

一个具有四方锥和三角双锥构型的线性混合桥连三核铜配合物

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摘要: 以反式-3-[*N,N*-二(2-吡啶甲基)氨基甲基]-2-羟基-5-甲基苯甲醛肟(H_2L)为配体, 合成了一个新颖的线性三核铜(II)配合物 $[Cu_3L_2(py)](ClO_4)_2 \cdot 2THF$ (**1**) (py =吡啶, THF =四氢呋喃), 对其进行了红外、紫外、热重和单晶结构表征。配合物 **1** 属于单斜晶系, 空间群为 $C2/c$, $a=2.969\ 0(7)$ nm, $b=1.302\ 8(3)$ nm, $c=2.057\ 4(9)$ nm, $\beta=132.435(2)^\circ$, $V=5.873(3)$ nm³, $Z=4$, $R_1=0.047\ 9$ 。单晶结构表明, 这是一个混合桥(-N-O-和 μ_2 -O-)连的线性五配位三核铜(II)配合物; 每个铜均由 3 个氮原子和 2 个氧原子配位, 中间的铜为扭曲的三角双锥构型, 而两侧的铜为扭曲的四方锥构型。变温磁化率显示 **1** 的铜离子间存在中等的反铁磁性($J=-33.3(5)$ cm⁻¹)。

关键词: 三核铜; 五配位; 晶体结构; 混合桥连; 反铁磁性

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A Mixed-Bridged Linear Trinuclear Copper(II) Complex Containing Both Square Pyramidal and Trigonal Bipyramidal Configuration

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Abstract: A novel trinuclear copper(II) complex, $[Cu_3L_2(py)](ClO_4)_2 \cdot 2THF$ (**1**) (H_2L =(*E*)-3-[*N,N*-di(2-pyridylmethyl)aminomethyl]-2-hydroxyl-5-methylbenzaldehyde oxime, py =pyridine, THF =tetrahydrofuran), has been successfully synthesized and characterized. **1** crystallizes in monoclinic system with space group $C2/c$, $a=2.969\ 0(7)$ nm, $b=1.302\ 8(3)$ nm, $c=2.057\ 4(9)$ nm, $\beta=132.435(2)^\circ$, $V=5.873(3)$ nm³, $Z=4$ with final $R_1=0.047\ 9$. X-ray crystallography analysis reveals that **1** is a mixed-bridged (-N-O-/ μ_2 -O-) linear tricopper(II) complex with all the copper cations being five-coordinated by three N and two O atoms: the central Cu(II) in a distorted trigonal bipyramidal configuration, whereas the peripheral Cu(II) in a distorted square pyramidal arrangement. Magnetic susceptibility measurement indicates that there is a medium antiferromagnetic exchange coupling between the Cu(II) ions with a J value of $-33.3(5)$ cm⁻¹. CCDC: 916132.

Key words: trinuclear copper; pentacoordinate; crystal structure; mixed-bridged; anti-ferromagnetism

Trinuclear Cu(II) complexes have received increasing attentions as models for the active sites of multicopper oxidases such as ascorbate oxidases, lac-

case and ceruloplasmin^[1-2]. A relatively large number of trinuclear Cu(II) complexes have been reported over the past three decades^[3-22]. Generally, the trinuclear

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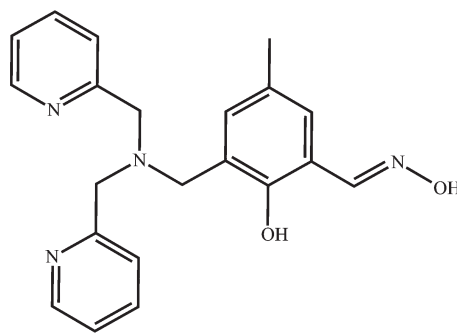
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Cu(II) complexes can be classified as triangular^[3-7] and linear arrangements^[8-22]. Up to now, linear trinuclear Cu(II) complexes with respective coordination numbers of 4, 5, 4^[9,14]; 4, 5, 5^[20]; 5, 4, 5^[19,21-22]; 5, 5, 5^[8-13,15-17]; 5, 6, 5^[18,21]; 5, 5, 6^[10] and 6, 6, 6^[10], have been found. However, most of trinuclear Cu(II) complexes with respective coordination numbers of 5, 5, 5 show the distorted square pyramidal configuration. Examples of five-coordinated trinuclear Cu(II) complexes containing both the distorted square pyramidal and trigonal bipyramidal configuration are very limited^[8]. Herein we present the synthesis and crystal structure of a rare linear pentacoordinate trinuclear Cu(II) complex: $[\text{Cu}_3\text{L}_2(\text{py})](\text{ClO}_4)_2 \cdot 2\text{THF}$ (**1**) ($\text{H}_2\text{L}=(E)\text{-3-[}N,N\text{-di(2-pyridylmethyl)aminomethyl]-2-hydroxyl-5-methylbenzaldehyde oxime}$, py=pyridine, THF=tetrahydrofuran), showing the simultaneous presence of the distorted square pyramidal and the trigonal bipyramidal geometries. Moreover, the central trigonal bipyramidal Cu(II) and the terminal square pyramidal Cu(II) ions are linked by $\text{-N-O-}\mu_2\text{-O-}$ mixed-bridging, which is also uncommon within trinuclear Cu(II) complexes^[11,17,22]. The spectral characterization, thermal stability and magnetic property of **1** are also reported.

1 Experimental

1.1 Materials and measurements

All chemicals used were of analytical grade. Solvents were purified by conventional methods. The ligand H_2L was prepared according to the literature method^[23] and its structure is shown in Scheme 1. Elemental analyses (C, H, N) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectrum was recorded on a Nicolet Avatar 380 FT-IR instrument with KBr pellets in the range of 4 000~400 cm^{-1} . UV-Vis spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer at room temperature in methanol solution. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449F3 thermal analyzer instrument under flowing N_2 with a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$. The temperature dependence of the magnetic susceptibility for **1** was measured on a Quantum Design MPMS-7 SQUID magnetometer in



Scheme 1 Structure of H_2L

the range of 1.8~300 K under 2 000 Oe of external field. Diamagnetic correction was made with Pascal's constants.

1.2 Synthesis of **1**

A solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.186 3 mmol) in distilled water (0.8 mL) was added dropwise to a solution of H_2L (0.124 2 mmol) in EtOH (1 mL). The mixture was stirred at room temperature for ten minutes, then the pyridine (5 μL) was added. Half an hour later, a solution of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.124 2 mmol) in distilled water (0.2 mL) was added and the dark green precipitate was immediately formed. After stirred for 8 h, the precipitate was separated by filtration, then washed with THF and dried under vacuum to give 55.4 mg (75%) of the complex. Diffusion from THF to the solution of the complex in pyridine afforded dark green single crystals of **1** suitable for X-ray crystallographic analysis. Elemental Analyses Calcd. for $\text{C}_{55}\text{H}_{61}\text{Cl}_2\text{Cu}_3\text{N}_9\text{O}_{14}$ (%): C 49.53, H 4.61, N 9.45; Found(%): C 49.20, H 4.54, N 9.80. IR data (KBr, cm^{-1}): $\nu(\text{C}=\text{N})$ 1 605 (s); $\nu(\text{C}=\text{C})$, 1 465 (m), 1 442 (s); $\nu(\text{Ar-O})$ 1 293 (m); $\nu(\text{C-O})$ 1 027 (s); $\nu(\text{Cl-O})$ 1 085 (vs), 936 (w), 627 (s).

1.3 Crystal structure determination

The well-shaped single crystals of **1** were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 296(2) K on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo $K\alpha$ ($\lambda=0.071\ 073\ \text{nm}$) radiation. The structure was solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELXTL software^[24]. All non-hydrogen atoms were anisotropically refined. Atoms O4, O5 and

O6 of ClO_4^- anion were found to be highly disordered with occupancy of 0.50. All H atoms were located from a difference map and refined isotropically. Cry-

talographic data are listed in Table 1. Selected bond distances and angles are given in Table 2.

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Table 1 Crystal data and structure refinement for 1

Complex	$[\text{Cu}_3\text{L}_2(\text{py})](\text{ClO}_4)_2 \cdot 2\text{THF}$	μ / mm^{-1}	1.239
Empirical formula	$\text{C}_{55}\text{H}_{61}\text{Cl}_2\text{Cu}_3\text{N}_9\text{O}_{14}$	$F(000)$	2 748
Formula weight	1 333.65	Crystal size / mm	0.20×0.16×0.14
Crystal system	Monoclinic	θ range / (°)	1.82~25.00
Space group	$C2/c$	Reflections collected	20 332
a / nm	2.969 0(7)	Independent reflections	5 166 ($R_{\text{int}}=0.027$ 5)
b / nm	1.302 8(3)	Reflections observed ($I>2\sigma(I)$)	4 062
c / nm	2.057 4(9)	Data / restraints / parameters	5 166 / 71 / 403
$\beta / (^\circ)$	132.435(2)	Goodness-of-fit on F^2	1.080
V / nm^3	5.873(3)	R_1 / wR_2 ($I>2\sigma(I)$)	0.047 9 / 0.147 1
Z	4	R_1 / wR_2 (all data)	0.062 1 / 0.156 9
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.508	$(\Delta\rho)_{\text{max}} (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	812, -538

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

Cu1-O1	0.194 6(3)	Cu2-N2	0.202 1(4)	O2-N4	0.137 6(4)
Cu1-N4	0.202 3(3)	Cu2-N3	0.201 9(3)	C15-O1	0.134 3(4)
Cu1-N5	0.235 6(5)	Cu2-O2 ⁱ	0.189 8(3)	C21-N4	0.128 2(5)
Cu2-N1	0.199 8(4)	Cu2-O1	0.217 0(2)	Cu1...Cu2	0.340 9(4)
O1-Cu1-N4	90.77(11)	O1-Cu2-N2	105.01(12)	N2-Cu2-N3	82.65(12)
O1-Cu1-N5	87.51(8)	O1-Cu2-N3	96.40(12)	O2 ⁱ -Cu2-N2	96.56(15)
O1-Cu1-O1 ⁱ	175.03(15)	O1-Cu2-O2 ⁱ	91.74(11)	O2 ⁱ -Cu2-N3	171.74(12)
N4-Cu1-N5	111.18(9)	N1-Cu2-N2	157.90(14)	C21-N4-O2	112.8(3)
N4-Cu1-N4 ⁱ	137.63(19)	N1-Cu2-N3	83.58(14)	Cu1-O1-Cu2	111.71(11)
O1-Cu2-N1	93.63(12)	O2i-Cu2-N1	94.59(14)	Cu2...Cu1...Cu2 ⁱ	161.64

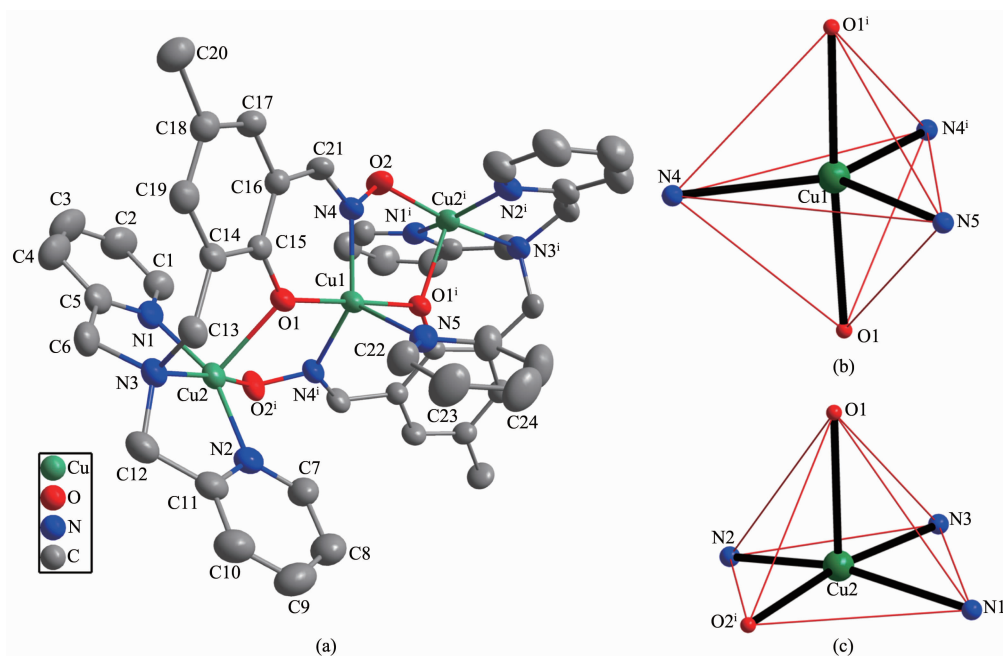
Symmetry code: ⁱ $-x, y, 1/2-z$.

2 Results and discussion

2.1 Crystal structure

Single crystal X-ray structure analysis shows that **1** crystallizes in the monoclinic space group $C2/c$. The asymmetric unit consists of three Cu(II) cations, two L^{2-} ligands, one pyridine, two perchlorate anions and two THF molecules. The structure of **1** with the atomic labeling system is shown in Fig.1a. The central Cu1 cation is situated on a two-fold axis which also goes through N5 and C24 atoms of pyridine. The Cu1 cation is coordinated by three nitrogen atoms (N4, N4ⁱ and N5) in the equatorial plane and two phenolic oxygen atoms (O1 and O1ⁱ) in the axial positions to form

a distorted trigonal bipyramidal configuration with the geometric parameter $\tau=0.623$ ^[25] (Fig.1b), whereas the peripheral Cu2 cation exhibits a distorted square pyramidal arrangement ($\tau=0.23$) where three nitrogen atoms (N1, N2 and N3) and one oxime group O2ⁱ atom form the basal plane and the phenolic O1 atom is in the apical position (Fig.1c). To the best of our knowledge, the simultaneous presence of a square pyramidal arrangement and a trigonal bipyramidal configuration within pentacoordinate trinuclear Cu(II) complexes is very rare^[8]. In addition, Cu1 and Cu2 atoms are double bridged by the phenolic μ_2 -O1- and oxime group (-O2ⁱ-N4ⁱ-), resulting in a linear trinuclear Cu(II) complex ($\angle \text{Cu2} \cdots \text{Cu1} \cdots \text{Cu2}^i=161.64^\circ$). The square-pyra-



30% thermal ellipsoids probability; Hydrogen atoms, counter ions and solvents are omitted for clarity; Symmetry code: ⁱ $-x, y, 1/2-z$

Fig.1 (a) Projection of the structure of **1** with the atomic labeling system; (b) Distorted trigonal bipyramidal configuration of Cu1; (c) Distorted square pyramidal arrangement of Cu2

midial Cu2 displaces 0.022 8 nm out of the basal plane consisting of N1, N2, N3 and O2ⁱ. The bond lengths of Cu-N are similar to those observed in the related trinuclear Cu(II) complexes^[8-13] though the Cu2-N2 and Cu2-N3 distances in **1** are nearly equal. Interestingly, the Cu2-O1 bond length is 0.027 2 nm longer than the Cu2-O2ⁱ one, while the Cu1-O1 bond distance is 0.022 4 nm shorter than Cu2-O1 one. Moreover, the Cu1-N5 distance is 0.033 3 nm longer

than Cu1-N4 one (Table 2). The distance of Cu1 and Cu2 atoms is 0.340 9 nm, which is larger than the sum of van der Waals radii of two copper atoms (0.28 nm), revealing no metallphilic Cu...Cu interaction in **1**.

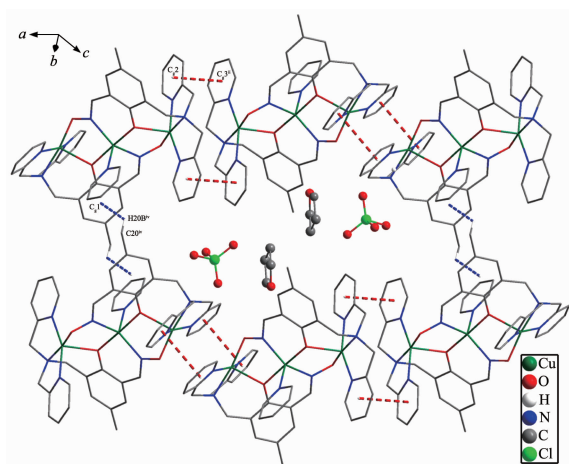
There are a lot of C-H...O hydrogen bond interactions in the structure of **1** (Table 3), which is significantly associated with the closer crystal packing. Mainly, these hydrogen bond interactions can be clas-

Table 3 Hydrogen bonding and π - π stacking interactions in **1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
C22-H22A...O1	0.093	0.252	0.309	120
C28-H28B...O2 ⁱⁱⁱ	0.097	0.260	0.353	161
C8-H8A...O5A	0.093	0.259	0.327	130
C3 ⁱⁱ -H3A ⁱⁱ ...O6A	0.093	0.252	0.345	174
C3 ⁱⁱ -H3A ⁱⁱ ...O6	0.093	0.257	0.337	144
C4-H4A...O7 ^v	0.093	0.260	0.341	146
C6-H6B...O6 ^v	0.097	0.252	0.342	154
C25-H25A...O5 ^v	0.097	0.254	0.350	171
C27-H27B...O6A ^v	0.097	0.237	0.326	151
C20 ^{iv} -H20B ^{iv} ...Cg1	0.096	0.295	0.363	129
π ... π interaction		Centroid...Centroid		Dihedral angle
$\pi(\text{Cg2})\cdots\pi(\text{Cg3})^{\text{ii}}$		0.364 3		6.9

Symmetry codes: ⁱⁱ $-x, 2-y, 1-z$; ⁱⁱⁱ $x, 2-y, 1/2+z$; ^{iv} $-x, 1-y, 1-z$; ^v $1/2+x, 3/2-y, 1/2+z$.

sified as three kinds: (1) one intramolecular C22–H22A \cdots O1 hydrogen bond involving pyridine and phenolic oxygen; (2) one intermolecular C28–H28B \cdots O2ⁱⁱⁱ hydrogen bond involving THF and oxime group's oxygen; (3) seven types of intermolecular C–H \cdots O hydrogen bond involving ClO₄[–]. In addition, there are one kind of intermolecular edge-to-face C–H \cdots π interaction involving –CH₃ and phenolic ring (C20^{iv}–H20B^{iv} \cdots C_g1, C_g1 is the centroid of the phenolic ring) and one kind of offset face-to-face $\pi\cdots\pi$ interaction between two pyridyl rings with the C_g2 \cdots C_g3ⁱⁱ distance of 0.364 3 nm and a dihedral angle of 6.9° (C_g2 and C_g3 is the centroid of pyridyl with N1 and pyridyl with N2, respectively). These interactions connect six trinuclear Cu(II) molecules to form a 2D layer with THF solvents and ClO₄[–] anions filled in the channel of a macrocycle (Fig.2).



THF solvents and ClO₄[–] anions are filled in the channel of a macrocycle; Symmetry codes: ⁱⁱ –x, 2–y, 1–z; ^{iv} –x, 1–y, 1–z

Fig.2 2D layer structure of **1** formed by face-to-face $\pi\cdots\pi$ stacking and edge-to-face C–H \cdots C_g1 interactions

2.2 Spectral characterization

In the IR spectrum of **1**, a strong band at 1 605 cm^{–1} can be assigned to the C=N stretching vibration of the coordinated pyridyl ring. A strong band at 1 027 cm^{–1} is attributed to the C–O stretching vibration of THF. The three bands at 1 085 (vs), 936 (w) and 627 (s) cm^{–1}, are attributable to the IR-allowed ν mode, IR-forbidden ν mode and the non-degenerate ClO₃ symmetrical bending vibrations of the ClO₄[–] anion, respectively^[26–28]. These features are in agreement with

the results of X-ray analysis.

The UV-Vis spectrum of **1** in CH₃OH solution is shown in Fig.3, an intense band at 205 nm is attributed to π – π^* transition of benzene ring (206 nm observed in the free H₂L ligand). Two shoulder bands at 234 and 256 nm are attributed to n – π^* transition of phenolic group in contrast to the single band at 262 nm for the free H₂L ligand. A band due to π – π^* transition of oxime group^[29] is found at 291 nm, a blue shift compared with the band at 319 nm for the free H₂L ligand, showing the conjugation between phenolic ring and oxime group decreases in **1** due to the coordination of the L^{2–} ligand. A band at 340 nm can be attributed to LMCT^[23].

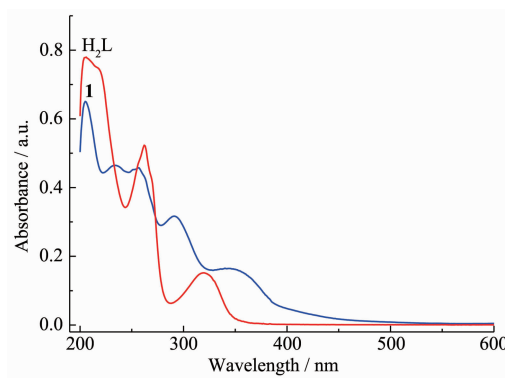


Fig.3 UV spectra of **1** and H₂L ligand in CH₃OH

2.3 TG analysis

TGA of **1** (Fig.4) was carried out in the range of 25 ~800 °C under nitrogen atmosphere. The first weight loss of 11% from 25 to 138 °C is attributed to the loss of two THF molecules (Calcd. 10.8%). The next weight loss of 5.8% from 138 to 225 °C corresponds to the loss of the coordinated pyridine molecule (Calcd. 6.7%). After that, **1** began to decom-

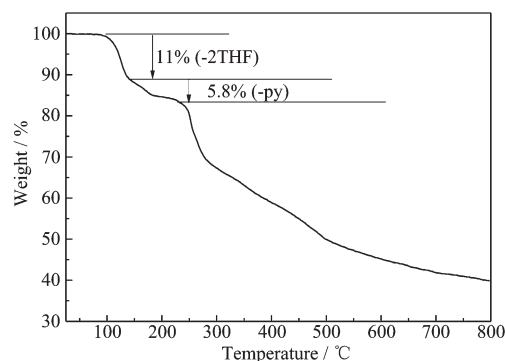


Fig.4 TGA curve of **1**

pose.

2.4 Magnetic property

As shown in Fig.5, the observed $\chi_M T$ value of **1** at 300 K is $1.25 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is slightly larger than expected for three isolated Cu(II) $S=1/2$ ions ($1.125 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for $g=2.0$). When further cooling, the $\chi_M T$ value decreases to reach $0.45 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 30 K that remains constant down to 5 K and decreases again below this temperature. This behavior shows the presence of predominant antiferromagnetic interactions between the Cu(II) ions. In fact, the presence of a plateau with a value of about $0.4 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ is expected for an antiferromagnetically coupled linear trinuclear Cu(II) complex where the central Cu(II) ion is coupled with the two terminal ones, but there is no coupling between the terminal ones. It corresponds to the spin ground state of $S=1/2$ for the trinuclear complex. According to these data and the structure of **1**, we can fit the magnetic properties to a simple symmetrical linear trimer Cu(II) model^[11]:

$$\chi = \frac{Ng^2\beta^2}{4kT} \times \frac{1 + e^{(2J-2J')/(kT)} + 10e^{3j/(kT)}}{1 + e^{(2J-2J')/(kT)} + 2e^{3j/(kT)}}$$

$$\chi_M = \frac{\chi}{1 - 2zj'\chi/(Ng^2\beta^2)}$$

J is based on the spin Hamiltonian $\hat{H} = -J \sum \vec{S}_i \cdot \vec{S}_{i+1}$ with $S=1/2$, N , k , T and β have the common meanings. The best fitting results from 1.8~300 K gave: $g=2.127(2)$, $J=-33.3(5) \text{ cm}^{-1}$ and $zj'=-0.66(1) \text{ cm}^{-1}$ with $R = \sum [(\chi_M T)_{\text{calc}} - (\chi_M T)_{\text{obs}}]^2 / \sum (\chi_M T)_{\text{obs}}^2 = 7.9 \times 10^{-8}$. The negative J value indicates the medium antiferromagnetic coupling between Cu(II) ions in **1**^[30]. In addition, the present J value is also compared with those observed

in the related linear trinuclear Cu(II) complexes^[11,18]. The negative value of zj' indicates that the face-to-face $\pi \cdots \pi$ stacking of pyridine rings of the ligands mediates the very weak antiferromagnetic interaction between molecules and corresponds to the decrease of $\chi_M T$ below 5 K.

3 Conclusions

A novel pentacoordinate trinuclear Cu(II) complex $[\text{Cu}_3\text{L}_2(\text{py})](\text{ClO}_4)_2 \cdot 2\text{THF}$ with (*E*)-3-[*N,N*-di(2-pyridylmethyl)aminomethyl]-2-hydroxyl-5-methylbenzaldehyde oxime (H_2L) has been synthesized and characterized by IR, UV-Vis, TGA and single crystal X-ray analysis. The central trigonal bipyramidal Cu(II) and two terminal square pyramidal Cu(II) ions are linked by -N-O/ μ_2 -O- mixed-bridging to form a linear trinuclear Cu(II) arrangement. A medium antiferromagnetic coupling between adjacent Cu(II) ions dominates the magnetic property of this complex.

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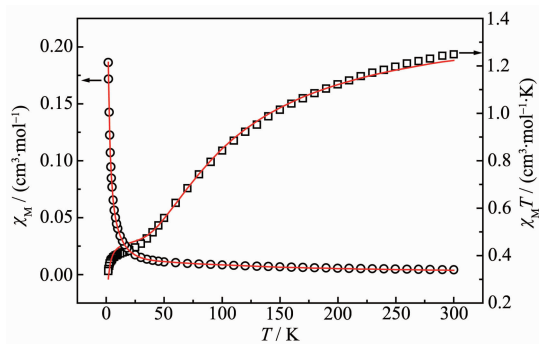


Fig.5 Thermal variation of the χ_M (○) and $\chi_M T$ (□) for **1**

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