^2-y^2}$. Crystal orbit overlap population show that the overlap population number of Cu(1) and Cu(1)^a is 0.225 186. These indicate that strong interaction between Cu atoms exists. The overlap population number of Cu(1) and O(1) is 0.073 000, which is consistent with the structure determination that the O(1) semi-coordinates with Cu(1). FMO figure (Fig.3) indicates that the active parts of the title compound locate mainly on amino group.

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