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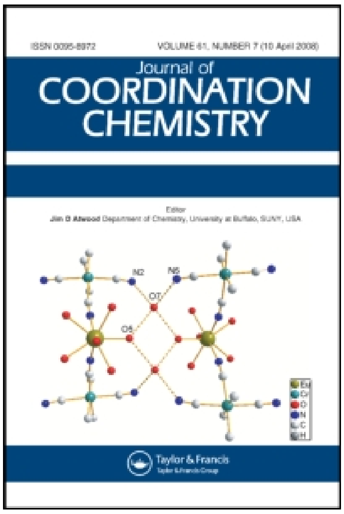

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A dinuclear diamagnetic copper(II) complex $[Cu_2(ophen)_2]Cl_2$ with hydroxylated phen

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A dinuclear diamagnetic copper(II) complex $[Cu_2(ophen)_2]Cl_2$ with hydroxylated phen

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A dinuclear diamagnetic copper(II) complex, $[Cu_2(ophen)_2]Cl_2$ (Hophen = 2-hydroxy-1, 10-phenanthroline), has been synthesized and characterized, providing good structural evidence for the long-debated Gillard mechanism.

Keywords: Copper(II) complex; Crystal structure; Hydroxylated phenanthroline; Hydrothermal

1. Introduction

Attention has focused on metal-directed supramolecular complexes due to their potential applications in novel magnetic materials, microporous phases and catalysts [1, 2]. Usually bi- or multi-dentate ligands containing N or O are used to bind metal centers [3]. For example, the chelate ligand 1,10-phenanthroline (phen) and its substituted derivatives have played an important role in the development of coordination chemistry. To interpret the anomalous properties of complexes such as $[M(phen)_3]^{n+}$ and $[M(bpy)_3]^{n+}$, Gillard adopted the idea of "covalent hydrates" from the organic chemistry and proposed an interesting mechanism [4]; the key component is nucleophilic attack of a hydroxide on coordinated heterocyclic ligand to form a covalent hydrate, which may react further by intramolecular shift of H_2O or OH^- onto the metal before formation of the final products. However, the mechanism was questioned [5, 6] owing to the lack of structural evidence for the covalent hydrate intermediate. In 2002, a Cu(I)–Cu(II) complex $[Cu_4(ophen)_4(tp)]$ provided structural evidence for Gillard's mechanism [8, 9] and later another two complexes, $[Cu_2(ophen)_2Cl]$ [10] and $[Cu_2(ophen)_2]H_2O$ [11], also were examples. But the Cu ions in these complexes are mixed (I, II) or (I, I) and are not the best examples for

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Gillard's mechanism. Herein, we describe a diamagnetic Cu(II)–Cu(II) complex with hydroxylated phen, $[Cu_2(ophen)_2]Cl_2$, and the possible reaction mechanism was also proposed.

2. Experimental

2.1. *Reagents and apparatus*

All the chemicals and the solvents were purchased from Xi'an Chemical Reagent Company of analytic grade. TGA analysis was carried out on a NETZSCH STA 449C instrument at heating rate of $10^{\circ}C\,min^{-1}$ under nitrogen. The X-ray single crystal structure was performed on a Bruker Smart-1000 CCD diffractometer. Variable temperature magnetic susceptibility data were collected on a Oxford UK Maglab system 2000 susceptometer.

2.2. *Synthesis of the complex*

$[Cu_2(ophen)_2]Cl_2$ was synthesized by a hydrothermal reaction with 2,2′-diphenic acid (0.484 g, 2 mmol), NaOH (0.160 g, 4 mmol) and $CuCl_2 \cdot 2H_2O$ (0.316 g, 2 mmol) dissolved in 12 mL of distilled water and solution of 1,10-phenanthroline (0.396 g, 2 mmol) in 2 mL of ethanol added. The resulting mixture was stirred at room temperature for 30 min until a homogeneous solution formed. The mixture was placed in the Teflon lined autoclave which was then sealed and heated to 160°C for 4 days. After cooling, dark needle crystals were filtered and dried in air (yield 60%, based on Cu). Elemental analysis (C, H, N) satisfied the formula: $C_{24}H_{14}C_{l2}Cu_2N_4O_2$.

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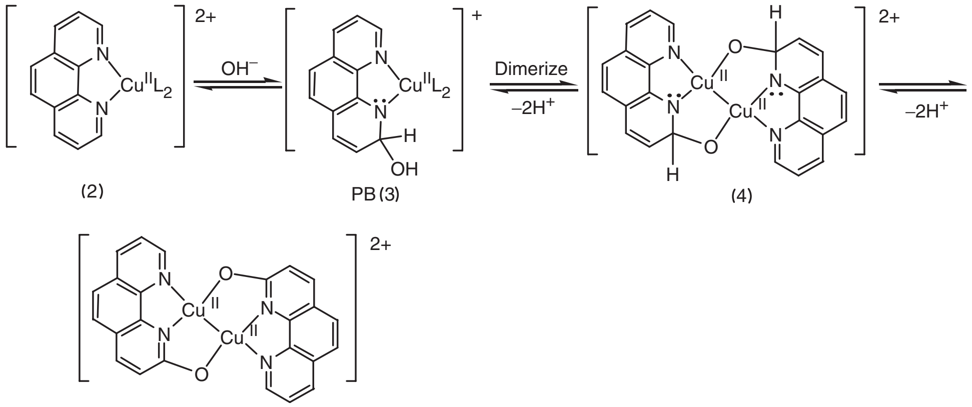
3. Results and discussion

3.1. *Synthesis and reaction mechanism*

Hydrothermal reactions have proved effective to prepare crystals [7], and is therefore useful to prepare hydrolated heterocyclic ligands. In our experiment, we attempted to synthesize a supramolecular complex of copper(II) with mixed ligands by the hydrothermal reaction of $CuCl_2 \cdot 2H_2O$ with phen, 2,2′-diphenic acid and NaOH. But the anticipated compound was not obtained and a dark dinuclear copper(II) complex $\left[Cu_2^{II}(ophen)_2\right]Cl_2$ was obtained, which is stable in air and insoluble in water and most organic solvents except for *N*,*N*-dimethylformamide (DMF). Although 2,2′-diphenic acid did not coordinate to Cu(II) ion in the title complex, experiments show it is impossible to prepare the complex without it. The 2,2′-diphenic acid may play a role of proton acceptor.

Hydroxylation of phen to produce Hophen is observed, providing structural evidence for the Gillard mechanism, i.e. covalent hydrate mechanism. Based on this mechanism and other well-known organic reactions, we propose a possible route for formation of our complex in scheme 1. First, because the α-carbon of phen can only be activated by



Scheme 1. Proposed formation mechanism of the title complex.

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coordination to Cu(II) ion, the intermediate $[\mathrm{M(phen)L_2}]^{2+}$ is formed, which can then be easily attacked by hydroxide to form a mononuclear covalent hydrate **2**, which deprotonates to form a pseudo-base **3**. The monomer **3** dimerizes to **4** and deprotonation of **4** produces the title complex.

In the second step, only the α-carbon atom in phen alters its hybridization from sp^2 to sp^3 and the N retains its sp^2 hybridization because the nucleophilic attack is by OH^-. The Cu^{2+} oxidation capability is weak and it is difficult to gain an electron from the N, so there is no intramolecular electron transfer. In this way, a dinuclear copper(II) complex is obtained.

3.2. *Crystal structure and magnetic susceptibility*

Diffraction data for the complex were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHEXTL-97 crystallographic software package. All of the non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were placed in calculated positions with fixed C–H distance (C–H, 0.93 Å). The crystallographic data are summarized in table 1. Selected bond distances and angles are given in table 2.

The structure of $[\mathrm{Cu_2(ophen)_2]Cl_2}$ is an infinite one-dimensional (1-D) chain framework. As shown in figure 1, each Cu(II) adopts trigonal geometry, being coordinated by two nitrogens from ophen and one oxygen from a deprotonated pyridyl hydroxy of another ophen. The average Cu–N bond distance of 2.0335 Å is longer than that of the Cu–O bond (1.898(8) Å) (table 1).

In this complex, the Cu(II)–Cu(II) distance of 2.530(3) Å is shorter than that of the corresponding Cu(I) complex $\left[\mathrm{Cu^{I}_2(ophen)_2}\right]$ (2.679(3) Å) [9], but longer than that of the mixed-valence $[\mathrm{Cu^{I}Cu^{II}(ophen)_2Cl}]\cdot \mathrm{H_2O}$ (2.4124(9) Å) [10]. The Cu–Cu distance is slightly shorter than the Cu–Cu separation of 2.56 Å in metallic copper [12], indicating very strong Cu–Cu interaction, which is also shown by the temperature-dependent magnetic susceptibility (figure 2). The complex shows diamagnetism ($\chi_\mathrm{M} < 0$)

Table 1. Crystal data and structure refinement for the title complex.

Empirical formula	$C_{24}H_{14}Cu_2N_4O_2Cl_2$
Formula weight	588.37
Crystal size (mm^3)	0.30 × 0.25 × 0.06
T (K)	293(2)
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cells and dimensions (Å, °)	
a	3.8680(10)
b	19.188(5)
c	26.952(7)
α	90.00
β	90.00
γ	90.00
V (Å^3)	2000.3(19)
Z	4
Density (g cm^{-3})	1.954
F(000)	1176
Data/restraints/parameters	1771/12/157
Goodness of fit (F^2)	1.012
Reflections collected/unique	9341/1771
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0825$, $wR_2 = 0.2877$
R indices (all data)	$R_1 = 0.1196$

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Table 2. Selected bond distances (Å) and angles (°).

Cu(1)–O(1)#1	1.898(8)	Cu(1)–N(1)	1.935(9)
Cu(1)–N(2)	2.132(10)	Cu(1)–Cu(1)#1	2.530(3)
O(1)#1–Cu(1)–N(1)	171.4(4)	O(1)#1–Cu(1)–N(2)	104.9(3)
N(1)–Cu(1)–N(2)	82.2(4)	O(1)#1–Cu(1)–Cu(1)1	89.4(2)
N(1)–Cu(1)–Cu(1)#1	83.2(3)	N(2)–Cu(1)–Cu(1)#1	165.1(3)

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z$.

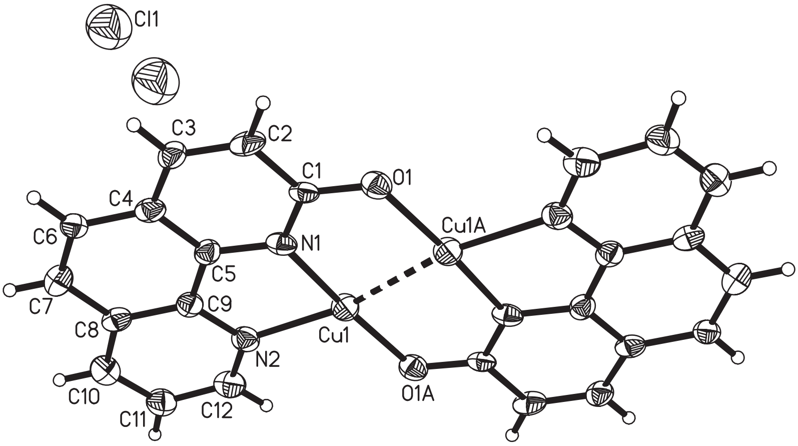

Figure 1. An ORTEP view of the title complex with atomic labeling.

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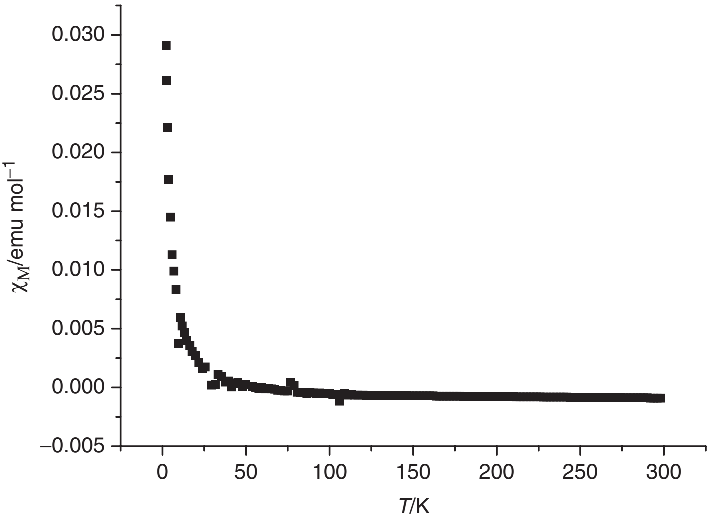

Figure 2. Plots of molar paramagnetic susceptibility χ_M *vs.* temperature T for the complex.

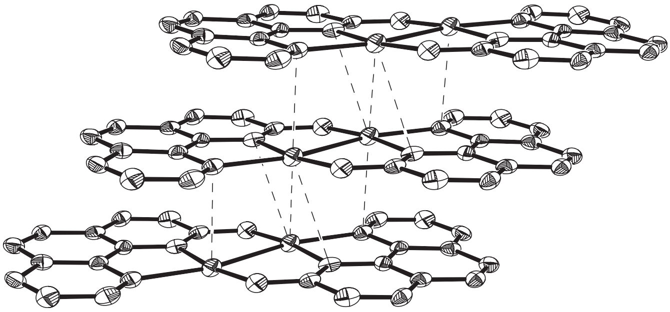

Figure 3. Perspective view showing the aromatic π–π stacking interactions and significant interactions between the Cu(II) ion and aromatic group in the cation of the complex.

at room temperature, indicating the single electron in each Cu(II) ion has been spin-paired due to the strong Cu(II)–Cu(II) interaction. This differs from the similar Cu_2(I,II) complex [9, 10, 13–15], which shows paramagnetism at room temperature and weak antiferromagnetic coupling at low temperatures. A very weak paramagnetism is also observed in the title complex when the temperature is under 20 K.

The bond angles around Cu are 82.2(4)°, 83.2(3)°, 104.9(3)° and 89.4(2), respectively, and remarkably, the total of the bond angles is 359.7° compared to 360° for an ideal planar structure. Furthermore, the two phen rings are approximately in one plane as well as the two copper atoms with deviation of 0.045 Å.

Adjacent cation planes of the complex are stacked through very strong, offset π–π aromatic stacking interactions [16] with face-to-face distance of 3.45 Å to furnish staircase-like one-dimensional (1-D) arrays (figure 3), while in the corresponding copper(I) complex $[Cu_2(ophen)_2]$, all molecular planes overlap [9]. Similar phenomena are observed in $[Ag_2(ophen)_2]$ [17], in which the offset face-to-face distance between adjacent molecules is 3.15 Å, and the complex is investigated as the first highly conducting, single-component molecular material ($\Omega = 14\,S\,cm^{-1}$).

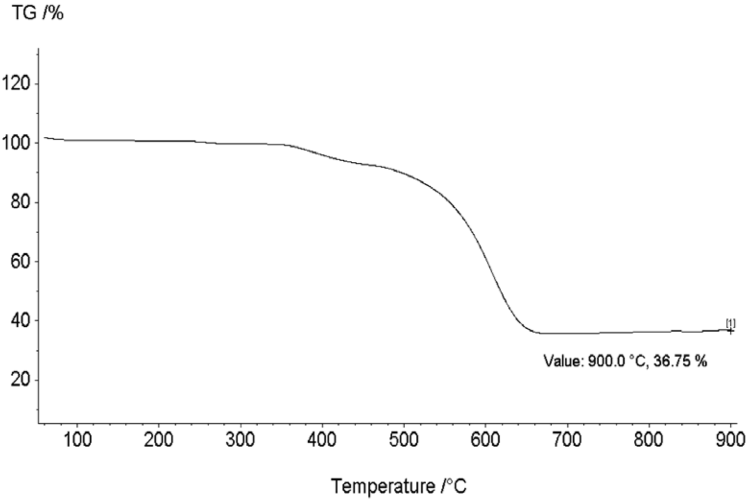

Figure 4. Thermal decomposition curve of the title complex.

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The room-temperature conductivity of the title complex in compacted pellets was also measured by the conventional two-probe technique, but the result showed a negligible conductivity.

3.3. *Thermal analysis*

TGA analysis (figure 4) shows that the complex is stable until 360°C and there is one main step of weight loss ending at 640°C. The observed weight loss corresponds to release of one water and two phen of 64.15% in agreement with calculated value (64.24%). The final product is admixture of $CuCl_2$ and CuO (chemometrics ratio is 1 : 1) after decomposition at 900°C (the residue value is 36.75%, calculated value is 36.39%).

4. Conclusion

A dinuclear copper(II) complex $[Cu_2(ophen)_2]Cl_2$ has been prepared in which $[Cu_2(ophen)_2]^{2+}$ cations are stacked through very strong, offset π–π interactions to furnish staircase-like one-dimensional (1-D) arrays. This complex provides good structural evidence for the long-debated Gillard mechanism. The magnetic data are interpreted in terms of antiferromagnetic coupling, consistent with a strong Cu–Cu interaction. The complex is stable until 360°C.

Supplementary materials

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC No. 235052. The data of temperature-dependent magnetic susceptibility can be obtained from the author.

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