

Synthesis, Structure and Magnetic Properties of Two New Homotrinnuclear Bis(oxamato) Copper(II) Complexes[†]

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Two new homotrinnuclear copper(II) complexes with 1,3-propylenebis(oxamato) (pba) and 2-hydroxy-1,3-propylenebis(oxamato) (pbaOH): $\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pba})](\text{DMSO})_2(\text{H}_2\text{O})\}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) and $\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pbaOH})](\text{DMSO})_2(\text{H}_2\text{O})\}(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (**2**) have been synthesized and their structures were determined. Both complexes have the similar homotrinnuclear unit and give rise to the bis-trinnuclear entity through weakly coordinated bonds and $\pi\text{-}\pi$ interaction. The temperature magnetic susceptibilities for **1** and **2** were analyzed by means of the Hamiltonian $\hat{H} = -2J(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu2}} + \hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu3}})$, leading exchange integral J to be -105.6 and -107.3 cm^{-1} for **1** and **2**, respectively.

Keywords crystal structure, homotrinnuclear copper(II) complex, magnetic property, bis(oxamato) complex

Introduction

Molecular magnetism of polynuclear complexes is of considerable interest for designing new magnetic materials and for investigating the relationship between the structure and the role of the polymetallic active sites in biological systems.¹⁻⁴ Journaux *et al.*⁵ have recently proposed that the way to obtain polynuclear complexes is mainly based on the following synthetic schemes: (1) the self-assembly method, (2) the use of poly-nucleating ligand, and (3) the use of complexes as ligands. A good example of "complex as ligand" is represented by the copper(II) complex of bis(oxamato), such as $[\text{Cu}(\text{pba})]^{2-}$, $[\text{Cu} \cdot$

$(\text{pbaOH})]^{2-}$, $[\text{Cu}(\text{opba})]^{2-}$ (pba = 1,3-propylenebis(oxamato), pbaOH = 2-hydroxy-1,3-propylenebis(oxamato), opba = *o*-phenylbis(oxamato)). From these precursors, it was possible to design binuclear and trinnuclear compounds,⁶⁻⁹ linear and zigzag chains,^{10,11} two-dimensional networks with an interlocked structure,¹²⁻¹⁴ and ladder compounds¹⁵ through rationally assembly. Some compounds exhibited a spontaneous magnetization below a critical temperature T_c by assembling ferromagnetic chains $[\text{AB}]_n$ within the crystal lattice in a ferromagnetic fashion^{16,17} and some compounds have irregular spin states with a higher ground state.⁶ In this paper, structures of two new homotrinnuclear copper(II) complexes: $\{[\text{Cu} \cdot (\text{phen})]_2[\mu\text{-Cu}(\text{pba})](\text{DMSO})_2(\text{H}_2\text{O})\}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) and $\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pbaOH})](\text{DMSO})_2(\text{H}_2\text{O})\}(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (**2**) and their magnetic properties were reported.

Experimental

Materials and physical measurements

All chemicals and solvents were of reagent grade and used as received without further purification. The copper(II) precursors $\text{Na}_2[\text{Cu}(\text{pba})] \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2 \cdot [\text{Cu}(\text{pbaOH})] \cdot 3\text{H}_2\text{O}$ were prepared according to the reported procedure.^{16,18}

The IR spectra were recorded as KBr disc on a Shi-

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madzu IR-408 infrared spectrophotometer in the region of 4000–600 cm^{-1} . C, H and N elemental analyses were carried out with a Perkin-Elmer analyzer model 240. Electronic spectra were measured with a Shimadzu UV-260 spectrometer in water and dimethyl sulphoxide mixture (2:1). Variable-temperature magnetic susceptibility measurements were performed on a LDJ 9600 Vibrating Sample Magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables).

Syntheses of complexes 1 and 2

A dimethyl sulphoxide solution (5 mL) of phen (99 mg, 0.5 mmol) was added to an aqueous solution (5 mL) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (185 mg, 0.5 mmol). To the mixture, a dimethyl sulphoxide solution (10 mL) containing $\text{Na}_2[\text{Cu}(\text{pba})] \cdot 6\text{H}_2\text{O}$ (0.25 mmol, 108 mg) was added. After being heated at 60–70 $^\circ\text{C}$ for half an hour, the mixture was filtered. The filtrate was left undisturbed, and well-formed green crystals of **1** were obtained by evaporation at room temperature after a month. Anal. calcd for $\text{C}_{35}\text{H}_{42}\text{Cl}_2\text{Cu}_3\text{N}_6\text{O}_{18}\text{S}_2$: C 35.94, H 3.68, N 7.19; found C 35.95, H 3.54, N 6.96.

Complex **2** was prepared in the same way as **1**, using $\text{Na}_2[\text{Cu}(\text{pbaOH})] \cdot 3\text{H}_2\text{O}$ (99 mg, 0.25 mmol) instead of $\text{Na}_2[\text{Cu}(\text{pba})] \cdot 6\text{H}_2\text{O}$. Anal. calcd for $\text{C}_{35}\text{H}_{43}\text{Cl}_2\text{Cu}_3\text{N}_6\text{O}_{18.5}\text{S}_2$: C 35.73, H 3.57, N 7.15; found C 35.60, H 3.47, N 6.97.

Determination of crystal structure

Crystals with dimensions of 0.30 mm \times 0.30 mm \times 0.20 mm for complex **1** and 0.30 mm \times 0.25 mm \times 0.20 mm for complex **2** were selected and mounted on a Bruker Smart 1000 diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.071073$ nm). Diffraction data were collected using ω -2 θ scans at room temperature (293 K). *LP* correction was applied to the data.

Both structures were solved by direct methods using SHELXS-97 program and refinement on F^2 was performed using SHELXL-97 by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms.^{19,20} Hydrogen atoms were added theoretically and refined with riding model position parameters and isotropically refined. For complex **2**, rotational disorder was observed in O(7) and S(2), refining to 70%:30% and

90%:10% partial occupancies, respectively.

The crystal data and refinement details are summarized in Table 1.

Results and discussion

Spectroscopic properties

The IR spectra of these two complexes are very similar, both displaying the presence of oxamato groups at 1615–1595 (s) ($\nu_{\text{C=O}}$) cm^{-1} . The absorption between 3500 (m) and 3300 (m) cm^{-1} may be assigned to the O–H stretching mode of lattice and/or coordinated water molecular, and the broad absorption centered in 1100 (s) cm^{-1} is attributed to the presence of ClO_4^- .

The electronic spectra of complexes **1** and **2** both show a strong absorption over 28000 cm^{-1} ($\epsilon = 10^4$ L/mol \cdot cm^{-1}) and a weak absorption at 15600 cm^{-1} ($\epsilon = 262$ L/mol \cdot cm^{-1} for complex **1** and $\epsilon = 237$ L/mol \cdot cm^{-1} for complex **2**). The former may be assigned to the intra-ligand and charge-transfer transitions in the Cu(II) chromophore and the latter to the $A_1 \rightarrow B_1$ transitions of copper(II) in a C_{2v} symmetry environment.

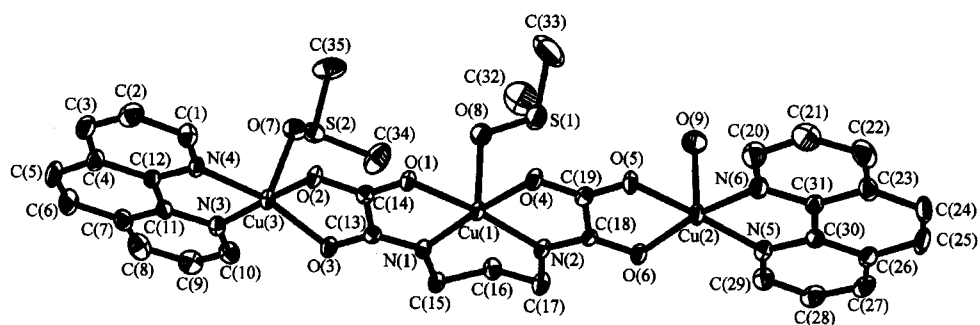
Description of the structure of 1

The structure of complex **1** consists of homotrinnuclear $\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pba})](\text{DMSO})_2(\text{H}_2\text{O})\}^{2+}$ cations, perchlorate anions, water and DMSO molecules. A perspective view of the trinuclear cation is depicted in Fig. 1 and the selected bond lengths and angles are listed in Table 2.

In the trinuclear cation, the central copper atom is ligated by two nitrogen and two oxygen atoms of oxamato bridge with a slight distorted square-planar geometry. The deviations of the four donor atoms from their mean plane are ± 0.0052 – 0.0053 nm. The average Cu–N distance (0.1950 nm) is significantly shorter than that of Cu–O (0.1995 nm), consistent with greater basicity of the deprotonated amido group. Moreover, an oxygen atom of DMSO is also coordinated to Cu(1) in the apical position (Cu–O 0.2281 nm). The Cu(2) and Cu(3) are also five-coordinated. In the basal plane, they are surrounded by two oxygen atoms from $[\text{Cu}(\text{pba})]^{2-}$ complex ligand and two nitrogen atoms from phen. The apical positions are occupied by oxygen atoms of H_2O for Cu(2) and DMSO for Cu(3) so as to form an unsymmetrical structure.

Table 1 Crystal data and details of structural determination for **1** and **2**

	1	2
Empirical formula	C ₃₅ H ₄₂ Cl ₂ Cu ₃ N ₆ O ₁₈ S ₂	C ₃₅ H ₄₃ Cl ₂ Cu ₃ N ₆ O _{18.5} S ₂
Crystal size (mm)	0.30 × 0.30 × 0.20	0.30 × 0.25 × 0.20
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 1.2908(4) nm <i>b</i> = 1.2983(3) nm <i>c</i> = 1.4143(4) nm α = 86.559(5)° β = 71.740(5)° γ = 89.066(5)°	<i>a</i> = 1.3040(5) nm <i>b</i> = 1.3088(5) nm <i>c</i> = 1.4248(6) nm α = 71.186(7)° β = 86.873(7)° γ = 89.577(7)°
<i>V</i> (nm ³)	2.2468(10)	2.2982(16)
<i>Z</i>	2	2
Calculated density (g/cm ³)	1.739	1.690
<i>F</i> (000)	1198	1192
μ (Mo K α) (mm ⁻¹)	1.702	1.663
θ range (°)	1.52 < θ < 25.02	1.64 < θ < 25.03
Limiting indices	-15 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 16	-15 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 15, -10 ≤ <i>l</i> ≤ 16
Total reflections	9369	9528
Independent reflections	7898 [<i>R</i> (int) = 0.0293]	8059 [<i>R</i> (int) = 0.0251]
Data/restraints/parameters	7898/0/595	8059/0/622
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0493, 0.1359	0.0525, 0.1434
<i>R</i> indices (all data)	0.0827, 0.1562	0.0960, 0.1691
Goodness-of-fit on <i>F</i> ²	1.021	1.033
Largest diff. peak and hole (e/nm ³)	716 and -636	963 and -490

**Fig. 1** Perspective view of **1** with the labeling scheme.

The dihedral angles between the equatorial plane around Cu(1) and the phen planes are 172.8° and 172.3°, respectively. That is to say, the whole cation is nearly planar when we do not take the coordinated solvent molecules into account. The deviations of Cu(1), Cu(2) and Cu(3) from the equatorial N(1)N(2)O(1)O(4) mean plane are only -0.01516, -0.05006 and 0.00506 nm. Cu(1)⋯Cu(2) and Cu(1)⋯Cu(3) distances are 0.5163 and 0.5265 nm, respectively.

As shown in Fig. 2, two $\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu} \cdot$

(pba)](DMSO)₂(H₂O)]²⁺ cations connect each other through six weakly coordinated bonds [Cu(2B)⋯O(3A) 0.3215 nm, Cu(3A)⋯N(5B) 0.3540 nm, Cu(1A)⋯N(2B) 0.3352 nm, Cu(1B)⋯N(2A) 0.3352 nm, Cu(2A)⋯O(3B) 0.3215 nm, Cu(3B)⋯N(5A) 0.3540 nm], giving rise to bis-trinuclear entity. Therefore, the coordination polyhedron of each Cu(II) ion can also be described as an octahedron with significant axial elongation. Another interesting thing is that the aryl rings of phen planes from different cations in the bis-trinuclear

are parallel and the distance between carbon atoms of phen ligands is the range of 0.3393–0.3622 nm, so there is probably existed the π - π interaction,²¹⁻²³ which may be another weak interaction to form the bis-trinuclear structure. The Cu(1A) \cdots Cu(1B) and Cu(2A) \cdots Cu(3B) distances are 0.3766 and 0.3920 nm, which are significantly shorter than the Cu \cdots Cu separation in the same cation.

Description of the structure of 2

The structure of complex 2 is very similar to 1, consisting of homotrinnuclear $\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pbaOH})]-(\text{DMSO})_2(\text{H}_2\text{O})\}^{2+}$ cations, perchlorate anions, water and DMSO molecules. A perspective view of the trinuclear cation is depicted in Fig. 3 and selected bond lengths and angles are listed in Table 3.

In the trinuclear cation, the Cu(II) ions are also five-coordinated. Besides the pbaOH⁴⁻ bridge and ligand phen, The apical positions are occupied by oxygen atoms of the solvent molecule H₂O for Cu(2) and DMSO for Cu(3) and Cu(1) to form an unsymmetrical structure. The dihedral angles between the equatorial N(1)N(2)-

O(1)O(2) planes around Cu(1) and the phen planes are 172.4° and 173.5°, respectively. The whole cation is also nearly planar when the solvent molecules were omitted. The deviations of Cu(1), Cu(2), Cu(3) from the equatorial N(1)N(2)O(1)O(2) mean plane are only 0.01276, 0.00254 and 0.04833 nm. Cu(1) \cdots Cu(2) and Cu(1) \cdots Cu(3) distances are 0.5183 and 0.5144 nm, respectively.

Fig. 4 shows the unique bis-trinuclear structure of 2. Two $\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pbaOH})](\text{DMSO})_2 \cdot (\text{H}_2\text{O})\}^{2+}$ cations connect each other through six weakly coordinated bonds [Cu(2B) \cdots O(6A) 0.3249 nm, Cu(3A) \cdots N(4B) 0.3568 nm, Cu(1B) \cdots N(2A) 0.3294 nm, Cu(1A) \cdots N(2B) 0.3294 nm, Cu(2A) \cdots O(6B) 0.3249 nm, Cu(3B) \cdots N(4A) 0.3568 nm]. The π - π interaction probably exist because the aryl rings of phen planes from different cations in the bis-trinuclear are parallel and the distance between carbon atoms of phen ligands is the range of 0.3398–0.3668 nm.²¹⁻²³ The Cu(1A) \cdots Cu(1B) and Cu(2A) \cdots Cu(3B) distances are 0.3723 and 0.3980 nm, which are also shorter than the Cu \cdots Cu separation in the same trinuclear cation.

Table 2 Selected bond lengths ($\times 10^{-1}$ nm) and angles ($^\circ$) for 1

Cu(1)—N(1)	1.949(4)	Cu(3)—O(3)	1.953(3)
Cu(1)—N(2)	1.950(4)	Cu(3)—O(2)	1.962(3)
Cu(1)—O(4)	1.990(3)	Cu(3)—N(4)	1.991(4)
Cu(1)—O(1)	2.001(3)	Cu(3)—N(3)	1.992(4)
Cu(1)—O(8)	2.281(4)	Cu(3)—O(7)	2.268(3)
Cu(2)—O(6)	1.963(3)		
Cu(2)—O(5)	1.967(3)		
Cu(2)—N(5)	1.989(4)		
Cu(2)—N(6)	1.989(4)		
Cu(2)—O(9)	2.285(4)		
N(1)-Cu(1)-N(2)	95.51(15)	N(5)-Cu(2)-N(6)	82.99(17)
N(1)-Cu(1)-O(4)	171.44(14)	O(6)-Cu(2)-O(9)	91.18(14)
N(2)-Cu(1)-O(4)	84.57(14)	O(5)-Cu(2)-O(9)	91.82(14)
N(1)-Cu(1)-O(1)	84.24(14)	N(5)-Cu(2)-O(9)	93.56(15)
N(2)-Cu(1)-O(1)	170.88(14)	N(6)-Cu(2)-O(9)	101.37(15)
O(4)-Cu(1)-O(1)	94.32(12)	O(3)-Cu(3)-O(2)	85.72(13)
N(1)-Cu(1)-O(8)	95.75(15)	O(3)-Cu(3)-N(4)	164.67(15)
N(2)-Cu(1)-O(8)	98.41(15)	O(2)-Cu(3)-N(4)	93.46(15)
O(4)-Cu(1)-O(8)	92.70(14)	O(3)-Cu(3)-N(3)	96.06(15)
O(1)-Cu(1)-O(8)	90.68(13)	O(2)-Cu(3)-N(3)	173.24(14)
O(6)-Cu(2)-O(5)	85.42(13)	N(4)-Cu(3)-N(3)	83.09(16)
O(6)-Cu(2)-N(5)	95.98(15)	O(3)-Cu(3)-O(7)	95.94(14)
O(5)-Cu(2)-N(5)	174.41(15)	O(2)-Cu(3)-O(7)	93.58(14)
O(6)-Cu(2)-N(6)	167.44(15)	N(4)-Cu(3)-O(7)	99.39(14)
O(5)-Cu(2)-N(6)	94.46(15)	N(3)-Cu(3)-O(7)	92.72(15)

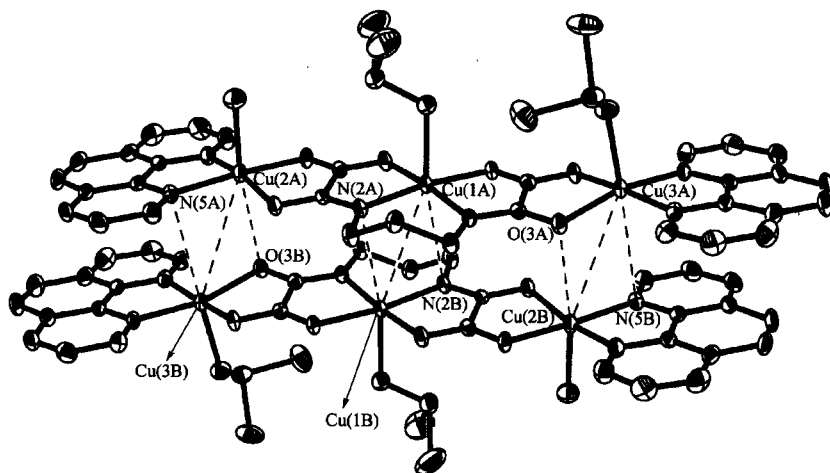


Fig. 2 Weakly coordinated bonds and bis-trinuclear structure of complex 1.

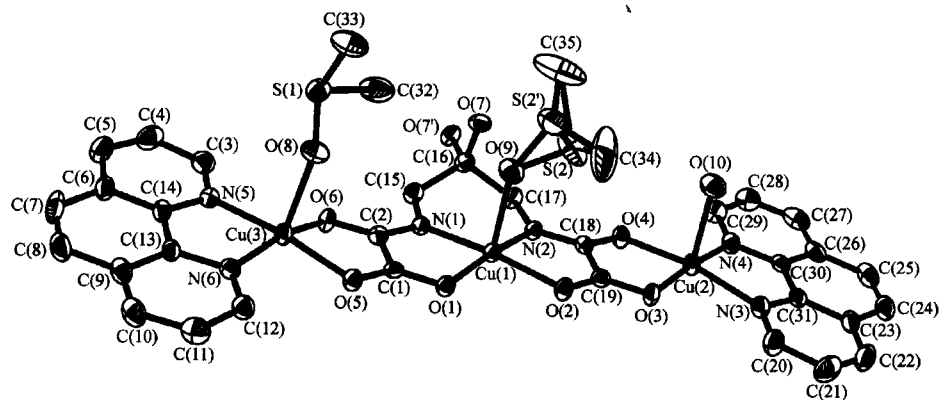


Fig. 3 Perspective view of complex 2 with the labeling scheme.

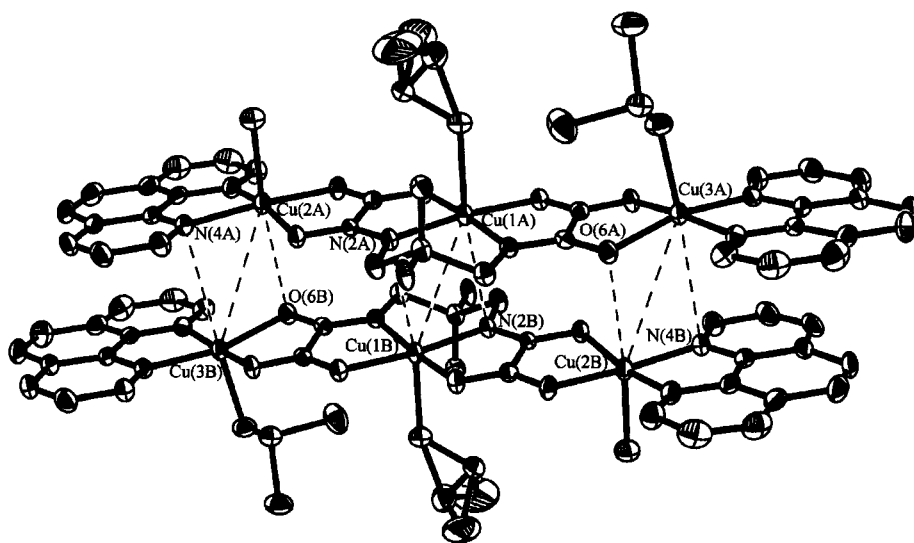


Fig. 4 Weakly coordinated bonds and bis-trinuclear structure of complex 2.

Table 3 Selected bond lengths ($\times 10^{-1}$ nm) and angles ($^\circ$) for **2**

Cu(1)—N(1)	1.952(4)	Cu(2)—N(4)	2.003(5)
Cu(1)—N(2)	1.955(4)	Cu(2)—O(10)	2.273(4)
Cu(1)—O(2)	1.988(4)	Cu(3)—O(5)	1.972(4)
Cu(1)—O(1)	1.994(3)	Cu(3)—O(6)	1.970(4)
Cu(1)—O(9)	2.337(4)	Cu(3)—N(6)	2.001(4)
Cu(2)—O(3)	1.974(4)	Cu(3)—N(5)	2.005(5)
Cu(2)—O(4)	1.979(4)	Cu(3)—O(8)	2.257(4)
Cu(2)—N(3)	1.997(5)		
N(1)-Cu(1)-N(2)	95.49(18)	N(3)-Cu(2)-N(4)	83.0(2)
N(1)-Cu(1)-O(2)	172.88(17)	O(3)-Cu(2)-O(10)	92.31(16)
N(2)-Cu(1)-O(2)	84.79(16)	O(4)-Cu(2)-O(10)	92.85(16)
N(1)-Cu(1)-O(1)	84.71(16)	N(3)-Cu(2)-O(10)	99.56(18)
N(2)-Cu(1)-O(1)	172.21(17)	N(4)-Cu(2)-O(10)	93.34(18)
O(2)-Cu(1)-O(1)	94.05(14)	O(5)-Cu(3)-O(6)	85.45(14)
N(1)-Cu(1)-O(9)	94.69(17)	O(5)-Cu(3)-N(6)	92.97(17)
N(2)-Cu(1)-O(9)	96.08(17)	O(6)-Cu(3)-N(6)	164.53(17)
O(2)-Cu(1)-O(9)	92.34(16)	O(5)-Cu(3)-N(5)	172.53(17)
O(1)-Cu(1)-O(9)	91.66(15)	O(6)-Cu(3)-N(5)	96.52(17)
O(3)-Cu(2)-O(4)	85.67(14)	N(6)-Cu(3)-N(5)	83.21(19)
O(3)-Cu(2)-N(3)	94.16(17)	O(5)-Cu(3)-O(8)	93.53(16)
O(4)-Cu(2)-N(3)	167.58(18)	O(6)-Cu(3)-O(8)	95.15(16)
O(3)-Cu(2)-N(4)	174.03(18)	N(6)-Cu(3)-O(8)	100.31(17)
O(4)-Cu(2)-N(4)	95.97(17)	N(5)-Cu(3)-O(8)	93.47(17)

Table 4 Some oxamato homotrinnuclear copper(II) compounds and their exchange integrals

Compound	Exchange integral (cm^{-1})	Ref.
$\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pba})](\text{DMSO})_2(\text{H}_2\text{O})\}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (1)	-105.6	This work
$\{[\text{Cu}(\text{phen})]_2[\mu\text{-Cu}(\text{pbaOH})](\text{DMSO})_2(\text{H}_2\text{O})\}(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (2)	-107.3	This work
$\{[\text{Cu}(\text{ebo})][\text{Cu}(\text{NO}_2\text{-phen})]_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (3)	-80.9	8
$\{[(\text{ettmd})\text{Cu}]_2[\mu\text{-Cu}(\text{pba})]\}(\text{ClO}_4)_2$ (4)	-137.1	9
$\{[(\text{pmd})\text{Cu}]_2[\mu\text{-Cu}(\text{Me}_2\text{pba})]\}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (5)	-128.1	9
$\{[(\text{bapa})\text{Cu}]_2[\mu\text{-Cu}(\text{Me}_2\text{pba})]\}(\text{ClO}_4)_2$ (6)	-92.1	9
$[\{\text{Cu}(\text{H}_2\text{O})(\text{tmen})\}_2]_2[\{\mu\text{-Cu}(\text{H}_2\text{O})(\text{opba})\}_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (7)	-156.1	7
$[\{\text{Cu}(\text{H}_2\text{O})(\text{tmen})\}_2]_2[\{\mu\text{-Cu}(\text{H}_2\text{O})(\text{Me}_2\text{pba})\}_2](\text{ClO}_4)_2$ (8)	-166.9	7
$[\{\text{Cu}(\text{H}_2\text{O})(\text{tmen})\}[\text{Cu}(\text{tmen})][\mu\text{-Cu}(\text{OHpba})]_n](\text{ClO}_4)_n \cdot n\text{H}_2\text{O}$ (9)	-167.9	7

Magnetic properties

The magnetic susceptibility was measured in the temperature range of 80–300 K on a LDJ 9600 Vibrating Sample Magnetometer in applied magnetic field of 5000 G. The room temperature value for μ_{eff} (2.40 B. M. for **1** and 2.38 B. M. for **2**, where μ_{eff} is the effective magnetic moment) is lower than that expected for three isolated Cu(II) ions ($\mu_{\text{eff}} = 3.00$ B. M.). Upon cooling to 80

K, the μ_{eff} value decreases rapidly, suggesting that an antiferromagnetic interaction among the copper ions is operative.

The magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J(\hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu2}} + \hat{S}_{\text{Cu1}}\hat{S}_{\text{Cu3}})$, where J is the exchange integral between Cu(1) and Cu(2) or Cu(3) ions. The best fitting for the

experimental data gives $J = -105.6 \text{ cm}^{-1}$, $g = 2.05$ for **1** and $J = -107.3 \text{ cm}^{-1}$, $g = 2.05$ for **2**. The agreement factor $R = \sum (\chi_{\text{obsd}} - \chi_{\text{calcd}})^2 / \sum \chi_{\text{obsd}}^2$ is 4.3×10^{-3} for **1** and 5.1×10^{-3} for **2**.

When comparing exchange integral J with those previously reported for homotrinuclear copper(II) species with similar oxamato bridge,⁷⁻⁹ we found that the present exchange integrals are close to all the others (Table 4). This is indicative of a small influence of the variation of the terminal ligands on J values.

References

- (a) Kahn, O. *Molecular Magnetism*, New York, VCH Publishers, **1993**.
(b) Kahn, O. *Struct. Bonding* **1987**, *68*, 89.
(c) Kahn, O. *Adv. Inorg. Chem.* **1996**, *4*, 179.
- Miller, S.; Epstein, J. *Chem. Eng. News*. **1995**, *2*, 30.
- Waller, B. J.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625.
- Solomon, E. I.; Brunold, T. C.; Davis, M. Z.; Kemsley, J. N.; Lee, S. K.; Lehnert, N.; Skulan, A. J.; Yang, Y. S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235.
- Aukaaloo, A.; Ottenwaelder, X.; Ruiz, R.; Journaux, Y.; Pei, Y.; Rivière, E.; Muñoz, M. C. *Eur. J. Inorg. Chem.* **2000**, 951 and references therein.
- Gao, E. Q.; Tang, J. K.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *Inorg. Chem.* **2001**, *40*, 3134.
- Tercero, J.; Diaz, C.; Fallah, M. S. E.; Ribas, J.; Solans, X.; Maestro, M. A.; Mahía, J. *Inorg. Chem.* **2001**, *40*, 3077.
- Miao, M. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Wang, G. L. *Polyhedron* **1995**, *14*, 1577.
- Solans, X.; Rodriguez, V. *Polyhedron* **1993**, *12*, 2697.
- Stumpf, H. O.; Pei, Y.; Kahn, O.; Sletten, J.; Renard, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 6738.
- Stumpf, H. O.; Pei, Y.; Ouahab, L.; Berre, F. L.; Cd-jovi, E.; Kahn, O. *Inorg. Chem.* **1993**, *32*, 5687.
- Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447.
- Vaz, M. G. F.; Pinheiro, L. M. M.; Stumpf, H. O.; Alcantara, A. F. C.; Golhen, S.; Ouahab, L.; Cadot, O.; Mathoniere, C.; Kahn, O. *Chem. Eur. J.* **1999**, *5*, 1486.
- Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866.
- Oushoorn, R. L.; Boubekour, K.; Batail, P.; Guillou, O.; Kahn, O. *Bull. Soc. Chim. Fr.* **1996**, *133*, 777.
- Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782.
- Guillou, O.; Begerat, P.; Kahn, O.; Bakalbassis, E.; Boubekour, K.; Batail, P.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 110.
- Nonoyama, K.; Ojima, H.; Nonoyama, M. *Inorg. Chim. Acta* **1976**, *20*, 127.
- Sheldrick, G. M. *SHELXS-97*. Program for X-Ray Crystal Structure Determination, Göttingen University, Germany, **1997**.
- Sheldrick, G. M. *SHELXL-97*. Program for X-Ray Crystal Structure Refinement, Göttingen University, Germany, **1997**.
- Chen, X. F.; Cheng, P.; Liu, X.; Zhao, B.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *Inorg. Chem.* **2001**, *40*, 2652.
- Nichols, P. J.; Raston, C. L.; Steed, J. W. *Chem. Commun.* **2001**, 1062.
- Lai, S. F.; Cheng, C. Y.; Lin, K. J. *Chem. Commun.* **2001**, 1082.

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