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Synthesis and Magnetic Properties of a New Binuclear Copper(II) Complex with Naphthalato-Bridged Ligand[1]

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Abstract—To utilized a bridged-ligand of 1,8-naphthalate dianion (NAPH) as building block by self-assembly technology, a new binuclear copper(II) compound $[Cu_2(\mu\text{-NAPH})_2(DMF)_4(H_2O)_2]$ (**I**) has been constructed and structurally characterized by X-ray crystallography. Complex **I** crystallizes in monoclinic, space group $C2/c$, with $a = 17.822(9)$, $b = 9.964(5)$, $c = 23.194(11)$ Å and $\beta = 102.385(5)°$. Magnetic measurements confirm that **I** presents a very weak antiferromagnetic interaction between the paramagnetic ions.

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INTRODUCTION

The design and synthesis of self-assembling supramolecular systems are an area of intense interest as a route to the rational generation of functional materials [1, 2]. Recent studies have also showed that supramolecular interactions played significant roles in drug enzyme complexes, protein folding and in model chemical systems [3–5]. The carboxylic complexes have attracted much attention of scientists as a type of building blocks. Besides its novel topological structure, these carboxylic complexes always have the potential application in these area [6–8]. Compared with flexible carboxylic acid coordination polymer, the rigid one could not change its orientation easily while it coordinate with metals. Thanks to this character, we could design and control the structure of the target product effortlessly. Therefore, scientists has attached a lot of importance to the complexes based on the building blocks of the naphthalic acid or naphthalene four formic acid which is the rigid polydentate ligand and provided much helpful experience to design the self-assembly carboxylic acid coordination polymers [9–14]. Herein, a NAPH-bridged ligand (NAPH = 1,8-naphthalate dianion) is utilized to constructed a new binuclear complex, $Cu_2(\mu\text{-NAPH})_2(DMF)_4(H_2O)_2$ (**I**). The magnetic property of **I** has also been investigated.

EXPERIMENTAL

Materials and methods. All reagents are of analytical grade and were used without further purification. Distilled water was used for all procedures. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer elemental analyzer (model 240). The infrared spectrum was obtained on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} region, using KBr pellets. Variable temperature magnetic susceptibilities were measured on a SQUID magnetometer from 2.0 to 300 K in a magnetic field of 1000 Oe, and the diamagnetic corrections were applied by using Pascal's constants.

Synthesis of I. In a DMF solution (10 mL) containing 1,8-naphthalic acid (43.2 mg, 0.2 mmol) and triethylamine (0.4 mmol), a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (148.2 mg, 0.4 mmol) in DMF (5 mL) was added and kept under magnetic stirring, a bluish-green solution was obtained. The resulting solution was filtered and kept at room temperature after several weeks to give bluish-green block crystals suitable for the X-ray structural analysis.

For $C_{36}H_{44}Cu_2N_4O_{14}$

anal. calcd., %:	C, 48.9;	H, 5.0;	N, 6.3.
Found, %:	C, 49.2;	H, 5.1;	N, 6.4.

IR (KBr; ν, cm^{-1}): 3433, 3055, 2868, 1597, 1414, 1096, 1015, 816, 712, 623.

X-ray crystallography. All measurements were made on a Rigaku XtaLAB mini CCD detector with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The empirical absorption corrections by semi-empirical from equivalents were carried out. The structure was solved by direct methods using the SHELXS-97 program and refined with SHELXL-97 [15] by full-matrix least-squares techniques on F^2. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for **I**

Parameter	Value
F_w	883.83
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	17.822(9)
b, Å	9.964(5)
c, Å	23.194(11)
β, deg	102.385(5)
V, Å^3	4023(3)
ρ, g cm^{-3}	1.459
Z	4
μ, mm^{-1}	1.127
F(000)	1832
Crystal size, mm	0.28 × 0.22 × 0.18
θ Range for data collection, deg	3.11–25.00
Limiting indices	$-21 \le h \le 21$, $-11 \le k \le 11$, $-27 \le l \le 27$
Reflections collected/unique (R_{int})	16842/3508 (0.0540)
Data/restraints/parameters	3508/7/262
Goodness-of-fit on F^2	1.076
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0351$, $wR_2 = 0.0865$
R indices (for all data)	$R_1 = 0.0425$, $wR_2 = 0.0911$
Largest diff. peak and hole, e/Å^3	0.400 and –0.476

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Cu(1)–O(7)	1.9626(19)	Cu(1)–O(4)$^{\#1}$	1.9631(19)
Cu(1)–O(2)	1.9654(19)	Cu(1)–O(5)	1.9840(19)
Cu(1)–O(6)	2.2974(19)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(7)Cu(1)O(4)$^{\#1}$	94.56(7)	O(7)Cu(1)O(2)	90.31(7)
O(4)$^{\#1}$Cu(1)O(2)	175.00(7)	O(7)Cu(1)O(5)	171.05(7)
O(4)$^{\#1}$Cu(1)O(5)	88.53(7)	O(2)Cu(1)O(5)	86.49(7)
O(7)Cu(1)O(6)	97.35(8)	O(4)$^{\#1}$Cu(1)O(6)	89.60(8)
O(2)Cu(1)O(6)	90.89(8)	O(5)Cu(1)O(6)	91.06(8)

* Symmetry code: $^{\#1}$ $-x + 3/2$, $-y + 1/2$, $-z + 1$.

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RESULTS AND DISCUSSION

Bluish-green block crystal of **I** can be obtained reproducibly by reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with NAPH dianion in DMF solution. The significant bands in the IR spectra of **I** exhibit two characteristic strong bands at 1647 and 1416 cm^{-1}, which may be attributed to the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretching vibrations of the carboxylato group [16]. The OH stretching frequency as a broad band is found at 3433 cm^{-1}.

Details of the structure analysis of complex **I** are given in Table 1. As shown in Fig. 1, the complex **I** is a binuclear complex, namely, $Cu_2(\mu\text{-NAPH})_2(DMF)_4(H_2O)_2$, where NAPH is 1,8-naphthalate dianion. Selected bond distances and angles are listed in Table 2. The central Cu^{2+} ion shows an axially elongated square-pyramidal with four Cu–O_{eq} bonds (Cu(1)–O(2) 1.9654(19), Cu(1)–O(4)$^{\#1}$ 1.9631(19) Å, symmetry code: $-x + 3/2$, $-y + 1/2$, $-z + 1$); Cu(1)–O(5) 1.9840(19), and Cu(1)–O(7) 1.9626(19) Å) occupying the equatorial plane, and the Cu–O_{ax} bond with bond length of 2.2974(19) Å (Cu(1)–O(6)) at the axial site, which is considerably longer than the Cu–O_{eq} bond distance of average 1.968 Å. The phenomena may be attributed to the Jahn–Teller effect of copper(II) ion. The crystal structure of complex **I** contains two NAPH and two Cu^{2+} ions. Two COO^- of μ-NAPH as a monodentate ligand coordinated to Cu atoms, respectively, and resulting in a cyclic structure. The packing of **I** is shown in Fig. 2. The intramolecular Cu(II)···Cu(II) distance is 4.702 Å.

Variable-temperature (2–300 K) magnetic susceptibility data are collected on polycrystalline samples and the magnetic behavior of **I** are represented in Fig. 3 in the form of χ_M and $\chi_M T$ versus T plot. At 300 K, the $\chi_M T$ value is 0.98 cm^3 K mol^{-1}. Upon cooling, $\chi_M T$ remains nearly constant, and decreases at $T < 10$ K, and reaching the minimum value of 0.59 cm^3 mol^{-1} K at 2 K implying a very weak antiferromagnetic coupling in this system. The experimental magnetic data have been fitted using the Bleaney–Bowers expression derived through the Hamiltonian operation, $\hat{H} = 2J\hat{S}_1\hat{S}_2$, with $S_1 = S_2 = 1/2$ (Eq. 1)

$$\chi = \frac{2Ng^2\beta^2}{kT}\left[\frac{1}{3 + \exp(-2J/kT)}\right](1 - \rho) + \frac{Ng^2\beta^2}{2kT}\rho + N_\alpha, \qquad (1)$$

where an additional coupling parameter zJ' was added in Eq. (2) to take a molecular field approximation into account the magnetic behavior at low temperature.

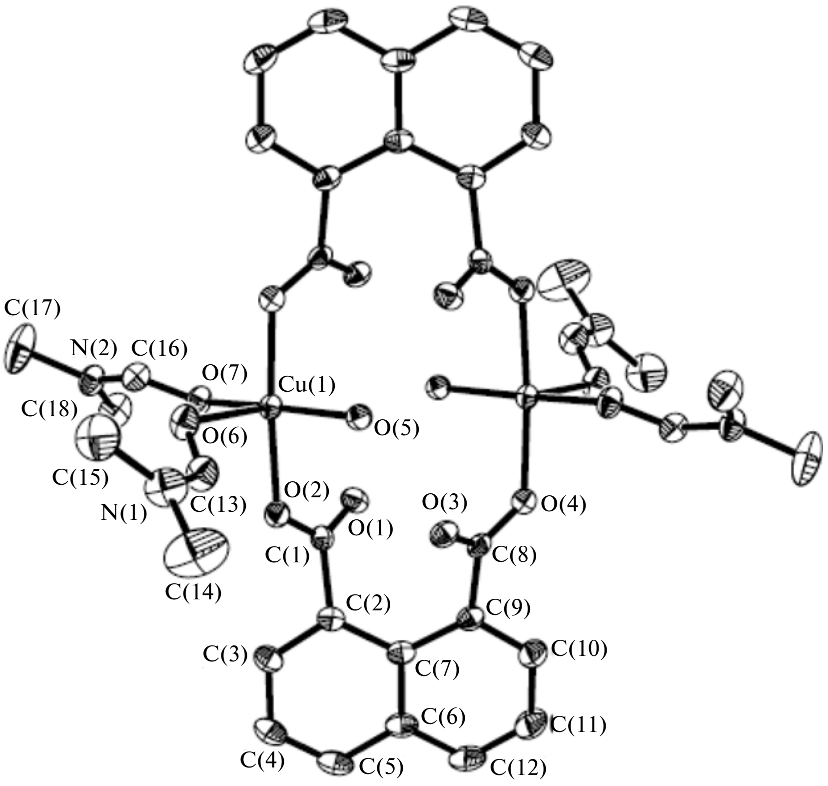

Fig. 1. ORTEP diagram of **I** with atom labeling scheme at the 30% probability level, hydrogen atoms are omitted for clarity.

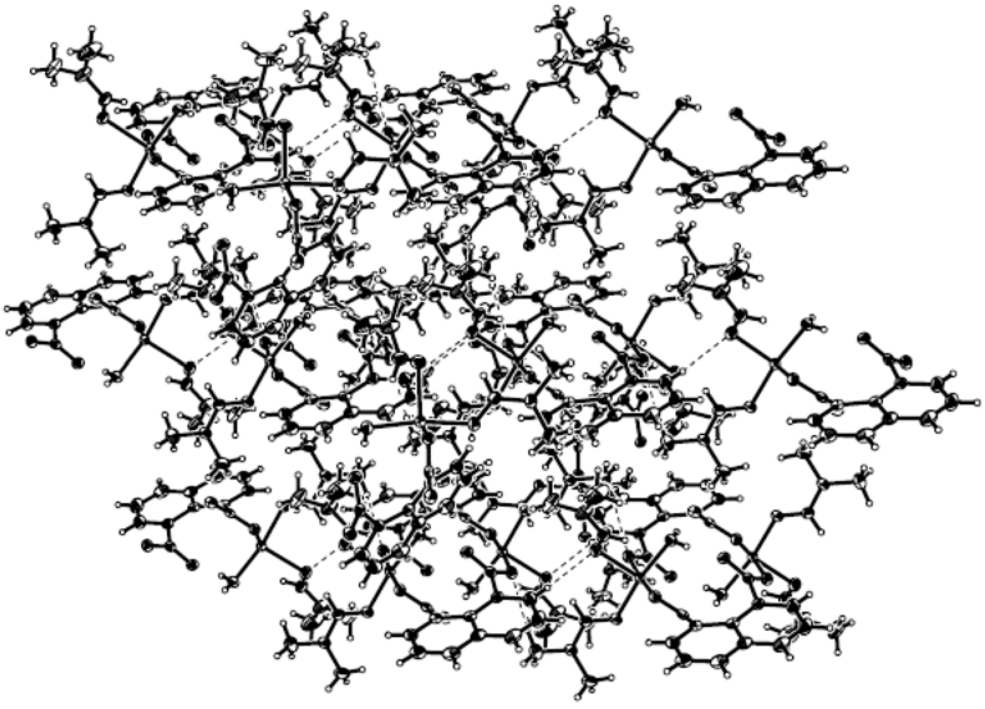

Fig. 2. View of the stacking of **I**.

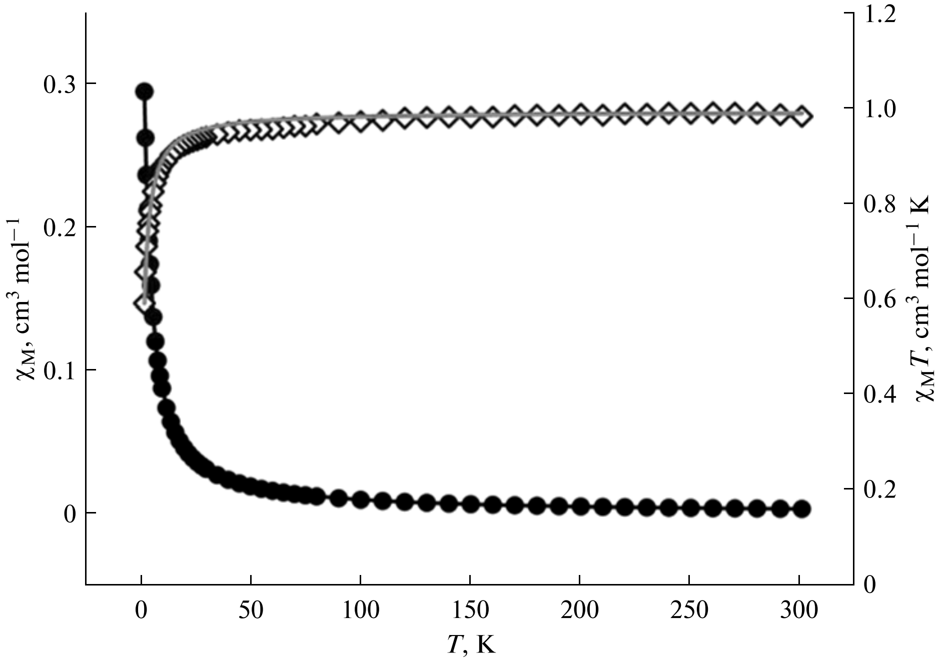

Fig. 3. Plots of $\chi_{\rm M}$ and $\chi_{\rm M}T$ of **I** versus T.

The total magnetic susceptibility is

$$\chi_{\rm M} = \frac{\chi}{1-(2zJ'/Ng^2\beta^2)\chi}. \qquad (2)$$

The magnetic parameters obtained by the simulation of the experimental data using the above expression are $J = -0.59$ cm^{-1}, $g = 2.30$, $zJ' = -0.97$, $\rho = 0.009$ and $R = 9.30 \times 10^{-5}$ (R value is defined as $R = \sum(\chi_{\rm obsd} - \chi'_{\rm cacld})^2 / \sum(\chi_{\rm obsd})^2$. The result further confirmers a very weak antiferromagnetic exchange interaction.

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