

以烟酸为配体的铜配合物的合成、晶体结构及磁学性质

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摘要: 以氯化铜和烟酸(Hnic)为原料,在水热条件下得到了一个配位聚合物 $[\text{Cu}_2(\text{nic})_4(\text{H}_2\text{O})]_n$ (**1**),并利用元素分析、红外光谱以及X-射线单晶衍射对其进行了表征。该晶体属单斜晶系, $P2_1/c$ 空间群, $a=1.071\ 56(3)\ \text{nm}$, $b=1.958\ 79(6)\ \text{nm}$, $c=1.379\ 50(3)\ \text{nm}$, $\beta=104.498\ (2)^\circ$, $V=2.803\ 31(13)\ \text{nm}^3$, $D_c=1.501\ \text{g}\cdot\text{cm}^{-3}$, $Z=4$, $F(000)=1\ 280$, $\text{Goof}=1.014$, $R_1=0.041\ 7$, $wR_2=0.113\ 2$ 。单晶结构分析显示,相邻的2个Cu(II)离子通过2个羧基和1个水分子体桥联形成双核铜单元,双核铜单元再通过烟酸配体连接形成五连接的三维($4^4\cdot6^6$)结构的金属有机骨架。变温磁化率研究显示,双核单元内铜离子之间存在反铁磁相互作用。

关键词: 铜配合物; 烟酸; 晶体结构; 磁性

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2013)09-1914-07

DOI: 10.3969/j.issn.1001-4861.2013.00.290

Synthesis, Crystal Structure and Magnetic Property of a Copper(II) Coordination Polymer Constructed from Nicotinic Acid

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Abstract: A new three-dimensional (3D) coordination polymer of $[\text{Cu}_2(\text{nic})_4(\text{H}_2\text{O})]_n$ (**1**) (Hnic=nicotinic acid) has been prepared and characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. The crystal is of monoclinic, space group $P2_1/c$ with $a=1.071\ 56(3)\ \text{nm}$, $b=1.958\ 79(6)\ \text{nm}$, $c=1.379\ 50(3)\ \text{nm}$, $\beta=104.498\ (2)^\circ$, $V=2.803\ 31(13)\ \text{nm}^3$, $D_c=1.501\ \text{g}\cdot\text{cm}^{-3}$, $Z=4$, $F(000)=1\ 280$, $\text{Goof}=1.014$, $R_1=0.041\ 7$, $wR_2=0.113\ 2$. Complex **1** shows a 3D uninodal 5-connected framework with $(4^4\cdot6^6)$ topology. Moreover, Magnetic susceptibility measurements demonstrate that complex **1** exhibits antiferromagnetic interaction within the binuclear units. CCDC: 921590.

Key words: Cu(II) complex; nicotinic acid; crystal structure; magnetism

0 Introduction

The rational design and controlled synthesis of metal-organic frameworks (MOFs) has become an exciting and expanding approach to novel functional materials in the realm of crystal engineering and supramolecular chemistry^[1]. Great interest has been focused on not only fine-tuning their structural diversities^[2] and interesting topologies^[3] but also their

potential applications as functional materials in many areas, such as photoluminescence^[4], magnetism^[5], catalysis^[6], gas storage^[7], conductivity^[8], non-linear optics (NLO)^[9], ion exchange^[10], ferroelectricity^[11], optoelectronic effects^[12], and spin-transition behaviour^[13]. The vast majority of work involves the use of polyfunctional organic ligands bonded to *d*-block transition metal atoms by metal coordination-directed self-assembly processes, which lead to the construction

收稿日期: 2013-01-26。收修改稿日期: 2013-03-30。

国家自然科学基金(No.20971004, 21271106)和教育部科学技术重点项目(No.210102)资助项目。

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of hybrid frameworks with fascinating topologies. However, some major challenges in this research field, such as, (i) how to control polymer dimensionality; (ii) how to improve framework stability; (iii) how to design novel structural compounds with desirable properties; (iv) how to synthesis desirable compounds in convenient ways, still remain.

Recent elaboration has demonstrated the dramatic influence of organic components on the framework of inorganic materials, such as how organic components modify the inorganic frameworks^[14]. Nicotinic acid (Hnic), which has two types of coordinating atoms (N and O), can be used as an electron transfer mediator or chelate ligand^[15-19]. The flexibility of the coordination sphere of nicotinic acid around transition metal ions, in combination with stereo and crystal packing forces, usually leads to tremendous network diversity. Taking advantage of some interesting properties of nicotinic acid and hydrothermal reactions, we present the synthesis, structural characterization, and magnetic properties of a new coordination polymer based on nicotinic acid, $[\text{Cu}_2(\text{nic})_4(\text{H}_2\text{O})]_n$ (**1**).

1 Experimental

1.1 Materials and general methods

All reagents for syntheses and analyses were purchased from commercial sources and used as received without further purification. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region. The X-band EPR spectra were recorded on a Bruker 2000-D-SRC spectrometer on polycrystalline material at room temperature. Variable-temperature susceptibilities were measured using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascals constants for all constituent atoms^[20].

1.2 Synthesis of $[\text{Cu}_2(\text{nic})_4(\text{H}_2\text{O})]_n$ (**1**)

A mixture of Hnic (0.4 mmol, 49.2 mg), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 mmol, 34.0 mg) and H_2O (15 mL) was stirred for 30 min, and the pH value of the solution was adjusted to about 5 with triethylamine. After stirring for

another 30 min, the mixture was transferred to a 25 mL Teflon-lined stainless steel vessel and heated at 120 $^{\circ}\text{C}$ for 2 d. Then the reaction system was cooled to room temperature, and blue block crystals of **1** were obtained. Yield: 62% (based on Hnic). Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_9\text{Cu}_2$ (%): C, 45.50; H, 2.86; N, 8.84. Anal. Found (%): C, 45.45; H, 2.88; N, 8.89. IR spectrum: 3 651, 3 062, 1 611, 1 584, 1454, 1 404, 1 381, 1 322, 1 260, 1 192, 1 155, 1 089, 1 057, 998, 882, 826, 701, 643, 575 and 545 cm^{-1} .

1.3 X-ray crystallography

The single crystals of complex **1** with approximate dimensions of 0.40 mm×0.40 mm×0.40 mm was placed on an Oxford Xcalibur Gemini Ultra diffractometer. The diffraction data were collected using a graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 290(2) K. Data reduction and empirical absorption correction were performed using the CrysAlisPro program^[21]. The structure was solved by the direct method using SHELXS-97^[22] and refined by full-matrix least squares on F^2 using SHELXL-97^[23]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated theoretically onto the specific atoms and refined with isotropic thermal parameters riding on the parent atoms. In addition, PLATON/SQUEZEE routine was used for their disordered solvent molecules in view of helps in crystallographic justification^[24]. The details of the crystal parameters, data collection and refinement for **1** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2.

CCDC: 921590.

2 Results and discussion

2.1 Crystal structure

Single-crystal X-ray diffraction of **1** reveals a complicated 3D coordination polymer that crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **1** contains two crystallographically unique Cu(II) ions, four individual nic anions and one coordinated water molecule. As shown in Fig.1, each of the two crystallographically distinct Cu(II) ions displays slightly

Table 1 Crystal data and structure refinement for **1**

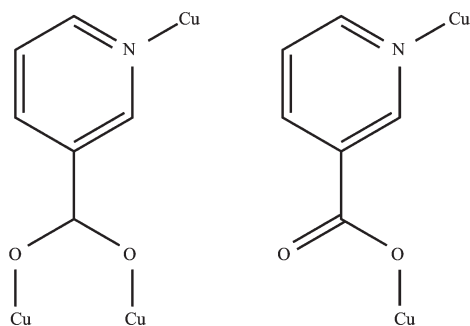
Formula	C ₂₄ H ₁₈ N ₄ O ₉ Cu ₂	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.501
Formula weight	633.50	Absorption coefficient / mm	1.572
Temperature / K	290(2)	θ range / (°)	2.41~25.50
Crystal system	Monoclinic	Limiting indices	$-13 \leq h \leq 13, -24 \leq k \leq 20, -17 \leq l \leq 16$
Space group	$P2_1/c$	$F(000)$	1 280
a / nm	1.071 56(3)	Reflections collected	17 587
b / nm	1.958 79(6)	Independent reflections	5 713 ($R_{\text{int}}=0.032$ 9)
c / nm	1.379 50(3)	Reflections observed ($I > 2\sigma(I)$)	4 094
α / (°)	90	Data/restraints/parameters	5 713/52/360
β / (°)	104.498(2)	Goodness-of-fit on R^2	1.014
γ / (°)	90	R_1, wR_2 ($I > 2\sigma(I)$)	0.041 7, 0.113 2
V / nm ³	2.803 31(13)	R_1, wR_2 (all data)	0.060 4, 0.117 1
Z	4	Largest difference peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	604, -574

Table 2 Selected bond lengths(nm) and angles(°) for **1**

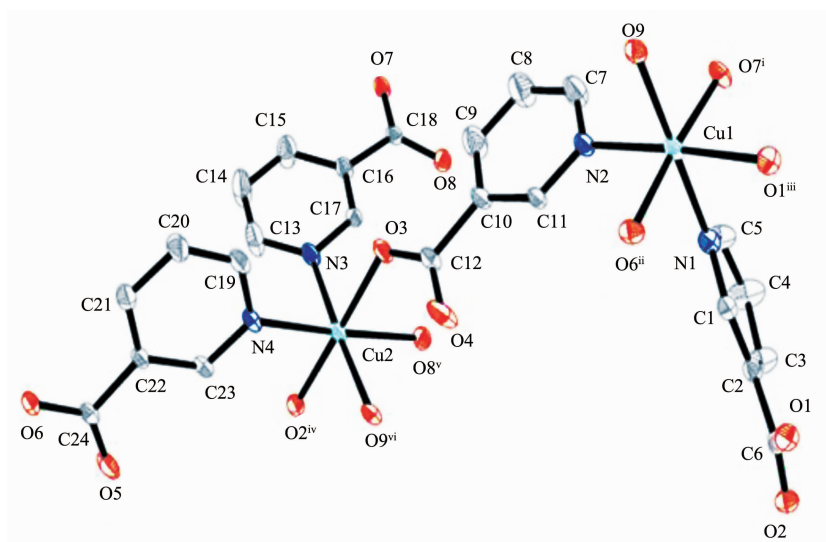
Cu(1)-O(7) ⁱ	0.202 0(2)	Cu(2)-O(2) ^{iv}	0.202 9(3)	Cu(1)-O(6) ⁱⁱ	0.207 7(2)
Cu(2)-O(3)	0.206 1(3)	Cu(1)-N(1)	0.208 1(3)	Cu(2)-N(3)	0.209 5(3)
Cu(1)-O(1) ⁱⁱⁱ	0.209 5(3)	Cu(2)-O(8) ^v	0.209 6(3)	Cu(1)-N(2)	0.211 0(3)
Cu(2)-O(9) ^{vi}	0.210 5(3)	Cu(1)-O(9)	0.212 3(3)	Cu(2)-N(4)	0.211 4(3)
O(7) ⁱ -Cu(1)-O(6) ⁱⁱ	175.33(10)	O(2) ^{iv} -Cu(2)-O(3)	177.06(11)	O(7) ⁱ -Cu(1)-N(1)	90.84(11)
O(2) ^{iv} -Cu(2)-N(3)	90.79(12)	O(6) ⁱⁱ -Cu(1)-N(1)	88.10(11)	O(3)-Cu(2)-N(3)	86.37(12)
O(7) ⁱ -Cu(1)-O(1) ⁱⁱⁱ	91.71(10)	O(2) ^{iv} -Cu(2)-O(8) ^v	95.87(11)	O(6) ⁱⁱ -Cu(1)-O(1) ⁱⁱⁱ	83.69(10)
O(3)-Cu(2)-O(8) ^v	83.36(11)	N(1)-Cu(1)-O(1) ⁱⁱⁱ	86.28(11)	N(3)-Cu(2)-O(8) ^v	89.36(11)
O(7) ⁱ -Cu(1)-N(2)	91.06(10)	O(2) ^{iv} -Cu(2)-O(9) ^{vi}	90.97(11)	O(6) ⁱⁱ -Cu(1)-N(2)	93.52(11)
O(3)-Cu(2)-O(9) ^{vi}	91.84(11)	N(1)-Cu(1)-N(2)	91.86(12)	N(3)-Cu(2)-O(9) ^{vi}	177.31(11)
O(1) ⁱⁱⁱ -Cu(1)-N(2)	176.68(10)	O(8) ^v -Cu(2)-O(9) ^{vi}	88.44(10)	O(7) ⁱ -Cu(1)-O(9)	91.23(10)
O(2) ^{iv} -Cu(2)-N(4)	88.58(11)	O(6) ⁱⁱ -Cu(1)-O(9)	89.72(10)	O(3)-Cu(2)-N(4)	92.21(11)
N(1)-Cu(1)-O(9)	177.49(11)	N(3)-Cu(2)-N(4)	90.86(12)	O(1) ⁱⁱⁱ -Cu(1)-O(9)	92.24(11)
O(8) ^v -Cu(2)-N(4)	175.54(11)	N(2)-Cu(1)-O(9)	89.52(12)	O(9) ^{vi} -Cu(2)-N(4)	91.22(11)

Symmetry code: ⁱ $-x, y-1/2, -z+3/2$; ⁱⁱ $-x+1, y-1/2, -z+5/2$; ⁱⁱⁱ $-x, -y, -z+2$; ^{iv} $-x, y+1/2, -z+5/2$; ^v $-x, -y+1, -z+2$; ^{vi} $x, -y+1/2, z+1/2$

distorted octahedral $[\text{CuN}_2\text{O}_4]$ coordination geometry. The arrangement of donor atoms about each of the two

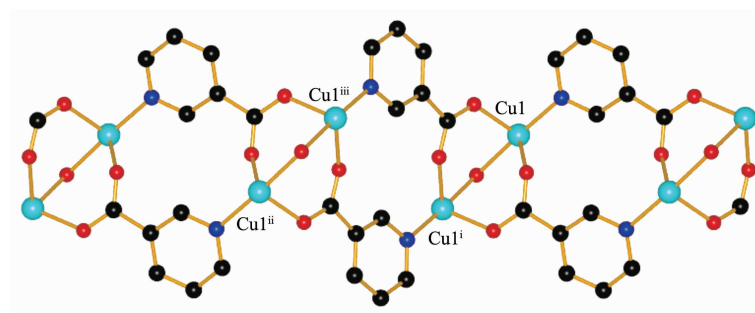
Scheme 1 Coordination modes of nic anion in **1**

Cu(II) ions is identical, albeit with subtly altered bond distances and angles. The two nitrogen donors, one belonging to an exobidentate μ_2 -nic anion and the other to an exotridentate μ_3 -nic anion, are disposed *cis* relative to each other. Oxygen atoms belonging to two different μ_3 -nic anions are also situated in a *cis* orientation. The remaining two coordination sites occupied by oxygen atoms from a μ_2 -nic anion and a μ_2 -water molecule, again in a *cis* disposition. The μ_3 -nic pyridyl nitrogen donor is arranged trans to the μ_2 -water molecule that bridge each pair of Cu(II) ions (Cu-O-Cu angles = 114.44 (12)°) into binuclear $[\text{Cu}(\mu\text{-H}_2\text{O})(\mu_3\text{-$



Hydrogen atoms are omitted for clarity. Symmetry code: ⁱ $-x, y-1/2, -z+3/2$; ⁱⁱ $-x+1, y-1/2, -z+5/2$; ⁱⁱⁱ $-x, -y, -z+2$; ^{iv} $-x, y+1/2, -z+5/2$; ^v $-x, -y+1, -z+2$; ^{vi} $x, -y+1/2, z+1/2$

Fig.1 Coordination environment of Cu(II) in complex **1** with thermal ellipsoids at 30% probability



Symmetry code: ⁱ $-x, -y+1/2, -1/2+z$; ⁱⁱ $-x, -y, 1-z$; ⁱⁱⁱ $-x, -1/2+y, 3/2-z+2$

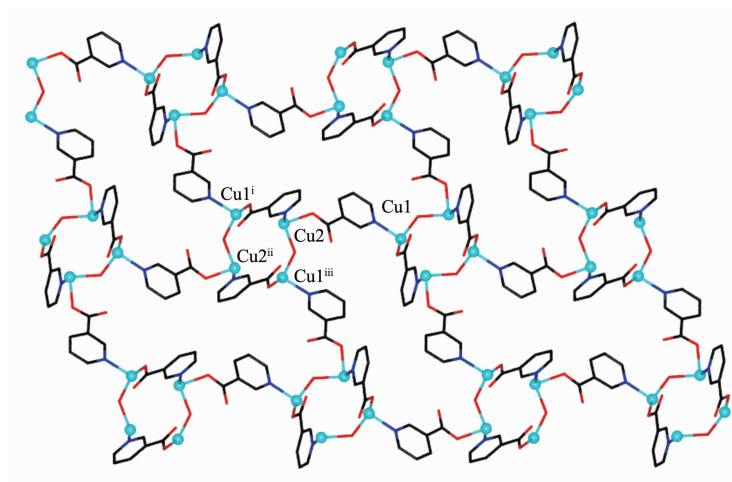
Fig.2 Views of helical 1-D chain of μ_3 -nic connected binuclear units in **1** along the c axis

nic) $_{2}\text{Cu}]^{2+}$ units with a Cu-Cu distance of 0.355 5 nm. The Cu-O distances range from 0.202 0(2) to 0.212 3(3) nm, and the Cu-N distances are between 0.208 1(3) and 0.211 4(3) nm. The O(N)-Cu-O(N) bond angles range from 83.69 (10) $^{\circ}$ to 177.49 (11) $^{\circ}$, which are similar to those observed in the reported complexes^[25].

As exhibited in Fig.2, each binuclear unit is turn connected to its neighbors through μ_3 -nic anions to form 1D $[\text{Cu}_2(\mu\text{-H}_2\text{O})(\mu_3\text{-nic})_2]$ helical chains that run down the c axis. The structure of **1** also contains rippled 2D cationic $[\text{Cu}_4(\mu\text{-H}_2\text{O})_2(\mu_2\text{-nic})_4]$ layers coincident with the bc plane, built from the junction of the two types of $[\text{Cu}_2(\mu\text{-H}_2\text{O})]^{4+}$ subunits through all of the μ_2 -nic anions (Fig. 3). This 2D layer stands in contrast to the $[\text{Co}_2(\mu\text{-H}_2\text{O})(\mu_2\text{-nic})_2]$ 1D double chain staircase motif observed in

the 3D open framework coordination polymer $[\text{Co}_2(\mu\text{-H}_2\text{O})(\mu_2\text{-nic})_4]$, which contains similar binuclear units^[26]. The 2D cationic layers in **1** are then stitched into the full 3D crystal structure through the aforementioned helical 1D $[\text{Cu}_2(\mu\text{-H}_2\text{O})(\mu_3\text{-nic})_2]$ chains.

Better insight into such elegant frameworks can be achieved using the topology method: Firstly, based on the considerations of their connectivity, the binuclear Cu_2 is viewed to be five-connected nodes (Fig.4); secondly, the CuO/N coordination bonds and nic ligands are simplified to be linear connectors; then the combination of nodes and connectors suggests the 5-connected frameworks for the present case. The topological notation for such 5-connected frameworks is $(4^4 \cdot 6^6)$ net (Fig.5). In the literature^[27-29], the uninodal 4-,



Symmetry code: ⁱ 1-x, y+1/2, 5/2-z; ⁱⁱ 1-x, 1-y, 3-z; ⁱⁱⁱ x, 1/2-y, 1/2+z

Fig.3 View of the undulating 2D network in **1** comprised of μ_2 -nic connected binuclear units

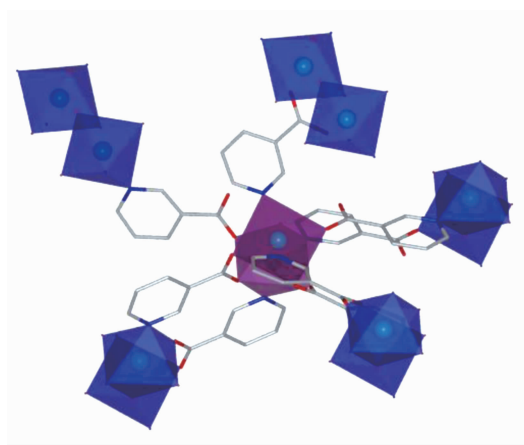


Fig.4 View of the linkages of a binuclear unit with four adjacent binuclear units in **1**

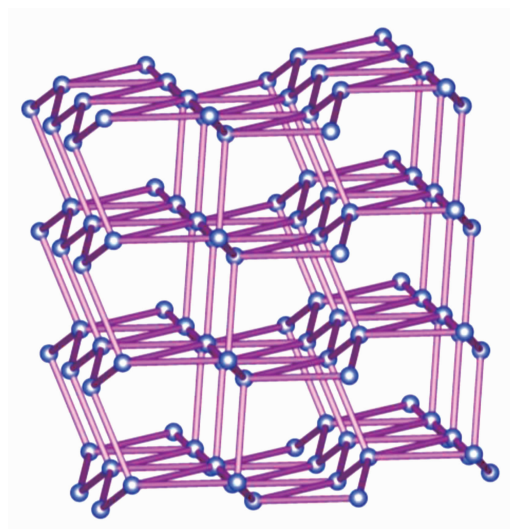


Fig.5 Topological illustration for the uninodal 5-connected ($4^4 \cdot 6^6$) net of **1**

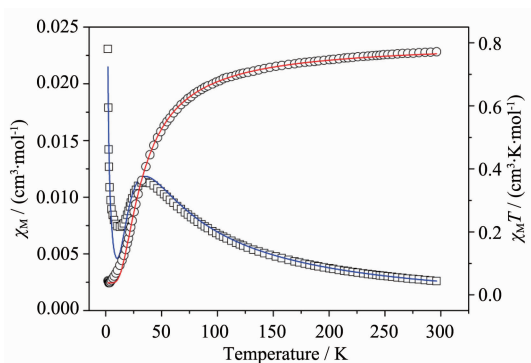
6- and 8-connected frameworks are often encountered, but we are not aware of a precedent characterized by such topology like that found in **1**.

2.2 IR spectra

The absence of such bands at around 1700 cm^{-1} in the IR spectrum indicates the complete deprotonation of nicotinic acid. The characteristic bands of carboxyl groups are shown in the range of $1584\sim 1611\text{ cm}^{-1}$ for antisymmetric stretching and 1381 cm^{-1} for symmetric stretching. The separations ($\Delta\nu$) between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ bands indicate the presence of different coordination modes. The bands in the region $643\sim 1322\text{ cm}^{-1}$ are attributed to the -CH- in-plane or out-of-plane bend, ring breathing, and ring deformation absorptions of pyridyl ring, respectively. Weak absorptions observed at 3062 cm^{-1} can be attributed to $\nu_{\text{C-H}}$ of benzene ring. The IR spectra exhibit the characteristic peaks of water molecule at 3651 cm^{-1} [30].

2.3 Magnetic properties and EPR

The $\chi_{\text{M}}T$ product has a value of $0.77\text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K, well in agreement with the expected value for two non-interacting Cu(II) ions with $S=1/2$ and $g=2.0$ (Fig.6). As the temperature decreases, so does the $\chi_{\text{M}}T$ product, indicating antiferromagnetic coupling between the Cu(II) ions in **1**. Accordingly, a maximum is seen in the susceptibility at 35 K, indicating the transition to a diamagnetic state below this temperature. As the temperature decreases further a plateau at a $\chi_{\text{M}}T$ value



Solid lines are the best fitting to the experimental data

Fig.6 Temperature dependence of $\chi_M T$ (○) and χ_M (□) for **1** of $0.045 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ is observed, as well as a rise in the susceptibility, clear indication of a small amount of paramagnetic impurity, probably a Cu(II) monomer or salt.

According to the crystal structure, complex **1** can be considered as binuclear from the viewpoint of magnetism, in which two Cu(II) ions are linked by two carboxylate and one μ_2 -water molecule bridges since the coupling through nic anions can almost be negligible. Taking into account the binuclear Cu(II) model, the magnetic susceptibility data are analyzed by using the familiar Bleaney-Bowers expression based on a Heisenberg Hamiltonian $H=JS_1 \cdot S_2$ ^[20]:

$$\chi_M = \frac{Ng^2\beta^2}{kT} \frac{1}{2 + \exp(-2J/kT)} (1-\rho) + \frac{Ng^2\beta^2}{4kT} \rho$$

$$\chi_M = \frac{\chi'_M}{1 - \left(\frac{2zJ}{Ng^2\beta^2}\right) \chi_M}$$

where N , g , b and k have their usual meanings. ρ is a variable fraction of paramagnetic impurities. zJ accounts for the interdimer interactions. The least-squares analysis of magnetic susceptibility data led to $J=-2.63 \text{ cm}^{-1}$, $zJ=0.041 \text{ cm}^{-1}$, $g=2.10$, $\rho=8.1\%$, and $R=7.23 \times 10^{-5}$. The fitting results indicate that the magnitude of the magnetic coupling between the adjacent Cu(II) ions in **1** is very weak. As is well known, the magnetic properties are closely related to the bridging conformation adopted by the carboxylate group in these polynuclear systems, the *syn-syn* carboxylato bridge is able to mediate very strong antiferromagnetic interactions in Cu(II) complexes, whereas the *syn-anti*

type will normally result in a weak magnetic exchange interaction^[31]. In **1**, the carboxylate groups of nic anion adopt a *syn-anti* fashion to link the Cu(II) ions and the resulting magnetic exchanges is weak.

The powdered EPR spectra of **1** were measured at room temperature and the spectra are shown in Fig.7. It is all typical Cu(II) signals having the character of axial eld. The g_{\parallel} and g_{\perp} values are 2.225 and 2.078, respectively. The order of $g_{\parallel} > g_{\perp} > 2.0023$ matches to all the Cu(II) complexes that the unpaired electron exists in $d_{x^2-y^2}$ orbital^[32], which is a typical occurrence for tetragonal or elongated octahedral Cu(II) coordination sphere. While the broadened signal of **1** with the G value of 3.48 (less than 4) indicates an antiferromagnetic interaction between the two Cu(II) ions of the binuclear complex^[33]. Similar magnetic and EPR data were observed for other copper(II) dimer^[34].

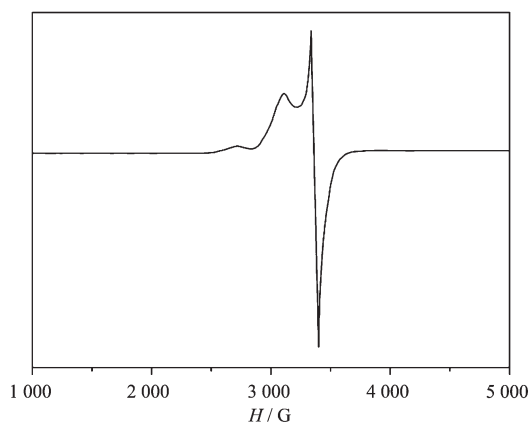


Fig.7 EPR spectra of **1** at room temperature

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