

## Syntheses and Structures of Two New Oxalate-bridged Transition-metal Supramolecular Polymers of $[M(2-NH_2py)_2(ox)]^*$

ZHANG Xiao, YI Zhi-hui, XUE Ming, XU Yan, YU Jie-hui, YU Xiao-yang and XU Ji-qing\*  
College of Chemistry, State Key Laboratory of Inorganic Synthesis and Preparative Chemistry,  
Jilin University, Changchun 130021, P. R. China

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Two new supramolecular polymers  $[M(2-NH_2py)_2(ox)]$  [ $M = Co$  (1),  $Ni$  (2); 2-NH<sub>2</sub>py = 2-aminopyridine; ox = oxalate] were hydrothermally synthesized and characterized by elemental analyses, IR and single-crystal X-ray diffraction analyses. The isomorphous compounds 1 and 2 both possess one-dimensional zigzag chain structures, which are composed of  $[M(2-NH_2py)_2]^{2+}$  units bridged by tetradentate oxalate ligands to form three-dimensional supramolecular network *via* the C—H···O hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. Compound 1 displays antiferromagnetic interaction.

**Keywords** Crystal structure; Oxalate ligand; Coordination polymer; Supramolecular interaction

### Introduction

Metal polycarboxylate frameworks are currently of great interest not only because of their wide variety of structural topologies but also because of their potential applications in several areas such as magnetism, non-linear optics, biological activity, electrical conductivity, and host-guest chemistry<sup>[1,2]</sup>. The coordination of oxalate with transition metal ions has been widely researched owing to its remarkable ability to mediate strong magnetic interactions between the metal centers<sup>[3–6]</sup>. Furthermore, the oxalate exhibits multiple type of coordination modes with transition metal centers and can provide abundant structural motifs<sup>[7–15]</sup>. Thus, oxalate is regarded as an excellent candidate of bridging ligands to build different kinds of coordination polymers including 1D, 2D and 3D network structures<sup>[6,7,11,12,15,16]</sup>. Up to now, the 1D chain system possessing zigzag structures with capping ligands composed of organic amines is the most often encountered, such as  $[(ox)M(DPA)]$  ( $M = Fe$ ,  $Ni$ <sup>[17]</sup>,  $Co$ <sup>[18]</sup>; DPA = 2, 2-dipyridylamine),  $[Zn(py)_2(ox)]$ <sup>[19]</sup>,  $[Zn(py)(ox)] \cdot H_2O$ <sup>[20]</sup>,  $[M_2(bpy)_2(ox)_2] \cdot 2H_2O$  ( $M = Cu$ <sup>[21]</sup>,  $Cd$ <sup>[22]</sup>; bpy = 2, 2'-bipyridine),  $[Fe(bzta)_2(ox)]$  (bzta = benzotriazole)<sup>[23]</sup>,  $[Cu(pyOH)_2(ox)]$  (pyOH = 3-hydroxypyridine)<sup>[24]</sup>,  $[Fe_2(im)_4(ox)_2]$  (im = imidazole)<sup>[25]</sup>,  $[Co_2 \cdot (im)_4(ox)_2]$ ,  $[Co(im)_2(ox)]$ ,  $[Mn(2,2'-bpy) \cdot (ox)]$ <sup>[26]</sup>, and  $[Cu(tmen)(ox)] \cdot 4H_2O$  (tmen = *N,N,N',N'*-tetramethyl ethylenediamin)<sup>[27]</sup>. The introduction of ancillary ligands with monodentate or biden-

tate N-donor is important in the syntheses of supramolecular compounds and may provide potential supramolecular recognition sites for hydrogen bond and  $\pi$ - $\pi$  aromatic stacking interaction to form interesting structures.

This article reports the syntheses and characterizations of two new supramolecular complexes based on oxalate as the bridging ligand forming an infinite 1D zigzag covalence chain decorated with the 2-NH<sub>2</sub>py ligands. Compound 1 displays antiferromagnetic interaction.

### Experimental

#### 1 Materials and General Methods

All chemicals were obtained commercially and were used without further purification.

Infrared spectra were recorded with KBr pellets on a Perkin-Elmer Spectrum One FTIR spectrometer in the 4000–400  $cm^{-1}$  region.

Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 element analyzer. Inductively coupled plasma (ICP) analyses for Co and Ni were conducted on a Perkin-Elmer Optima 3300 DV spectrometer.

Variable temperature magnetic susceptibility measurement was performed on a Quantum Design MPMS XL-5 SQUID magnetometer.

#### 2 Synthesis

##### 2.1 Synthesis of $[Co(2-NH_2py)_2(ox)]$ (1)

A mixture of  $CoCl_2 \cdot 6H_2O$  (0.25 g, 1.1 mmol),  $C_2H_2O_4 \cdot 2H_2O$  (0.2 g, 1.5 mmol), 2-NH<sub>2</sub>py (0.4 g,

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\*\* To whom correspondence should be addressed. E-mail: xjq@mail.jlu.edu.cn

4 mmol), and distilled water (12 mL) in a molar ratio of 2:3:8:1300 was continuously stirred for 1 h in air at room temperature, and the pH of the mixture was adjusted to 5.5 with an aqueous solution of sodium hydroxide. The resulting solution was sealed in a 20 mL Teflon-lined stainless steel reactor and heated at 170 °C for 3 d. After cooling to room temperature, the red block crystals were isolated, washed with distilled water, and dried at ambient temperature. Yield: 0.10 g (56% based on Co). IR (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3481 (m) and 3358 (m) for  $\nu(\text{N—H})$ , 3211 (w) for  $\nu(\text{C—H})$ , 1685 (s) and 1630 (s) for  $\nu(\text{CO}_2)$ , 1599 (s) and 1565 (m) for  $\nu_{\text{as}}(\text{C}=\text{C})$  and  $\nu_{\text{as}}(\text{C}=\text{N})$ , 1495 (s) and 1449 (s) for  $\nu(\text{C—N})$ , 1355 (w) and 1315 (w) for  $\nu_s(\text{CO}_2)$ , 1260 (w) and 1166 (w) for  $\delta(\text{C—H})$ , 1059 (w) and 1006 (w) for  $\nu_s(\text{CO})$ , 853 (w), 797 (w) and 768 (m) for  $\delta(\text{CO}_2)$ . Elemental anal. (%) calcd. for  $\text{C}_6\text{H}_6\text{Co}_0.5\text{N}_2\text{O}_2$ : C 43.00, H 3.61, N 16.72, Co 17.58; found: C 42.97, H 3.59, N 16.71, Co 17.61.

## 2.2 Synthesis of $[\text{Ni}(\text{2-NH}_2\text{py})_2(\text{ox})](2)$

Compound **2** was prepared under conditions similar to that of synthesizing compound **1** except with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.25 g, 1.1 mmol) instead of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . The green block crystals were isolated. Yield: 0.08 g (43% based on Ni). IR (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 3485 (m) and 3357 (m) for  $\nu(\text{N—H})$ , 3217 (w) for  $\nu(\text{C—H})$ , 1687 (s) and 1630 (s) for  $\nu(\text{CO}_2)$ , 1597 (s) and 1566 (m) for  $\nu_{\text{as}}(\text{C}=\text{C})$  and  $\nu_{\text{as}}(\text{C}=\text{N})$ , 1496 (s) and 1450 (s) for  $\nu(\text{C—N})$ , 1355 (w) and 1315 (w) for  $\nu_s(\text{CO}_2)$ , 1259 (w) and 1166 (w) for  $\delta(\text{C—H})$ , 1060 (w) and 1007 (w) for  $\nu_s(\text{CO})$ , 853 (w), 800 (w), 767 (m) and 738 (w) for  $\delta(\text{CO}_2)$ . Elemental anal. (%) calcd. for  $\text{C}_6\text{H}_6\text{Ni}_0.5\text{N}_2\text{O}_2$ : C 43.03, H 3.61, N 16.73, Ni 17.52; found: C 43.05, H 3.59, N 16.75, Ni 17.50.

## 2.3 X-ray Single-crystal Structure Determination

Single crystals of compounds **1** and **2** were determined on a SIEMENS SMART CCD diffractometer using the  $\omega$  scan technique at room temperature under graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.071073$  nm) radiation. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares via SHELXTL 97<sup>[28,29]</sup>. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from difference Fourier maps and refined with isotropic temperature factors.

The crystallographic and refinement details of compounds **1** and **2** are listed in Table 1, the selected bond lengths and bond angles are listed in Table 2.

**Table 1** Crystal data and structure refinement parameters of compounds **1** and **2**

Empirical formula	$\text{C}_6\text{H}_6\text{Co}_0.5\text{N}_2\text{O}_2$ (1)	$\text{C}_6\text{H}_6\text{Ni}_0.5\text{N}_2\text{O}_2$ (2)
Formula weight	167.59	167.48
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
$a/\text{nm}$	1.3878(4)	1.38477(14)
$b/\text{nm}$	1.1029(3)	1.10873(11)
$c/\text{nm}$	0.8761(2)	0.86401(8)
$\beta/(\circ)$	94.037(4)	93.721(2)
$V/\text{nm}^3$	1.3377(6)	1.3237(2)
$Z$	8	8
$D_c/(\text{g} \cdot \text{cm}^{-3})$	1.664	1.681
$F(000)$	684	688
$\theta$ Range	2.36°—26.49°	2.36°—28.16°
$h/k/l$	−12, 17/−13, 13/−10, 10	−8, 10/−13, 14/ −11, 10
Number of reflections collected	3475	4108
Unique data [ $I > 2\sigma(I)$ ]	1355	1513
Goodness of fit on $F$	1.029	1.001
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0280, 0.0741	0.0388, 0.0886
$R_1, wR_2$ (all data)	0.0303, 0.0794	0.0472, 0.0917
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}/e \cdot \text{nm}^{-3}$	325, −336	582, −345

**Table 2** Selected bond lengths (nm) and bond angles ( $\circ$ ) of compounds **1** and **2**\*

Compound 1		Compound 2	
Co1—O2	0.21056(14)	Ni1—O2	0.20823(16)
Co1—O1	0.21295(14)	Ni1—O1	0.20894(16)
Co1—N1	0.21480(17)	Ni1—N1a	0.21180(2)
O2a—Co1—O2	160.00(8)	O2a—Ni1—O2	162.83(9)
O2a—Co1—O1	86.96(6)	O2a—Ni1—O1	87.53(6)
O2—Co1—O1	78.42(5)	O2—Ni1—O1	79.91(6)
O1—Co1—O1a	86.12(8)	O1—Ni1—O1a	86.06(9)
O2a—Co1—N1	100.39(6)	O2a—Ni1—N1a	92.19(7)
O2—Co1—N1	93.09(6)	O2—Ni1—N1a	99.56(7)
O1—Co1—N1	89.36(6)	O1—Ni1—N1a	176.16(7)
O1a—Co1—N1	175.38(6)	O1a—Ni1—N1a	90.12(7)
O1—Co1—N1a	175.38(6)	O1—Ni1—N1	90.12(7)
N1—Co1—N1a	95.17(9)	N1a—Ni1—N1	93.71(11)

\* Symmetry code: (a)  $-x+2, y, -z+3/2$ .

## Results and Discussion

### 1 Description of the Structures

The structure determination shows that compounds **1** and **2** are isomorphous and both crystallize in the monoclinic system with space group  $C2/c$ . The asymmetric units of compounds **1** and **2** are both composed of eleven independent non-hydrogenic atoms (Fig. 1), which include one metal center M (M = Co for compound **1** and Ni for compound **2**), which is located on special position (0, 0.150789, 0.75 for Co in compound **1** and 0.5, 0.147493, 0.25 for Ni in compound **2**) with the site occupancy factor being 0.5, one 2-NH<sub>2</sub>py molecule, and half an oxalate ligand. Each transition metal center M<sup>2+</sup> is covalently bonded to two

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