DALTON
FULL PAPER

Heterobinuclear copper(II)–manganese(II) complexes behaving as three-dimensional supramolecular networks *via* both macrocyclic oxamido-bridges and hydrogen bonds

Jin-Kui Tang,[a] Li-Ya Wang,[a] Lei Zhang,[a] En-Qing Gao,[b] Dai-Zheng Liao,*[a,b] Zong-Hui Jiang,[a] Shi-Ping Yan[a,c] and Peng Cheng[a]

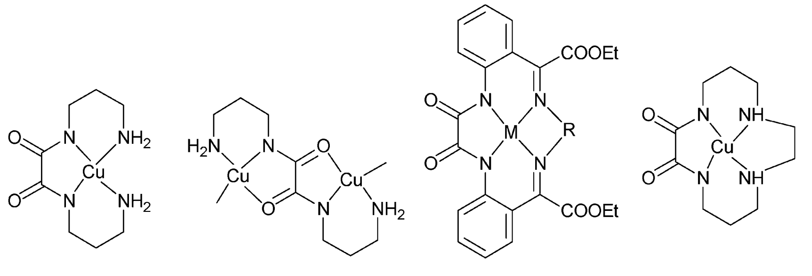
[a] *Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China. E-mail: coord@nankai.edu.cn*
[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China*
[c] *State Key Laboratory of Chemistry and Application of Rare Earth Materials, Peking University, Beijing 100871, P. R. China*

Received 15th October 2001, Accepted 2nd January 2002

Two novel oxamido-bridged heterobinuclear copper(II)–manganese(II) complexes derived from macrocylic oxamido compounds incorporating different blocking ligands were synthesized and characterized by IR and electronic spectroscopy. They are of formula $[Cu(L)Mn(phen)_2](ClO_4)_2\cdot 1.5H_2O$ (**1**) and $[Cu(L)Mn(ntb)](ClO_4)_2\cdot H_2O$ (**2**), where L = 1,4,8,11-tetraazacyclotetradecane-2,3-dione, phen = 1,10-phenanthroline and ntb = tris(2-benzimidazolylmethyl)-amine. The crystal structures of the two complexes have been determined and they consist of binuclear units in which the copper(II) ion is in a square-planar environment and linked to the manganese(II) ion *via* the *exo–cis* oxygen atoms of the oxamido macrocyclic ligand, with Cu ··· Mn separations of 5.421 (**1**) and 5.486 Å (**2**), respectively. The packing of the molecules along the *a* orientation in **2** results in open channels, which were extended into a three-dimensional hydrogen-bonded supramolecular network. The temperature dependence of the magnetic susceptibility for **1** and **2** were analyzed by means of the Hamiltonian, $\hat{H} = -2J\hat{S}_{Mn}\hat{S}_{Cu}$, leading to $J = -14.2$ and -14.7 cm^{-1} for **1** and **2**, respectively.

Introduction

Molecular magnetism has seen a rapid development in the last two decades or so.[1–3] Particular emphasis has been placed on heterobimetallic complexes.[3,4] The magnetic interaction between two non-equivalent paramagnetic centers may lead to situations which cannot be encountered with species containing only one kind of center. One of the best strategies to design and synthesize heteronuclear species is the "complex as ligand" approach, *i.e.* using mononuclear complexes that contain potential donor groups for another metal ion.[1,3–11] A good example of "complex ligands" is represented by the mononuclear Cu(II) complexes of N,N′-bis(coordinating group substituted) oxamides,[6–11] such as [Cu(oxpn)] (Scheme 1). The versatility of oxpn (where oxpn = the *N*,*N*′-bis(3-aminopropyl)-oxamido dianion) as a polynucleating ligand lies in the fact that it can adopt either *cis* or *trans* conformation.[6] Although the flexibility can give rise to a rich variety of complexes and extended structures, it allows much less control over the final type of complex obtained.[6] The macrocyclic oxamides, in which the *exo–cis* conformation of the oxygen donors is enforced, allow us to synthesize heterobimetallic systems and model magnetic systems in a more controlled fashion *via* the stepwise complexation of the macrocyclic and the *exo* donors (Scheme 1).[12] Compared with the rich variety of polymetallic systems of non-cyclic oxamides, those containing macrocyclic oxamides are rather limited,[12–16] although polymetallic complexes of macrocyclic ligands have been of great interest to supramolecular and coordination chemists for their special structures, properties and/or functionalities.[17] Christodoulou *et al.*[13] reported two such binuclear macrocyclic complexes [Ni(α-diketo-TAD-Me$_4$)]ZnCl$_2$ and [Ni(α-diketo-TAD-Me$_4$)][Cu(NO$_3$)$_2$] (α-diketo-TAD-Me$_4$ is 2,3-dioxo-5,6:13,14-dibenzo-7,12-dimethyl-9,10-(4′,5′-dimethylbenzo)-1,4,8,11-tetraazacyclotetradeca-7,11-diene) by using the Ni(II) precursor as a "complex ligand", but the diamagnetic nature of the Ni(II) ions in these



[Cu(*cis*-oxpn)] [Cu$_2$(*trans*-oxpn)] [Cu(cyclam)] [Cu(L)]

Scheme 1

DOI: 10.1039/b107418k

complexes precluded studies of magnetic interactions between the metal ions.

With these facts in mind and in continuation of our interest in polynuclear macrocyclic complexes,[14–16,18] by using the macrocyclic oxamide with the paramagnetic Cu(II) ion as precursors, with diamines and a cyclam as blocking ligands, the two Cu^{II}-Mn^{II} complexes $[Cu(L)Mn(phen)_2](ClO_4)_2\cdot 1.5H_2O$ (**1**) (L = 1,4,8,11-tetraazacyclotetradecane-2,3-dione) and $[Cu(L)Mn(ntb)](ClO_4)_2\cdot H_2O$ (**2**) were prepared and characterized. The crystal structures and magnetic properties were investigated.

Experimental

Materials and synthesis

All chemicals were of A. R. grade and used as received. The mononuclear precursors Cu(L)[16] (L = 1,4,8,11-tetraazacyclotetradecane-2,3-dione) and ntb[19] were prepared as described elsewhere.

Preparations

$[Cu(L)Mn(phen)_2](ClO_4)_2\cdot 1.5H_2O$ (1). An aqueous solution (5 ml) of $Mn(ClO_4)_2\cdot 6H_2O$ (1 mmol, 362 mg) was added to a suspension of Cu(L) (1 mmol, 289 mg) in 10 ml of water. To the resulting solution was added dropwise an ethanol solution (10 ml) of phen (2 mmol, 396 mg) with constant stirring. Red crystals were obtained by slow evaporation of the resulting solution at room temperature. IR (KBr): 3500w, 3200w, 2900w, 1600vs, 1510m, 1440m, 1340w, 1080vs (br), 840s, 720s. Anal. Calc. for $C_{34}H_{39}Cl_2CuN_8MnO_{11.5}$: C, 43.85; H, 4.01; N, 12.04. Found: C, 43.89; H, 4.01; N, 11.94%.

$[Cu(L)Mn(ntb)](ClO_4)_2\cdot H_2O$ (2). To a suspension of Cu(L) (1 mmol, 289 mg) in water (10 ml) was added an ethanol (20 ml) solution of ntb (1 mmol, 408 mg) and an aqueous solution (5 ml) of $Mn(ClO_4)_2\cdot 6H_2O$ (1 mmol, 362 mg). The mixture was stirred under reflux for 3 h and then filtered. Red crystals were obtained by slow evaporation of the filtrate at room temperature. IR (KBr): 3350m, 2900w, 1610 (sh), 1450m, 1340w, 1270w, 1140vs, 1110vs, 1080vs, 740m. Anal. Calc. for $C_{34}H_{41}Cl_2CuN_{11}MnO_{11}$: C, 42.13; H, 4.27; N, 15.90. Found: C, 41.81; H, 4.43; N, 15.82%.

Physical measurements

Elemental analyses (C, H, N) were performed on a Perkin–Elmer 240 analyser. Electronic spectrum: Shimadzu UV-2401 PC spectrophotometer, in MeCN. IR spectra: Shimadzu IR-408 spectrometer; KBr pellets; only main bands are given in cm^{-1}. Variable-temperature magnetic susceptibilities: Quantum Design MPMS-7 SQUID magnetometer; diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[20]

X-Ray crystallography

Determination of the unit cell and data collection were performed at room temperature on a Siemens SMART (**1**) and BRUKER SMART 1000 (**2**), all using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using Siemens SHELXTL (**1**) and SHELXS-97 (**2**) and refined by least-squares procedures on F_o^2 with SHELXL-97 by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors, respectively.[21] The hydrogen atoms of solvent molecules were not added, and the other hydrogen atoms were located geometrically and refined isotropically. One of the perchlorate ions in **2** is seriously disordered. The chloride atom was wholly split into three parts with occupancies being 0.50 : 0.35 : 0.15 and the occupancy factors of 0.50 : 0.35 : 0.15 were assumed for corresponding oxygen atoms of this perchlorate ion. Crystal data collection and refinement parameters are given in Table 1.

CCDC reference numbers 171324 and 171325.

See http://www.rsc.org/suppdata/dt/b1/b107418k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Description of the structure of 1

The structure of complex **1** consists of the heterobinuclear complex cation $[Cu(L)Mn(phen)_2]^{2+}$, 1.5 solvent molecules, and 2 perchlorate ions. A perspective view of the binuclear cation is depicted in Fig. 1, and selected bond lengths and angles are listed in Table 2.

The copper(II) atom is in a slightly distorted square-planar environment with the four donor atoms deviated from their mean plane by −0.1632 (N1), 0.142 (N2), −0.1569 (N3) and 0.1558 Å (N4), and the copper atom is 0.0212 Å out of the plane. The copper atom is connected to the manganese atom *via* the *exo–cis* oxygen atoms of the oxamido macrocyclic ligands with a Cu–Mn separation of 5.421 Å. The coordination sphere of the manganese atom is completed by four nitrogen atoms from two phen ligands. The coordination polyhedron can be considered as a distorted octahedron. The copper and manganese atoms are displaced towards the opposite side of the bridge plane by −0.0674 and 0.0642 Å, respectively. The oxamido bridging plane and the mean equatorial plane of the copper ion form a dihedral angle of 13.0°. The sum of the angles around the amidate nitrogen atoms of the oxamido macrocyclic ligand is very close to 360°. This fact, together with the values of the bond lengths involved and the planarity of the oxamido skeleton, reveal that the amidate nitrogens are sp^2-hybridized and that the π-carbonyl electrons are delocalized to form a conjugated system.

Description of the structure of 2

The structure of complex **2** consists of the heterobinuclear complex cation $[Cu(L)Mn(ntb)]^{2+}$, 2 perchlorate ions and a water molecule. A perspective view of the binuclear unit is depicted in Fig. 2 and selected bond lengths and angles are listed in Table 3.

The copper atom resides in the coordination cavity formed by the four nitrogen donors of the macrocyclic oxamide, with a distorted square-planar geometry. The deviations of donor atoms from the N_4 mean plane are 0.1760 (N1), −0.1753 (N2), 0.1677 (N3) and 0.1684 Å (N4), and the copper atom is 0.0461 Å out of the plane. The Cu- and Mn-atoms are bridged by an oxamido group with a separation of 5.486 Å, and the Mn atom assumes an asymmetrical distorted octahedral environment, with the two carbonyl O-atoms O(1) and O(2) of the macrocyclic oxamido ligand and the two N-atoms N(5) and N(8) of the tripodal ligand ntb in equatorial positions, and the other two nitrogen atoms (N6, N10) of ntb in axial positions. The copper and manganese atoms are displaced towards the opposite side of the bridge plane by −0.1124 and 0.0486 Å. The oxamido bridging plane and the mean equatorial plane of the copper ion form a dihedral angle of 11.7°. Similar to that in **1**, the amidate nitrogens are sp^2-hybridized and the π-carbonyl electrons are delocalized to form a conjugated system. The packing of the molecules along the *a* orientation results in open channels (Fig. 3). Meanwhile, the channels are connected in two orientations through different hydrogen bonds. Along the *b* axis orientation, adjacent channels are linked by hydrogen bonds [N11 ··· O2($-x+2$, $-y+2$, $-z$), 2.763 Å] formed between two binuclear entities from different channels (Fig. 4), while along the *c* axis orientation, they are connected through hydrogen bonds [N7 ··· O13($x+1$, y, $z-1$), 2.959 Å, N9 ··· O3($-x+1$, $-y+1$, $-z$), 2.890 Å] formed between the binuclear units and

Table 1 Crystallographic data for complexes **1** and **2**

	1	**2**
Formula	$C_{34}H_{37}Cl_2CuMnN_8O_{11.50}$	$C_{34}H_{41}Cl_2CuMnN_{11}O_{11}$
M	931.10	969.21
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	31.133(6)	9.7676(11)
b/Å	16.989(3)	15.3391(18)
c/Å	14.827(3)	16.1155(19)
α/°	90	113.477(2)
β/°	97.25(3)	97.085(2)
γ/°	90	98.055(3)
V/Å^3	7780(3)	2149.7(4)
Z	8	2
D_{calc}/g cm^{-3}	1.590	1.464
F(000)	3806	953
μ(Mo-Kα)/mm^{-1}	1.080	0.980
T/K	293(2)	293(2)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0709, 0.1389	0.0676, 0.1435
R_1, wR_2 [all data]	0.1171, 0.1690	0.1530, 0.1770

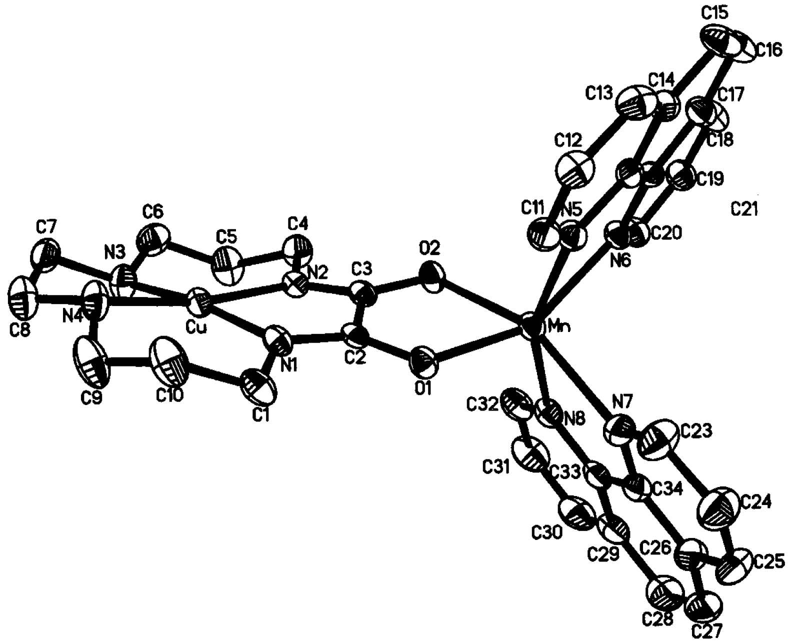


Fig. 1 ORTEP view of the binuclear cations in **1**. The thermal ellipsoids are drawn at the 30% possibility level.

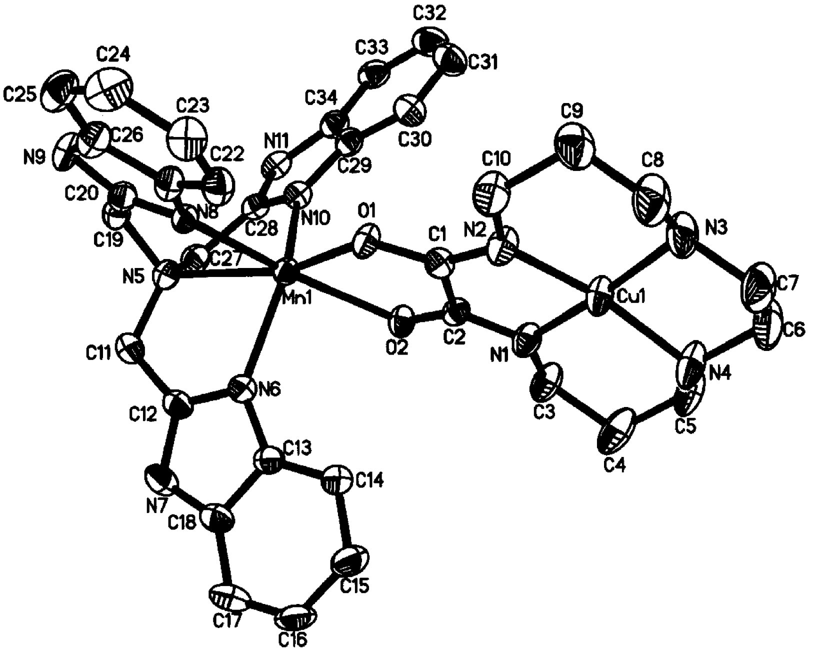


Fig. 2 ORTEP view of the binuclear cations in **2**. The thermal ellipsoids are drawn at the 30% possibility level.

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

Cu(1)–N(1)	1.935(5)	Mn(1)–N(7)	2.279(6)
Cu(1)–N(2)	1.955(5)	N(1)–C(2)	1.301(8)
Cu(1)–N(4)	1.997(6)	N(1)–C(1)	1.466(8)
Cu(1)–N(3)	2.002(6)	N(2)–C(3)	1.296(8)
Mn(1)–O(1)	2.143(4)	N(2)–C(4)	1.453(8)
Mn(1)–O(2)	2.165(4)	O(1)–C(2)	1.265(7)
Mn(1)–N(6)	2.254(5)	O(2)–C(3)	1.267(7)
Mn(1)–N(8)	2.269(6)	C(2)–C(3)	1.534(8)
Mn(1)–N(5)	2.273(5)		
N(1)–Cu(1)–N(2)	84.2(2)	O(2)–Mn(1)–N(7)	110.92(18)
N(1)–Cu(1)–N(4)	96.4(2)	N(6)–Mn(1)–N(7)	93.34(19)
N(2)–Cu(1)–N(4)	171.9(2)	N(8)–Mn(1)–N(7)	72.7(2)
N(1)–Cu(1)–N(3)	169.3(2)	N(5)–Mn(1)–N(7)	157.2(2)
N(2)–Cu(1)–N(3)	94.8(2)	C(2)–N(1)–C(1)	119.0(5)
N(4)–Cu(1)–N(3)	86.0(3)	C(2)–N(1)–Cu(1)	113.3(4)
O(1)–Mn(1)–O(2)	77.50(16)	C(1)–N(1)–Cu(1)	126.9(4)
O(1)–Mn(1)–N(6)	91.62(18)	C(3)–N(2)–C(4)	119.3(6)
O(2)–Mn(1)–N(6)	152.75(18)	C(3)–N(2)–Cu(1)	112.9(4)
O(1)–Mn(1)–N(8)	155.9(2)	C(4)–N(2)–Cu(1)	127.2(4)
O(2)–Mn(1)–N(8)	95.5(2)	O(1)–C(2)–N(1)	128.7(6)
N(6)–Mn(1)–N(8)	103.7(2)	O(1)–C(2)–C(3)	117.4(6)
O(1)–Mn(1)–N(5)	110.18(19)	N(1)–C(2)–C(3)	113.9(5)
O(2)–Mn(1)–N(5)	87.04(18)	O(2)–C(3)–N(2)	128.7(6)
N(6)–Mn(1)–N(5)	73.22(19)	O(2)–C(3)–C(2)	116.9(5)
N(8)–Mn(1)–N(5)	92.3(2)	N(2)–C(3)–C(2)	114.4(6)
O(1)–Mn(1)–N(7)	88.1(2)		

Table 3 Selected bond lengths (Å) and angles (°) for **2**

Cu(1)–N(2)	1.941(5)	Mn(1)–O(2)	2.297(4)
Cu(1)–N(1)	1.946(5)	O(1)–C(1)	1.288(6)
Cu(1)–N(4)	1.988(6)	O(2)–C(2)	1.272(6)
Cu(1)–N(3)	1.997(6)	C(1)–C(2)	1.510(8)
Mn(1)–O(1)	2.106(4)	N(1)–C(3)	1.460(7)
Mn(1)–N(6)	2.163(5)	N(2)–C(10)	1.486(8)
Mn(1)–N(10)	2.183(5)	N(1)–C(2)	1.305(7)
Mn(1)–N(8)	2.217(5)	N(2)–C(1)	1.278(7)
N(2)–Cu(1)–N(1)	84.1(2)	N(10)–Mn(1)–N(8)	102.92(17)
N(2)–Cu(1)–N(4)	167.2(3)	O(1)–Mn(1)–O(2)	75.09(14)
N(1)–Cu(1)–N(4)	95.6(2)	N(6)–Mn(1)–O(2)	86.92(16)
N(2)–Cu(1)–N(3)	96.1(2)	N(10)–Mn(1)–O(2)	86.91(16)
N(1)–Cu(1)–N(3)	172.6(2)	N(8)–Mn(1)–O(2)	164.35(15)
N(4)–Cu(1)–N(3)	85.9(3)	C(2)–N(1)–C(3)	119.1(5)
O(1)–Mn(1)–N(6)	116.14(17)	C(2)–N(1)–Cu(1)	112.2(4)
O(1)–Mn(1)–N(10)	111.46(17)	C(3)–N(1)–Cu(1)	127.4(4)
N(6)–Mn(1)–N(10)	128.38(17)	C(1)–N(2)–C(10)	118.5(5)
O(1)–Mn(1)–N(8)	89.87(16)	C(1)–N(2)–Cu(1)	113.1(4)
N(6)–Mn(1)–N(8)	96.10(17)	C(10)–N(2)–Cu(1)	128.3(4)

perchlorate ions and water molecules, which both lie between the channels, thus yielding a three-dimensional hydrogen-bonded supramolecular network, as shown in Fig. 5.

Spectroscopic characterization

The IR spectra of binuclear species **1** and **2** show two strong bands at *ca.* 1600 and *ca.* 1440 cm^{-1}, attributed to the ν(N–C–O) stretching bands, which are characteristic of the bridging oxamido group[7] and a broad strong band at *ca.* 1080 cm^{-1} which is characteristic of perchlorate ions.[22]

The electronic absorption spectra of the two binuclear complexes in MeCN below 400 nm are dominated by intense bands due to intraligand and charge-transfer transitions in the Cu(II) chromophore.[18] In the 500–900 nm region, relatively strong bands centered at 504–512 nm are attributed to the spin-allowed d–d transitions of Cu(II) in an environment close to square-planar.[7] The coordination environment of manganese(II) in the Cu–Mn complex is a distorted octahedron. Thus, according to ligand field theory and assuming O_h symmetry, the ground state of manganese(II) is $^6A_{1g}$. Because d–d transitions of manganese(II) ($^6A_{1g} \longrightarrow {}^4T_{1g}(G)$, $^4T_{2g}(G)$, $^4A_{1g} \cdots$) are spin-forbidden, in the spectra of the complexes no characteristic band of manganese(II) was found.[23]

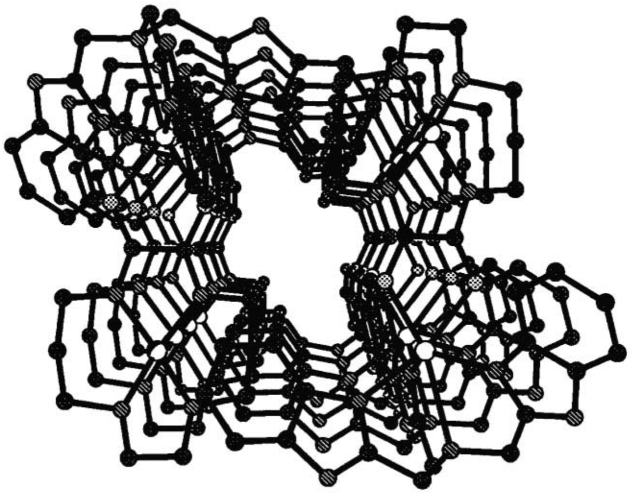


Fig. 3 View of the packing of the molecules of **2** along the *a* orientation, showing channels.

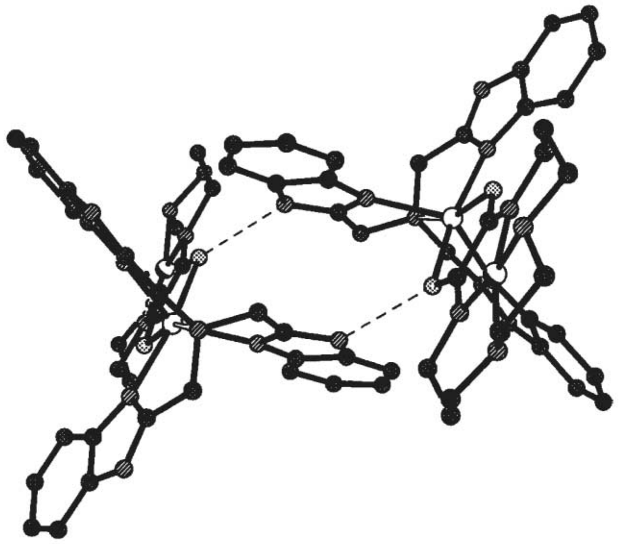


Fig. 4 A diagram showing the hydrogen bonds between two binuclear entities in **2**.

Magnetic properties

The temperature dependence of the molar magnetic susceptibility (χ_M) and its product with temperature ($\chi_M T$) for **1** and **2** are shown in Fig. 6. The $\chi_M T$ values at room temperature are 4.40 and 4.16 $\text{cm}^3\ \text{mol}^{-1}$ K for **1** and **2**, respectively, lower than the spin-only value (4.75 $\text{cm}^3\ \text{mol}^{-1}$ K) expected for the uncoupled Cu(II)–Mn(II) unit. They decrease smoothly upon cooling and reach a plateau below 30 K with $\chi_M T$ between 2.60–3.00 $\text{cm}^3\ \text{mol}^{-1}$ K. The plateau corresponds to the temperature range where only the quintet ground state is thermally populated. These features are typical of Cu(II)–Mn(II) pairs with antiferromagnetic intramolecular interaction. The presence of this plateau in the low-temperature range indicates that the zero-field splitting within the $S = 2$ ground state is too small to be detected by magnetic studies down to 5 K.

On the basis of the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Mn}}\hat{S}_{\text{Cu}}$, the expression of the magnetic susceptibility for a CuMn pair is:

$$\chi_M = \frac{N\beta^2}{kT}\left(\frac{28g_3^2 + 10g_2^2\exp(-6J/kT)}{7 + 5\exp(-6J/kT)}\right) + N\alpha$$

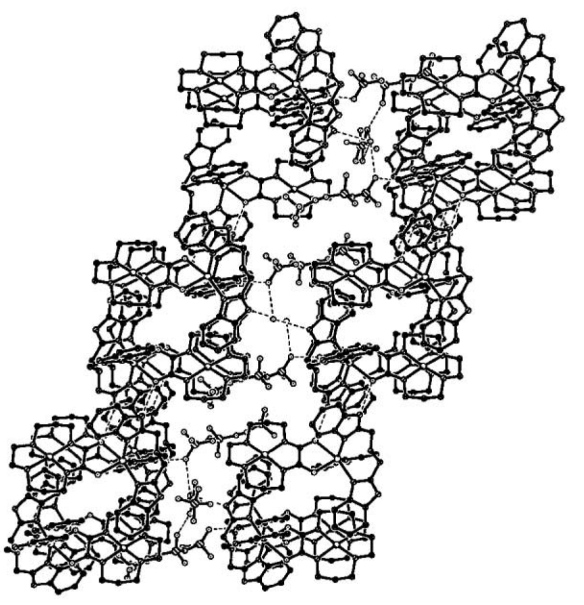


Fig. 5 Three-dimensional frameworks in the crystal structure of **2**.

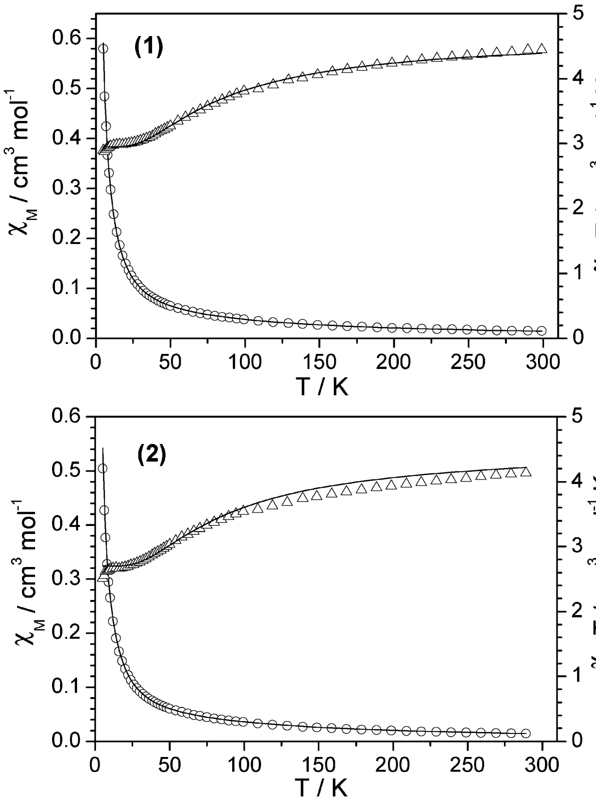


Fig. 6 χ_M (○) *vs.* T and $\chi_M T$ (Δ) *vs.* T plots for complexes **1** and **2**.

where the g_S ($S = 2, 3$) factors are related to local g factors by, $g_2 = (7g_{Mn} - g_{Cu})/6$, $g_3 = (5g_{Mn} + g_{Cu})/6$, $N\alpha$ is the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1}), and the other symbols have their usual meanings. The parameters obtained by the simulation of the experimental data using the above expression are $J = -13.9$ cm^{-1}, $g_{Cu} = 2.08$, $g_{Mn} = 1.99$, $R = 1.58 \times 10^{-4}$ (**1**), $J = -15.44$cm^{-1}, $g_{Cu} = 2.20$, $g_{Mn} = 1.94$, $R = 2.2 \times 10^{-3}$ ($R = \Sigma(\chi_{obsd} - \chi_{calc})^2/\Sigma\chi_{obsd}^2$).

According to Kahn,[1,3,4] the antiferromagnetic interaction between Cu(II) and Mn(II) arises from the non-zero overlap between the $d_{x^2-y^2}$ magnetic orbitals centered on the two metal ions and delocalized towards ligands. The larger the overlap, the stronger the interaction. The difference in the magnetic exchange may be explained on the basis of structural distortions. In this regard, one of the relevant factors is the value of the dihedral angle (γ) between the mean equatorial plane of the metal ion and the oxamido plane:[24,25] the greater the value of γ the smaller the antiferromagnetic coupling. The similar γ value of these two complexes (13.07 for **1** and 11.7° for **2**) results in comparable J values for the two complexes.

Conclusions

By using the macrocyclic oxamido–copper(II) complex as a complex ligand and phen and ntb as auxiliary ligands, two novel oxamido-bridged heterobinuclear copper(II)–manganese(II) complexes have been obtained. Both complexes consist of cationic binuclear Cu–Mn entities. The packing of the molecules along the *a* orientation in **2** results in open channels, which were extended into a three-dimensional hydrogen-bonded supramolecular network. The temperature dependence of the magnetic susceptibility for **1** and **2** were analyzed by means of the Hamiltonian $\hat{H} = -2J\hat{S}_{Mn}\hat{S}_{Cu}$, leading to $J = -14.2$ and -14.7 cm^{-1} for **1** and **2**, respectively.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20071019, 20071020,50172021 and 90101028).

References

1 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
2 *Molecular Magnetism: From Molecular Assemblies to the Devices*, ed. E. Coronado, P. Delhaès, D. Gatteschi and J. S. Miller, Kluwer, The Netherlands, 1996.
3 O. Kahn, *Adv. Inorg. Chem.*, 1996, **43**, 179.
4 O. Kahn, *Struct. Bonding (Berlin)*, 1987, **68**, 89.
5 (*a*) S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1805; (*b*) N. B. O'Brien, T. O. Maier, I. C. Paul and R. S. Drago, *J. Am. Chem. Soc.*, 1973, **95**, 6640.
6 (*a*) H. Ojima and K. Nonoyama, *Coord. Chem. Rev.*, 1988, **92**, 85; (*b*) R. Ruiz, J. Faus, F. Lloret, M. Julve and Y. Journaux, *Coord. Chem. Rev.*, 1999, **193–195**, 1069.
7 F. Lloret, Y. Journaux and M. Julve, *Inorg. Chem.*, 1990, **29**, 3967.
8 (*a*) H. Okawa, Y. Kawahara, M. Masahiro and S. Kida, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 549; (*b*) L. Banci, A. Bencini, C. Benelli and D. Getteschi, *Inorg. Chem.*, 1981, **20**, 1399; (*c*) Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem.*, 1985, **24**, 4063; Y. Journaus, J. Sletten and O. Kahn, *Inorg. Chem.*, 1986, **25**, 439; (*d*) K. Nakatani, J. Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J. P. Renard, Y. Pei, J. Sletten and M. Verdaguer, *J. Am. Chem. Soc.*, 1989, **111**, 5739; (*e*) F. Lloret, M. Julve, J. Faus, R. Ruiz, I. Castro, M. Mollar and M. Philoche-Levisalles, *Inorg. Chem.*, 1992, **31**, 784; (*f*) A. Escuer, R. Vicente, J. Ribas, R. Costa and X. Solans, *Inorg. Chem.*, 1992, **31**, 2627; (*g*) F. Lloret, M. Julve, R. Ruiz, Y. Journaux, K. Nakatani, O. Kahn and J. Sletten, *Inorg. Chem.*, 1993, **32**, 27; (*h*) C. Mathoniére, O. Kahn, J. C. Daran, H. Hilbig and F. H. Köhler, *Inorg. Chem.*, 1993, **32**, 4057.
9 Z.-Y. Zhang, D.-Z. Liao, Z.-H. Jiang, S.-Q. Hao, X.-K. Yao, H.-G. Wang and G.-L. Wang, *Inorg. Chim. Acta*, 1990, **173**, 201.
10 (*a*) J. A. Real, R. Ruiz, J. Faus, M. Julve, Y. Journaux, M. Phioche-Levisalles and C. Bois, *J. Chem. Soc., Dalton, Trans.*, 1994, 3769; (*b*) J. L. Sanz, R. Ruiz, A. Gleizes, F. Lloret, J. Faus, M. Julve, J. J. Borrás-Almenar and Y. Journaux, *Inorg. Chem.*, 1996, **35**, 7384; (*c*) J. Larionova, S. A. Chavan, J. V. Yakhmi, A. G. Frøystein, J. Sletten, C. Sourisseau and O. Kahn, *Inorg. Chem.*, 1997, **36**, 6374; (*d*) Z.-N. Chen, H.-X. Zhang, K.-B. Yu, B.-S. Kang, H. Cai, C.-Y. Su, T.-W. Wang and Z.-L. Lu, *Inorg. Chem.*, 1998, **37**, 4475; (*e*) J. Ribas, C. Diaz, R. Costa, J. Tercero, X. Solans, M. Font-Bardía and H. Stoeckli-Evans, *Inorg. Chem.*, 1998, **37**, 223.
11 (*a*) J. M. Dominguez-Vera, J. M. Moreno, N. Galvez, J. Suarez-Varela, E. Colacio, R. Kivekas and M. Klinga, *Inorg. Chim. Acta*, 1998, **281**, 95; (*b*) C. Diaz, J. Ribas, R. Costa, J. Tercero, M. S. El Fallah, X. Solans and M. Font-Bardía, *Eur. J. Inorg. Chem.*, 2000, 675; (*c*) I. Castro, M. L. Calatayud, J. Sletten, M. Julve and F. Llort, *C. R. Acad. Sci., Ser. IIc: Chim.*, 2001, 235.
12 L. Cronin, A. R. Mount, S. Parsons and N. Robertson, *J. Chem. Soc., Dalton Trans.*, 1999, 1925.

13 D. Christodoulou, M. G. Kanatzidis and D. Coucouvanis, *Inorg. Chem.*, 1990, **29**, 191.
14 E.-Q. Gao, G.-M. Yang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan and G.-L. Wang, *J. Chem. Res. (S)*, 1999, 278.
15 (*a*) E.-Q. Gao, G.-M. Yang, J.-K. Tang, D.-Z. Liao, Z.-H. Jiang and S.-P. Yan, *Polyhedron*, 1999, **18**, 3643; (*b*) E.-Q. Gao, D.-Z. Liao, Z.-H. Jiang and S.-P. Yan, *Polyhedron*, 2001, **20**, 923.
16 E.-Q. Gao, J.-K. Tang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan and G.-L. Wang, *Helv. Chim. Acta*, 2001, **84**, 908.
17 (*a*) *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979; (*b*) P. A. Vigato, S. Tamburini and D. E. Fenton, *Coord. Chem. Rev.*, 1990, **106**, 25; (*c*) C. T. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293.
18 E.-Q. Gao, W.-M. Bu, G.-M. Yang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan and G.-L. Wang, *J. Chem. Soc., Dalton Trans.*, 2000, 1431.
19 A. R. Oki, P. K. Bommarreddy, H. M. Zhang and N. Hosmane, *Inorg. Chim. Acta*, 1995, **231**, 109.
20 P. W. Selwood, *Magnetochemistry*, Interscience, New York, 1956, p. 78.
21 G. M. Sheldrick, SHELXS-97 and SHELXL-97, Software for Crystal Structure Analysis, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1997.
22 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 5th edn., 1997, Part B, p. 83.
23 D.-Z. Liao, J. Shi, Z.-H. Jiang, S.-P. Yan, P. Cheng and G.-L. Wang, *Polyhedron*, 1992, **11**, 2621.
24 S. Alvarez, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 4500.
25 J. L. Sanz, B. Cervera, R. Ruiz, C. Bois, J. Faus, F. Lloret and M. Julve, *J. Chem. Soc., Dalton, Trans.*, 1996, 1359.