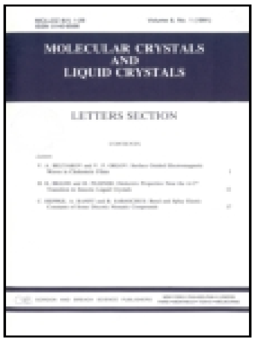

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One Dinuclear Copper(II) Complex: Synthesis, Structure, and Properties

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*The reaction of $Cu(AC)_2{\cdot}H_2O$ with 4-diethylamino-2-hydrogen-benzaldehyde (Hdahb) in methanol and water under solvothermal conditions leads to the formation of a novel dinuclear complex $[Cu_2(dahb)_4]$ (**1**) ($C_{44}H_{56}Cu_2N_4O_8$, Mr = 896.03, D_{calcd} = 1.404 g cm^{-3}). The compound belongs to the monoclinic system space group $P2_1/c$, and was characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. It consists of dinuclear unit, which is bridged by μ_2-phenolato oxygen. The $\{Cu_2^{II}O_2\}$ core displays dominant antiferromagnetic interactions from the nature of the binding modes through μ_2-O.*
[Supplemental materials are available for this article. Go to the publisher's online edition of Molecular Crystals and Liquid Crystals to view the free supplemental file.]

Keywords Crystal structure; dinuclear copper; magnetism

1. Introduction

Recently, the rational design and synthesis of novel coordination polymers have drawn considerable attention in the field of supramolecular chemistry and crystal engineering due to their interesting topologies and potential applications in magnetism, molecular adsorption, catalysis, electrical conductivity, and nonlinear optics [1–6].

Generally, there are many factors that affect self-assembly of coordination assemblies: such as chemical structure of the ligands chosen, the coordination geometry preferred by the metals ions, the reaction temperature and the solvent system, the counterions and the methods of crystallization [7–11]. In our previous study, we have reported a series tetra- and heptanuclear clusters based on 2-hydrogen-benzaldehyde ramification [12]. we found that the position and bulk of substituent group maybe influence the structure of the coordination complexes. Herein, choosing another 2-hydrogen-benzaldehyde ramification 4-diethylamino-2-hydrogen-benzaldehyde (Hdahb) as reagent, we obtained a novel dinuclear complex. The complexes of Hdahb have not been reported, through Schiff bases' complexes based on Hdahb have been reported several examples [13–16]. We reported the first dinuclear copper complex $[Cu_2(dahb)_4]$ based on Hdahb.

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2. Experimental

2.1. Material and Physical Measurements

All chemicals were commercially available and used as received without further purification. The C, H, N microanalyses were carried out with a PE 2400 series II elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrophotometer. The crystal structure was determined by single-crystal X-ray diffraction and using SHELXS-97, SHELXL-97 software for structure solution and refinement, correspondingly. Magnetization measurements were carried out with a Quantum Design MPMS-XL7 SQUID.

2.2. Synthesis

A mixture of Hdahb (0.097 g, 0.5 mmol), $Cu(AC)_2{\cdot}H_2O$ (0.199 g, 1 mmol), methanol (7.0 mL) and H_2O (7.0 mL) was placed in a teflon-lined stainless steel vessel, heated to 120^{o}C for 120 hr, and then cooled to room temperature. Blue block crystals were obtained. Phase-pure crystals were obtained by manual separation (yield: 56 mg, 50.00% based on Hdahb). *Anal. Calcd.* (%) for $C_{44}H_{56}Cu_2N_4O_8$: C, 58.98; H, 6.3; N, 6.25. Found (%): C, 58.76; H, 6.46; N, 6.32. IR data (KBr, cm^{-1}): 3429 (m), 2931 (w), 2823 (w), 1616 (s), 1539 (m), 1439 (s), 1339 (m), 1241 (s), 1207 (s), 1048 (m), 963 (w), 860 (w), 737 (m), 647 (w).

2.3. Crystal Structure Determination

The diffraction data sets were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 293 K using the ω–θ scan mode in the range $2.92^\circ \leq \theta \leq 25.01^\circ$. Raw frame data were integrated with the SAINT program [17]. The structure was solved by direct methods using SHELXL-97 and refined by fullmatrix least-squares on F^2 using SHELXS-97 [17]. An empirical absorption correction was applied with the program SADABS [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode. Calculations and graphics were performed with SHELXTL [17]. The crystallographic details are provided in Table 1, while the selected bond distances and angles are listed in Table 2.

3. Results and Discussion

3.1. Structural Description

Single-crystal X-ray structure analysis reveals that $Cu_2(dahb)_4$ crystallizes in a monoclinic system space group $P2_1/c$. It is shown in Fig. 1 that the symmetrical unit contains two copper atoms, four $danb^-$ ligands. Cu1 is coordinated by four oxygen atoms from two different $dahb^-$ ligands and the fifth oxygen atom from the third $dahb^-$ ligand formed tetragonal pyramid geometry with O3A (symmetry code: (A) $1-x$, $1-y$, $1-z$) at the apical position with bond lengths in the range of 1.896–2.502 Å and the O–Cu1–O angles in the range of 84.22°–94.62° and 171.12°–175.8°. Each pair of Cu(II) ions is bridged by a pair of μ_2-O of the $dahb^-$ ligands into a dimer with an intramolecular Cu···Cu distance of 3.272(1) Å which

Table 1. Crystallographic and experimental data for the complex **1**

Complex	**1**
Formula	$C_{44}H_{56}Cu_2N_4O_8$
Formula mass	896.03
Crystal system	Monoclinic
Space group	$P2_1/C$
a (Å)	7.0533 (2)
b (Å)	16.4883(6)
c (Å)	18.3538 (7)
β (°)	96.689 (4)
V (Å^3)	2119.96(13)
Z	2
D_{calcd} (g cm^{-3})	1.404
μ (mm^{-1})	1.060
θ range (°)	2.91–25.01
R_{int}	0.0491
Goof	1.026
Completeness	99.2%
$F000$	940
R_1[a] ([$I > 2\sigma$])	0.0879
wR_2[b]	0.2177

Notes. [a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w(|F_o{}^2|)^2]^{1/2}$.

is shorter than the copper distances in the dimer copper(II) complex [$Cu_2L(O_2CC_6H_4$-p-NH_2)]] (where L is a trianionic pentadentate Schiff base ligand *N*,*N*′-(2-hydroxypropane-1,3-diyl) bis(salicylaldimine)) (3.472(1) Å) [18], and longer than copper···copper distances in the dimeric copper(II) carboxylates (2.59–2.747 Å) [19] and dimeric copper(II) 1H-benzimidazol-2-yl-methanol complex (3.043(1) Å) [20]. The dimmer further constructed

Table 2. Selected bond lengths (Å) and bond angles (°) of **1**

Cu1—O1	1.896(5)	Cu1—O2	1.959(5)
Cu1—O3	1.920 (5)	Cu1—O4	1.961 (6)
Cu1—O3A	2.502 (5)	O3—Cu1—O4	93.9 (2)
O1—Cu1—O3	175.8 (2)	O3A—Cu1—O1	98.6 (2)
O1—Cu1—O2	94.6 (2)	O3A—Cu1—O2	87.9 (2)
O1—Cu1—O4	86.6 (2)	O3A—Cu1—O3	85.4 (2)
O2—Cu1—O4	171.1 (2)	O3A—Cu1—O4	100.6 (2)
O3—Cu1—O2	84.2 (2)	O3—Cu1—O4	93.9 (2)
O1—Cu1—O3	175.8 (2)	Cu1—O3—Cu1A	94.6 (2)

Notes. Symmetry codes: (A) $1 - x$, $1 - y$, $1 - z$.
One dinuclear copper(II) complex: syntheses, structures, and properties.

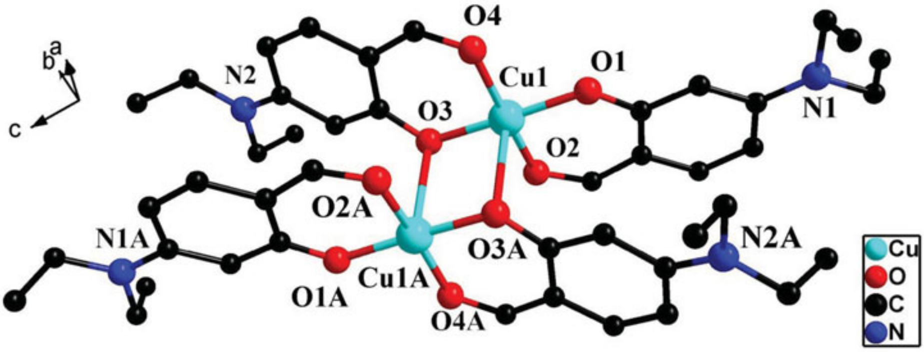

Figure 1. Crystal structure of the complex **1** and hydrogen atoms have been omitted for clarity.

one-dimensional (1D) through C–H···O hydrogen bonds (C7-H7···O4^{i}, 3.229(1) Å, C18-H18···O4^{ii}, 3.198(1) Å, symmetry code: (i) $x-1, y, z$; (ii) $x+1, y, z$) (Fig. 2(b)) which formed a 3D through weak C–H···π interaction (C22–H22a···X1A^{iii}, 3.563(1) Å, C8-H8b···X1A^{iv}, symmetry code: (iii) x, $1.5-y$, $0.5+z$; (iv) $1-x$, $-0.5+y$, $0.5-z$. X1A is the centroid of the one benzene ring of the ligand of **1**, which is the centroid of C1, C2, C3, C4, C5 and C6 or C12 C13 C14 C16 and C17, Fig. 2(a), Fig. S1).

3.2. Magnetic Properties

The magnetic susceptibilities of **1** were measured by using a crushed single crystalline sample. The dc susceptibilities of the complex were measured under an applied field of 1 KOe for **1** at temperatures ranging from 2 to 330 K.

For the complex **1**, at 330K, spin–orbital coupling of Cu^{II} ion gives rise to a $\chi_M T$ product of 2.50 cm^3 K mol^{-1}. With decreasing T, $\chi_M T$ value linearly reduces to a minimum of 0.79 cm^3 K mol^{-1} at 2 K. The temperature dependence of the reciprocal susceptibility $\chi_M{}^{-1}$ above 150 K follows the Curie–Weiss law [$\chi_M = C/(T-\theta)$] with a Weiss constant of $\theta = -334.12$ K and Curie constant of $C = 5.0$ cm^3 Kmol^{-1} (Figure S2). The negative Weiss constant indicates dominant intramolecular antiferromagnetic interaction between adjacent Cu^{II} ions through the two μ_2-oxygen exchange bridges (Fig. 3).

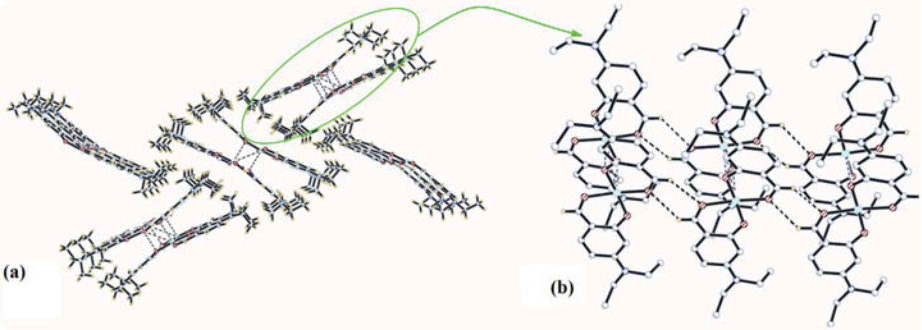

Figure 2. Packing drawing of 1(a); 1D chain through C–H···O hydrogen bonds of 1(b).

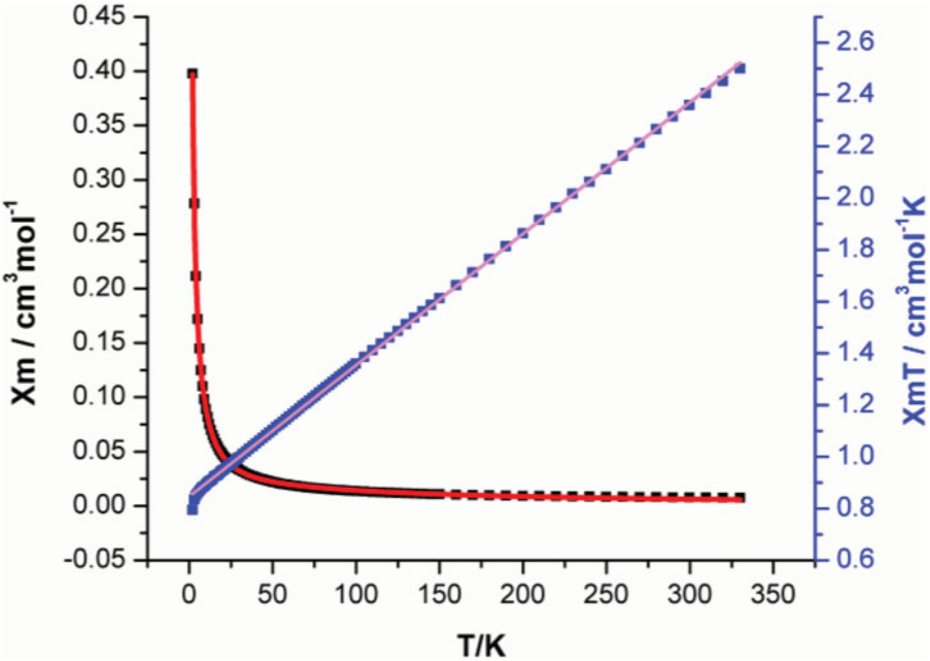

Figure 3. Plot of χ_m–T and $\chi_m T$–T for complex **1**.

According to Hodgson [21] antiferromagnec interaction becomes stronger with the increasing of Cu–O–Cu angle. As well known, antiferromagnec interaction among di-μ-alkoxo-dicopper(II) complexes generally fall in line with this rule in the range of Cu—O—Cu angle 94°–105° [22]. It has been revealed that spin coupling between copper(II) ions in di-μ-hydroxo-dicopper(II) complexes is deeply dependent on the Cu—O—Cu angle [23]. Herein, the Cu—O—Cu angle is 94.6° and Cu···Cu distance is 3.272 Å. Inspection of the molecular structure reveals that one main exchange pathway exists: J, the interaction between Cu1···Cu1A by two μ_2–O bridges. The Van Vleck's equation using Kambe's method [24] as follows with Hamiltonian: $\hat{\mathrm{H}} = -2J\vec{\mathrm{S}}_1 \cdot \vec{\mathrm{S}}_2$

$$x = (1-\rho)\left(\frac{2N\mu_B^2 g^2}{kT} \times \frac{1}{3+\exp\left(\frac{-2J}{kT}\right)}\right) + \rho\left(\frac{N\mu_B^2 g^2}{2kT}\right) \tag{1}$$

The best fitting gave: $J = -\ 0.399\ \mathrm{cm}^{-1}$, $g = 2.24$.

3.3. IR Spectra

The IR spectral data of the compound **1** and the ligand are shown in Fig. 4. There are indications that broad bands in the range of 2976 cm^{-1} can be assigned to the stretching frequency of the intermolecule hydrogen bond between atom O and H of the free ligand. The ν(C—O) phenolic of the free ligand at 1239 cm^{-1} was shifted to lower frequency (1207 cm^{-1}) in the complex, suggesting its participation the chelation [25]. The ν(C=O) carbonyl group of the free ligand at 1633 cm^{-1} was shifted to lower frequency (1616 cm^{-1}) in the complex, also indicating the O atom of the carbonyl group participation coordination [26]. The complex showed two new strong bands at 1241 cm^{-1} and at 1048 cm^{-1} which

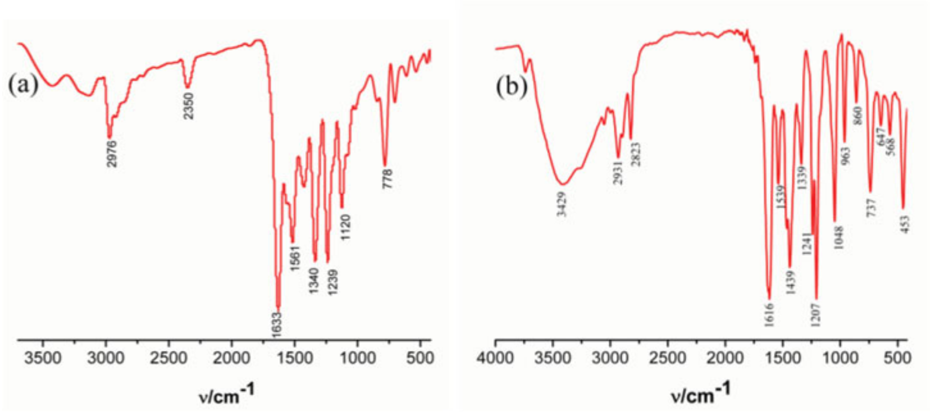

Figure 4. IR spectra of free ligand (a) and **1** (b).

may be assigned to the ν (C—N) stretching frequencies. The peaks observed at 453 cm^{-1} can be assigned to ν (Cu—O), probably originating from the coordination of the ligand [27].

4. Conclusion

Using 4-(diethylamino)-2-hydroxybenzaldehyde, the binuclear complex has been synthesized. The coordinated environment of metal ions in the synthesis system seems to be the most important synthetic parameter in formation of the complex. Magnetic studies indicate that the complex displays a dominant antiferromagnetic interaction between the Cu^{II} ions through the two μ_2-oxygen exchange bridges.

Funding

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Notes

Electronic Supplementary Information (ESI) available: [C—H···π hydrogen bonds of **1;** Plot of $\chi_m{}^{-1}$–T for **1**]. CCDC 974254 contain the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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