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Structures and magnetic properties of two noncentrosymmetric coordination polymers based on carboxyphosphinate ligand

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ABSTRACT

Two novel coordination polymers have been hydrothermally synthesized by reactions of Cu(II), Mn(II) salt with 2-carboxyethyl(phenyl)phosphinic acid (H_2L), namely, $[Cu(L)(H_2O)]_n$ (**1**) and $[Mn(HL)_2]_n$ (**2**). Both compounds were well characterized by single crystal X-ray diffraction, elemental analysis, IR spectroscopic, power X-ray diffraction and magnetic studies. Compound **1** crystallizes in a noncentrosymmetric monoclinic *Cc* space group and presents an inorganic two-dimensional (2D) network, whereas compound **2** adopts a noncentrosymmetric $Pca2_1$ space group and exhibits a 2D layer structure. Magnetic studies reveal a dominant ferromagnetic interaction in **1**, and weak antiferromagnetic coupling between the Mn(II) ions in **2** mediated by phosphinico group, respectively.

1. Introduction

The rational design and synthesis of coordination compounds with previously fixed specific properties such as magnetism [1], catalysis [2], luminescence [3], nonlinear optics [4] and molecular sensing [5], as well as their intringuing structural optics [6] had been studies for decades. The previous studies showed that the structure and properties of MOFs depend on factors such as the metal ions with definite coordination geometry, the nature of organic ligands, the counteranions, the reaction conditions, and so on [7]. For example, copper(II), cobalt(II), nickel(II), and manganese(II) ions with unpaired electrons are often employed for the syntheses of compounds with magnetic properties [8], while lanthanide ions with f-f electronic transitions are often used to prepare compounds with luminescent properties [9]. And we also found that a suitable reaction pH value [10] may be a strong influence on the self-assembly synthesis process [11].

Recently, phosphonate ligands are involved to construct organic–inorganic hybrid materials with beautiful architectures as well as interesting physical properties, such as sorption, catalysis, optical properties and magnetism [12]. Although many fruitful works have been reported on phosphonate compounds, the compounds based on phosphinic acid derived from phosphonic acid have rarely been investigated [13]. Compared with mono-organic-group-attached carboxylate or phosphonate moieties, carboxyphosphinate ligand can allow a better modulation of the structure of the resultant metal compounds [14]. We employed a V-shaped semi-rigid carboxyphosphinate ligand of 2,2'-phosphinico-dibenzoic acid to build coordination polymers with sophisticated framework and interesting properties [15]. 2-Carboxyethyl(phenyl) phosphinic acid (H_2L) is a flexible ligand, which has been utilized to prepare coordination polymers with diverse structures and physical properties by us and other groups [16]. As part of our ongoing interest in the construction of coordination polymers from the carboxyphosphinate ligands, the systems of Cu(II)/Mn(II) and H_2L have been investigated. Here we harvest two novel noncentrosymmetric compounds of copper(II) and manganese(II) with H_2L, namely, $[Cu(L)(H_2O)]_n$ (**1**), $[Mn(HL)_2]_n$ (**2**). Here, we report the syntheses, crystal structures and the magnetic properties of the two compounds in details.

2. Experimental

2.1. Materials and methods

All reagents and solvents used in the present work were of

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analytical grade as obtained from commercial sources without further purification. FT-IR spectra were carried on KBr pellets in the range from 4000 to 400 cm^{-1} on a Nicolet Avatar A370 spectrophotometer. Elemental analyses for C, H were performed on a Vario EL-III elemental analyzer. Powder X-ray diffraction (PXRD) data for **1** and **2** were collected on a DX-2700 diffractometer with (Cu Kα) radiation ($\lambda = 1.5406$ Å) over the 2θ range of 5–30° at room temperature. Variable temperature (2–300K) magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID magnetometer at an applied field of 1000 Oe. The diamagnetic corrections were applied by using Pascal's constants.

2.2. Synthesis of $[Cu(L)(H_2O)]_n$ (1)

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.15 mmol) with H_2L (0.1 mmol) and $Na_2SiO_3 \cdot 9H_2O$ (0.02 mmol) in 8 mL of distilled water was stirred at room temperature for 30 min, and a solution of NaOH (1 mol L^{-1}) was added to adjust pH ~ 6, then sealed in a 15 mL Teflon-lined stainless steel autoclave and heated at 85 °C for 3 days. After cooling to room temperature at a rate of 5 °C°h^{-1}, blue crystals of **1** were obtained in 75% yield based on Cu. Elemental analysis calcd (%) for $C_9H_{11}O_5PCu$ (293.70): C, 36.80; H, 3.77. Found: C, 36.74; H, 3.65%. IR/cm^{-1} (KBr): 3399(m), 3073(w), 2910(w), 1639(w), 1432(s), 1384(m), 1197(w), 1119(s), 1058 (s), 997(w), 925(w), 829(m), 732(s), 701(w), 659(w), 614(w), 528 (m), 507(w).

2.3. Synthesis of $[Mn(HL)_2]_n$ (2)

A mixture of $MnCl_2 \cdot 4H_2O$ (0.2 mmol) with H_2L (0.1 mmol), and 4,4-bipy (0.05 mmol) in 8 mL of distilled water was stirred at room temperature for half an hour. The pH value of the solution was adjusted to 7.00 by addition of 13°μL triethylamine. The solution was sealed in a 15 mL Teflon-lined stainless steel autoclave and heated at 85 °C for 3 days. After cooling to room temperature at a rate of 5 °C°h^{-1}, colorless crystals were isolated by filtration and washed by water in 87% yield based on Mn. Elemental analysis calcd (%) for $C_{18}H_{20}O_8P_2Mn$ (481.22): C, 44.93; H, 4.19. Found: C, 45.01; H, 4.22%. IR/cm^{-1} (KBr): 3416(m), 3075(w), 2948 (w), 2500(m), 1857(m), 1667(s), 1458(m), 1410(m), 1353(s), 1276(s), 1211(w), 1143(s), 1041(s), 957(m), 795(m), 691(m), 534(s), 493(w), 438(w).

2.4. X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature using the *phi* and *omega* scan technique. Data reduction was conducted with the Bruker SAINT package. Absorption correction was performed using the SADABS program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-2000 with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model. Crystallographic data and structural refinement results are summarized in Table 1. Important bond distances for **1** and **2** are listed in Table 2.

Table 1
Crystal data and structure refinement information for **1** and **2**.

Compounds	1	2
Formula	$C_9H_{11}O_5PCu$	$C_{18}H_{20}O_8P_2Mn$
Formula weight	293.70	481.22
Crystal system	Monoclinic	Orthorhombic
Space group	*Cc*	$Pca2_1$
a (Å)	4.9470(9)	15.531(4)
b (Å)	27.508(5)	5.4879(13)
c (Å)	8.0697(14)	22.947(5)
α (°)	90.00	90.00
β (°)	104.504(2)	90.00
γ (°)	90.00	90.00
V ($Å^3$)	1063.1(3)	1955.9(8)
Z	4	4
Dc (g cm^{-3})	1.829	1.634
μ (mm^{-1})	2.206	0.883
F (000)	592	988
GOF on F^2	1.008	1.037
R_1[a],wR_2[b][I > 2σ(I)]	0.0309, 0.0604	0.0234, 0.0584
R_1[a],wR_2[b] (all data)	0.0342, 0.0622	0.0253, 0.0595

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(|F_o^2|-|F_c^2|)^2/\sum w(|F_o^2|)^2]^{1/2}$.

Table 2
Selected bond distances (Å) for compounds **1** and **2**.

1			
Cu1–O1A	1.938(3)	Cu1–O2	2.244(3)
Cu1–O3	2.003(3)	Cu1–O4B	1.928(3)
Cu1–O5	1.992(3)	P1–O3	1.517(3)
P1–O4	1.505(3)		
2			
Mn1–O5C	2.289(3)	Mn1–O3B	2.076(3)
Mn1–O7	2.204(3)	Mn1–O4	2.241(3)
Mn1–O1A	2.242(3)	Mn1–O8D	2.078(3)
P1–O3	1.492(3)	P1–O4	1.522(3)
P2–O7	1.511(3)	P2–O8	1.502(3)

Symmetry codes for **1**: A: x–1/2, –y+1/2, z–1/2; B: x–1, y, z.
Symmetry codes for **2**: A: x+1/2, –y+2, z; B: x, y–1, z; C: x–1/2, –y+1, z; D: x, y+1, z.

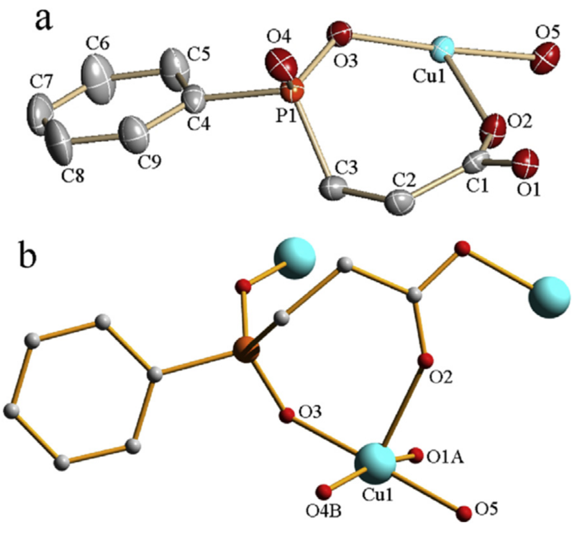

Fig. 1. (a) Molecular structure of **1** with 50% probability displacement ellipsoids. (b) coordination mode of L^{2-} ligand. Hydrogen atoms are omitted for clarity. Symmetry codes: A: x – 1/2, –y + 1/2, z – 1/2; B: x – 1, y, z.

3. Results and discussion

3.1. Structure description for 1

The single crystal X-ray analysis reveals that compound **1** crystallizes in the noncentrosymmetric space group *Cc* and is extended a 2D network, in which the ligand H_2L is deprotonated completely. As shown in Fig. 1a, the asymmetric unit contains one Cu^{2+} ion, one L^- anion and one coordinated water molecule. The coordination geometry around Cu1 ion has a distorted square pyramidal geometry which is surrounded by two phosphinico oxygen, two carboxylate oxygen atoms from two L^- ligands as well as one