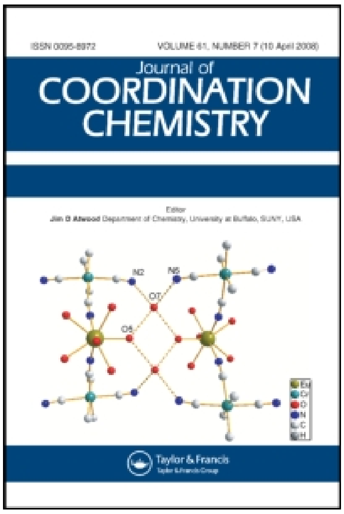

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Synthesis, crystal structure and magnetic properties of a new 1-D oxamidate-bridged Cu(II)-Mn(II) polymer

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Synthesis, crystal structure and magnetic properties of a new 1-D oxamidate-bridged Cu(II)-Mn(II) polymer

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A new coordination polymer, $\{[Cu(aeop)Mn(H_2O)_3]_2\}_n$ ($H_4aeop = N'$-(2-aminoterephthalic acid)-N''-(1,3-propanediamine)oxamidate), has been synthesized and characterized structurally and magnetically. This complex features a 1-D ladder-like chain structure constructed from neutral tetranuclear units through the *syn-anti* carboxylate bridges. This crystal forms in the triclinic system, space group $P\bar{1}$, with $a = 9.653(1)$ Å, $b = 9.686(1)$ Å, $c = 10.903(1)$ Å, $\alpha = 80.984(1)^\circ$, $\beta = 69.776(1)^\circ$, $\gamma = 80.729(1)^\circ$ and $z = 2$. The relationship between its magnetic properties and structure has also been investigated.

Keywords: Oxamidate-bridged; Coordination polymer; Crystal structure; Magnetic properties

1. Introduction

The design of metal-containing building blocks to spontaneously assemble into interesting molecular architectures is of considerable interest in view of the nature of magnetic exchange interactions between metal ions through bridging ligands [1]. Molecules that contain two kinds of metal ions play an important role in molecular magnetism [2]. One strategy to design and synthesize heteronuclear species is the ‘‘complex as ligand’’ approach, where anionic precursors are particularly suitable for heterobinuclear complexes or heterobimetallic chain compounds playing an important role in development of molecular magnetism [3–9].

Oxamidate derivatives are versatile organic ligands which can chelate as well as bridge to construct discrete and extended structures, depending on the ‘‘second’’ metal ion conformation [10]. The *cis*-oxamidates usually give discrete polynuclear species, whereas *trans*-isomers can afford extended structures. These ligands in

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trans-conformation allow formation of *trans*-oxamidato-bridged binuclear copper units, which can behave as building blocks to be linked together by a "second" bridging group such as azide [11, 12], cyanate [13], 4,4′-bipyridine [14], pyrimidine [14, 15], carboxylate [16, 17], cyanide [18], hydroxide [19], etc., to construct extended 1-D or 2-D polymers.

Carboxylate ligands play an important role in coordination chemistry, adopting various binding modes such as terminal monodentate, chelating to one metal center, bridging in *syn–syn*, *syn–anti* and *anti–anti* configuration to two metal centers, and bridging tridentate to two metal centers [20]. Carboxylate is also a bridging ligand having interesting magnetic properties. The most common are the *syn–syn* and *syn–anti* conformations that mediate large antiferromagnetic and weak antiferromagnetic or ferromagnetic interactions [21, 22].

In this paper, a new dissymmetrical ligand N′-(2-aminoterephthalic acid)-N″-(1,3-propane-diamine)oxamidate, abbreviated as H_4aeop, has been designed and prepared. Based on this ligand, we describe the synthesis, crystal structure and the magnetic properties of the new coordination polymer.

2. Experimental

2.1. *Materials*

All chemicals were of reagent grade and used without further purification.

2.2. *Synthesis of H_4aeop*

A 5 mmol (0.6826 g) portion of ethyl oxalyl chloride in 10 mL of THF was added dropwise into a 50 mL THF solution of 5 mmol (0.93 g) of 2-aminoterephthalic acid. After 1 h, 20 mL of absolute ethanol was further added and the mixture was added dropwise into the solution which contained 20 mL of absolute ethanol and 4.2 mL of 1,3-propanediamine at 0°C. The resulting solution was stirred for 2 h, when H_4aeop precipitated as a white powder, which was washed with absolute ethanol and dried under vacuum. Yield: 1.38 g, 89%. Anal. Calcd for $C_{13}H_{15}N_3O_6$(%): C, 50.49; H, 4.89; N, 13.59. Found: C, 50.46; H, 4.93; N, 13.56. IR (KBr, cm^{-1}): ν_{NH2} 3430(s); $\nu_{C=O}$ (oxamidate group) 1632 (m); $\nu_{as(COO)}$ (ν_{COOH}) 1668 (s).

2.3. *Synthesis of the copper(II) precursor*

1 mmol (0.3093 g) of H_4aeop and 4 mmol (0.160 g) of NaOH were dissolved in 20 mL of water. Aqueous solution (10 mL) containing 1 mmol (0.1705 g) of $CuCl_2 \cdot 2H_2O$ was then added. The resulting violet-red solution was filtered and concentrated to 5 mL. Ethanol was then added slowly into the filtrate, and $Na_2[Cu(aeop)] \cdot 3H_2O$ precipitated as a red polycrystalline powder and was washed with ethanol and dried under vacuum at room temperature. Yield: 0.404 g, 86.2%. Anal. Calcd for $C_{13}H_{17}N_3O_9Na_2Cu$(%): C, 33.30; H, 3.66; N, 8.96; Cu, 13.56. Found: C, 33.28; H, 3.69; N, 8.93; Cu, 13.59. IR (KBr, cm^{-1}): ν_{NH2} 3407 (s); $\nu_{(COO^-)}$ 1609 (s).

2.4. *Preparation of {[Cu(aeop)Mn(H₂O)₃]₂}ₙ (1)*

A 0.1 mmol (0.0469 g) amount of $Na_2[Cu(aeop)] \cdot 3H_2O$ was dissolved in 17 ml of water and 17 mL of DMF solution containing 0.1 mmol (0.0244 g) $Mn(CH_3COO)_2 \cdot 4H_2O$ was added under constant stirring. The resulting violet solution was filtered, and well-shaped violet single crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the solution. Yield: 0.0463 g, 90%. Anal. Calcd for $C_{13}H_{21}CuMnN_3O_{11}$(%): C, 30.39; H, 4.12; N, 8.18; Cu, 12.37; Mn, 10.69. Found: C, 30.42; H, 4.15; N, 8.15; Cu, 12.39; Mn, 10.72. IR (KBr, cm^{-1}): $\nu_{C=O}$ 1616 (s).

2.5. *Physical measurements*

Elemental analyses for C, H and N were carried out on a Perkin-Elmer elemental analyzer, model 2400II. The metal contents were determined by EDTA titration [23]. The infrared spectra were recorded on an Avater-360 spectrometer using KBr pellets from 400–4000 cm^{-1}. Thermogravimetric analysis was carried out on an EXSTAR6000 TG/DTA6300 SII type analyzer in a nitrogen atmosphere, and the complex was heated to 900°C at a heating rate of 10°C min^{-1}. Magnetic measurement was carried out on polycrystalline samples with a MPMS-7SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all atoms.

2.6. *X-ray analysis*

The single crystal used for data collection of compound **1** was selected and mounted on a Bruker Smart APEX diffractometer with a CCD detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lorentz and polarization factors were made for the intensity data and absorption corrections were performed using SADABS [24]. The crystal structures were solved using SHELXTL and refined using full matrix least-squares [25]. The hydrogen atom positions were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbon atoms. Crystal data collection and refinement parameters are given in table 1.

3. Results and discussion

3.1. *IR spectra*

The ligand H_4aeop exhibits one $\nu_{C=O}$ vibration of the oxamidate group at ca 1632 cm^{-1} [26], one $\nu_{as(COO)}$ (ν_{COOH}) vibration band at ca 1668 cm^{-1} [27], and the bands of the $\nu_{N–H}$ group (oxamidate group) at ca 3012 and 3129 cm^{-1}. These bands are all missing in the spectrum of the Cu(II) complex because of the loss of protons of both the COOH and N–H (oxamidate group) groups, indicating coordination of COO^- and deprotonated amide to Cu(II). One new sharp strong band observed in the Cu(II) complex (1613 cm^{-1}) and **1** (1616 cm^{-1}) is the result of overlapping between $\nu_{as(coo)}$ of the ionized carboxylate group and vibration of the oxamidate group ($\nu_{C=O}$) acting in bidendate mode. In addition, the $–NH_2$ vibration at ca 3430 cm^{-1} for H_4aeop was

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

Formula	$C_{13}H_{21}N_3O_{11}CuMn$
M	513.81
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.656(1)
b	9.686(1)
c	10.903(1)
α	80.984(1)
β	69.776(1)
γ	80.729(1)
V (Å^3)	938.7(2)
F(000)	524
Z	2
D_{Calcd} (g · cm^{-3})	1.818
μ (mm^{-1})	1.870
Crystal size (mm^3)	0.20 × 0.13 × 0.09
θ range (deg)	2.00 to 26.02
Independent reflns.	3603 [$R_{\mathrm{int}} = 0.0452$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0412$, $wR_2 = 0.1030$
R indices (all data)	$R_1 = 0.0539$, $wR_2 = 0.1086$

present for the complex and with small shift (3407 cm^{-1}). Such a red shift indicates that the nitrogen of $-NH_2$ coordinates to the copper ion.

3.2. *Thermal properties*

Thermogravimetric analysis (TGA) shows that the Cu(II) complex loses 10.7% (expected, 11.5%) in the 26–150°C range corresponding to loss of three water molecules. Compound **1** loses 16.4% of total weight in the 26–150°C range, corresponding to loss of 4.5 molecules of water for the formula unit (expected, 16.3%). We also found that this compound decomposes at about 375°C, and the temperature is higher than that of the Cu(II) complex (at about 320°C). This indicates that **1** is thermally more stable than the Cu(II) complex.

3.3. *Description of the structure*

Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$. The structural unit consists of a binuclear neutral molecule, three coordination waters and two solvation water molecules (figure 1). Two symmetrically related binuclear molecules are linked through coordination between carboxylic oxygens (O6 and O6#1) and Mn to give a tetranuclear neutral loop in the *ac* plane. The tetranuclear neutral loops are further connected by coordination bonds between carboxylate oxygens (O5) and Cu ions to form a new 1-D ladder-like chain structure along the *b* axis (figure 2).

The Cu(II) ions are all distorted square pyramidal with CuN_3O_2. The Cu1 is displaced 0.010 Å from the equatorial plane toward the apical position, occupying an inner site of the trideprotonated ligand with a CuN_3O environment in equatorial plane. The apical position of Cu1 is occupied by one carboxylate oxygen (O5#2) from another tetranuclear unit with a Cu1–O5#2 apical bond length 2.505 Å.

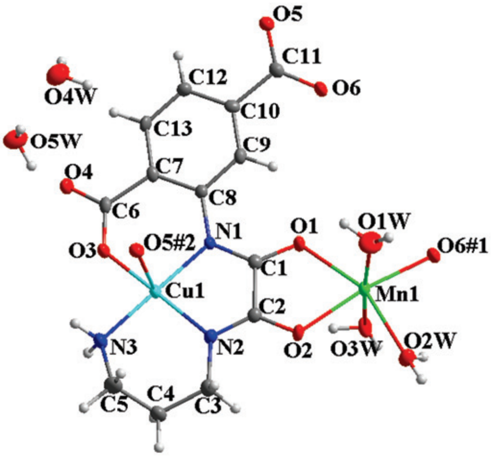

Figure 1. Molecular structure of **1**; the labels of hydrogen atoms are omitted for clarity. Symmetry code: #1: $1-x$, $-y$, $1-z$; #2: $1-x$, $1-y$, $1-z$.

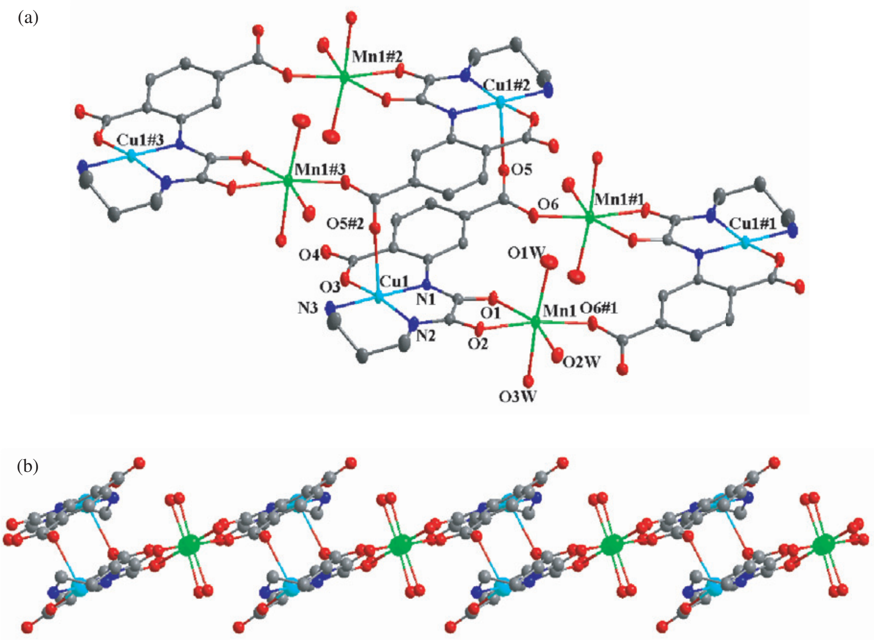

Figure 2. (a) ORTEP view and atom labeling of the segment of 1-D ladder-like chain of **1** (50% thermal ellipsoids). Symmetry transformations used to generate equivalent atoms: #1: $1-x$, $-y$, $1-z$; #2: $1-x$, $1-y$, $1-z$; #3: x, $1+y$, z. (b) 1-D ladder-like chain structure of **1**, the hydrogen atoms and solvent waters are omitted for clarity.

The Mn(II) ions have distorted octahedral environments with four coplanar bonds of nearly equivalent length (Mn1–O6#1, 2.122(3); Mn1–O2W, 2.257(2); Mn1–O1, 2.209(2); Mn1–O2, 2.155(2) Å) and two apical bonds (Mn1–O1W, 2.150(3); Mn1–O3W, 2.172(3) Å).

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

Cu1–O3	1.934(2)	Cu1–N1	1.985(3)
Cu1–N2	1.936(3)	Cu1–N3	1.999(3)
Cu1–O5#2	2.505(3)		
Mn1–O6#1	2.122(3)	Mn1–O1W	2.150(3)
Mn1–O2	2.155(2)	Mn1–O3W	2.172(3)
Mn1–O1	2.209(2)	Mn1–O2W	2.257(2)
O3–Cu1–N2	168.13(12)	O3–Cu1–N1	92.76(11)
N2–Cu1–N1	84.76(12)	O3–Cu1–N3	87.43(11)
N1–Cu1–N3	179.64(13)	N2–Cu1–N3	95.00(13)
O6#1–Mn1-O1W	87.08(11)	O6#1–Mn1–O2	171.67(10)
O1W–Mn1–O2	98.94(11)	O6#1–Mn1–O3W	85.94(10)
O1W–Mn1–O3W	172.64(11)	O2–Mn1–O3W	88.24(10)
O6#1–Mn1–O1	110.81(10)	O1W–Mn1–O1	91.57(11)
O2–Mn1–O1	74.96(10)	O3W–Mn1–O1	88.75(10)
O6#1–Mn1–O2W	90.39(10)	O1W–Mn1–O2W	97.33(10)
O2–Mn1–O2W	83.17(10)	O3W–Mn1–O2W	85.04(10)
O1–Mn1–O2W	157.44(10)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y$, $-z+1$; #2: $1-x$, $1-y$, $1-z$.

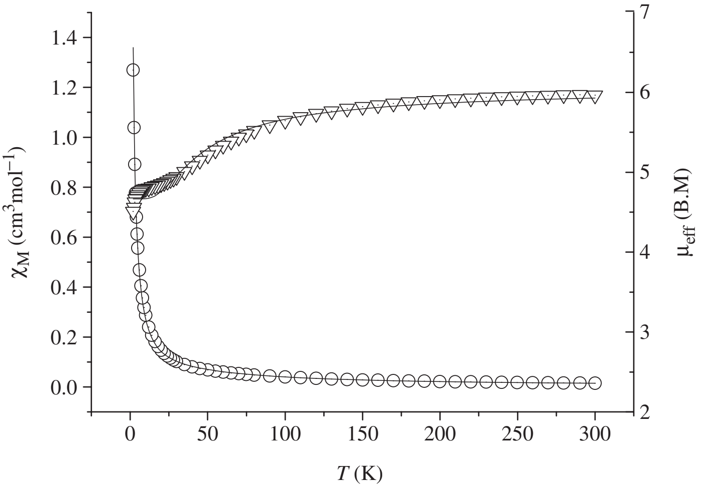

Figure 3. χ_M *vs.* T and μ_{eff} *vs.* T plots for **1**.

The Cu1–Mn1 distances through the the oxamidate bridge are 5.4889(9) Å. The equatorial plane of Cu1 (N1, N2, N3 and O3) and the equatorial plane of Mn1 (O6#1, O2W, O2 and O1) make angles of 179.25° and 175.784° with the bridge plane (O1, O2, N1, N2) and 175.646° with each other (table 2).

3.4. *Magnetic properties*

The magnetic behavior of **1** is investigated in the 2.0–300 K temperature range and indicative of an overall antiferromagnetic coupling, as shown in figure 3. The room temperature value for μ_{eff} is 5.92 B.M. Upon cooling the μ_{eff} values decrease regularly, approaching a minimum around 2.00 K with $\mu_{\text{eff}} = 4.50$ B.M.

There are at least three kinds of magnetic interactions for the present systems, namely: (i) Cu1–Mn1 through a *cis*-oxamidate bridge; (ii) Cu1–Mn1 binuclear units through the 2-aminoterephthalic acid ligand; (iii) Cu1–Mn1#3 and Mn1#1–Cu1#2 through the *syn–anti* carboxylate oxygen bridges, as shown in figure 2(a).

The Cu(II) ions are square-pyramidal with a long apical bond (Cu1–O5#2 = 2.505 Å). The unpaired electron around Cu1 is described by a $d(x^2-y^2)$ magnetic orbital pointing from the metal toward the four nearest neighbor atoms, N1, N2, N3, and O3 in the equatorial plane, which diminish the coupling between dz^2 with the orbital of other ions. The magnetic orbital overlaps the $d(x^2-y^2)$ magnetic orbital centered on Mn(II) through the *cis*-oxamidate bridge and through the *syn–anti* carboxylate oxygen bridge. This interaction (i) in **1** is well-known to favor an exceptionally strong antiferromagnetic interaction [28]. For (iii), it is evident that copper(II) orbitals are mismatched for interaction to take place through this *syn–anti* carboxylate group, since this exchange pathway Cu(II)–O–C–O–Mn(II) involves an axial position on Cu1 [$d(z^2)$] direction [29], which should cause a weak magnetic interaction. The ferromagnetic contribution is weak when the metal ions are bridged by polyatomic extended ligands for (ii) [30].

On the basis of these considerations, we can take the system as an isolated binuclear moiety with (i) Cu1–Mn1 through a *cis*-oxamidate bridge and take (ii) and (iii) into account in the interactions of these binuclear moieties. The magnetic analysis was then carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Mn1}}$. The expression of the magnetic susceptibility for Cu1–Mn1 system is [31]

$$\chi_{\mathrm{M}} = \frac{2N\beta^2}{KT}\left[\frac{14g_3^2 + 5g_2^2\exp(-6J/KT)}{7 + 5\exp(-6J/KT)}\right] + N_\alpha$$

with,

$$g_2 = \frac{(7g_{\mathrm{Mn}} - g_{\mathrm{Cu}})}{6}$$
$$g_3 = \frac{(5g_{\mathrm{Mn}} + g_{\mathrm{Cu}})}{6}$$
$$N_\alpha = 200 \times 10^{-6}\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$$

using molecular field approximation to deal with magnetic exchange interactions between the binuclear systems.

$$\chi'_{\mathrm{M}} = \frac{\chi_{\mathrm{M}}}{1 - (2zj'/Ng^2\beta^2)\chi_{\mathrm{M}}}$$

where J is the exchange integral between Cu1–Mn1 ions in the binuclear moiety, zj' is the magnetic interaction between binuclear systems. $N\alpha$ is the temperature independent paramagnetism.

The best fit to the experimental data gives $J = -8.46\,\mathrm{cm}^{-1}$, $g_{\mathrm{Cu}} = 2.26$, $g_{\mathrm{Mn}} = 1.94$, $zj' = -1.18\,\mathrm{cm}^{-1}$. The agreement factor $\mathrm{R} = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2/\sum\chi^2_{\mathrm{obsd}}$ is 2.02×10^{-3}, which corresponds to a good agreement as shown in figure 3. The negative J and zj' values suggest that interaction between Cu1-Mn1 ions and the interaction between binuclear units are both antiferromagnetic.

4. Conclusion

In this paper, the "bridging ligand complex" $Na_2[Cu(aeop)]\cdot 3H_2O$ plays a very important role during construction of the heterobimetallic coordination polymers. Through self-assembly, a 1-D ladder-like chain coordination polymer bridged by oxamidate and carboxylate groups has been obtained. The magnetism of this complex has also been discussed in connection with its structure. We are in the process of producing a series of heterometallic compounds with this and related ligands.

Supplementary material

CCDC-676084 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

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