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Structure characterization of several oxalate-bridged transition-metal coordination polymers

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Abstract

Four oxalate-bridged transition-metal supramolecular compounds $[Co_2(im)_4(ox)_2]$ 1, $[Co(im)_2(ox)]$ 2, [Mn(2,2'-bpy)(ox)] 3 and $[Fe(H_2O)_2(ox)]$ 4 (im, imidazole; ox, oxalate; bpy, bipyridine) were obtained from the simple hydrothermal reactions of $M^{n+}-ox-L$ (M, transition metal; L, aromatic N-donor ligand) system. They all exhibit the 1-D chain structures, consisting of the ML_2^{2+} (or ML^{2+}) units linked by oxalate bridges. Interestingly, the 1-D oxalate chains in the title compounds are further self-assembled into the 3-D supramolecular networks through the interchain various secondary bonding interactions. Because the ML²⁺ units adopt the different configuration, the oxalate chains show either zigzag type as in compounds 1-3 or linear type as in compound 4. Compounds 1 and 2 are isomeric, and only in packing modes of interchain im molecules there exists the difference.

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Keywords: Oxalate; Aromatic N-donor ligand; Molecular structure; Hydrothermal synthesis

1. Introduction

In the past several years, a prevalent synthetic strategy of constructing supramolecular compounds with special topological structures is to select a mixed ligand of organic acid and organic base as the precursors due to potential variety of the role played by either or both of the mixed ligands. The material roles include (1) the pH level of synthetic system, one of the important synthetic factors, can be effectively adjusted by any of them; (2) the protonated organic acid or organic base can service as the guests to template the construction of host frameworks [1]; (3) the O or N atoms from organic acid or organic base can act as the hydrogen-bonded donor or acceptor, extending the molecular units into high-dimension networks [2]; (4) some new organic templates may be obtained via the in situ reactions between organic acids or organic bases [3]. Recently,

a series of reactions of M^{n+} -ox-L (L, aromatic N-donor ligand and aromatic amine) system were investigated by our group under the hydrothermal conditions. Some interesting results are listed in Table 1 including mononuclear $[Zn(H_2O)_4(na)_2]$ (na, nicotinate) [4], [Cd(2,2'-bbim)- SO_4]·H₂O (bbim. bibenzoimidazole) [5]. 1-D $[Fe_2(im)_4(ox)_2]$ [6], $[Fe(bta)_2(ox)]$ (bta, benzotriazole) [7] and 2-D [Zn(bta)₂], [Zn(im)(ox)] as well as 3-D [Cd₂(ox)(OH)₂] [4]. Herein, we report the structure characterization of the other four coordination polymers [Co₂(i $m_{4}(ox)_{2}$] 1, [Co(im)₂(ox)] 2, [Mn(2,2'-bpy)(ox)] 3 and $[Fe(H_2O)_2(ox)]$ 4.

2. Experimental

2.1. Preparations

The syntheses were carried out in 30 ml Teflon-lined stainless steel vessels under auto-genous pressure. The single crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature.

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Table 1 Compounds from M^{n+} -ox-L-H₂O system

Entry	M^{n+} —ox—L— H_2O system	Product			Reference
1	$CdCl_2 \cdot 2.5H_2O$ —ox—im— H_2O	$[Cd_2(ox)(OH)_2]$	3D	Colorless	Ref. [4]
2	$3CdSO_4 \cdot 8H_2O - ox - pda - H_2O$	$[Cd(2,2'-bbim)_2SO_4] \cdot H_2O$	0D	Colorless	Ref. [5]
3	$Zn(OAc)_2 \cdot 2H_2O$ —ox—im— H_2O	[Zn(im)(ox)]	2D	Colorless	Ref. [4]
4	$Zn(OAc)_2 \cdot 2H_2O$ —ox—bta— H_2O	$[Zn(bta)_2]$	2D	Colorless	Ref. [4]
5	$Zn(OAc)_2 \cdot 2H_2O$ —ox—na— H_2O	$[Zn(H_2O)_4(na)_2]$	0D	Colorless	Ref. [4]
6	K_3 [Fe(ox) ₃]—im—H ₂ O	$[Fe_2(im)_4(ox)_2]$	1D	Red	Ref. [6]
7	K_3 [Fe(ox) ₃]-bta-H ₂ O	$[Fe(bta)_2(ox)]$	1D	Orange	Ref. [7]
8	$K_3[Fe(ox)_3]$ —na— H_2O	$[Fe(H_2O)_2(ox)]$ 4	1D	Yellow	This work
9	$K_3[Co(ox)_3]$ —im— H_2O	$[Co_2(im)_4(ox)_2]$ 1	1D	Purple	This work
10	$Co(ox) \cdot 2H_2O$ -bdc-im- H_2O	$[Co(im)_2(ox)]$ 2	1D	Purple	This work
11	$CrCl_3 \cdot 6H_2O - MnCl_2 \cdot 4H_2O - ox - bpy - H_2O$	[Mn(2,2'-bpy)(ox)] 3	1D	Yellow	This work

pda, o-phenylenediamine; bdc, 1,4-benzenedicarboxylic acid.

[$Co_2(im)_4$ ($ox)_2$] 1. The purple needle crystals of **1** were obtained from a simple hydrothermal reaction of K₃[Co(ox)₃] (440 mg, 1.0 mmol), im (140 mg, 2.0 mmol), and H₂O (20 ml) in a molar ratio of 1:2:1100 at 160 °C for 3 days with a yield of ca. 50% based on Co. IR (KBr, cm⁻¹) v: 1677 (s), 1610 (s), 1540 (m), 1442 (w), 1360 (m), 1318 (m), 1142 (w), 1095 (w), 1069 (s), 830 (m), 946 (w), 797 (s), 752 (m), 662 (s), 619 (m). Anal. Calcd. for Co₂C₁₆H₁₆N₈O₈: C, 33.94; H, 2.85; N, 19.79%. Found: C, 33.90; H, 2.83; N, 20.00%.

[$Co(im)_2(ox)$] 2. The isomeric compound **2** with **1** was got from another simple hydrothermal reaction. A typical reaction mixture of Co(ox) \cdot 2H₂O (180 mg, 1.0 mmol), bdc (250 mg, 1.5 mmol), im (100 mg, 1.5 mmol), KOH(180 mg, 3.0 mmol), H₂O (20 ml) in a molar ratio of 1:1.5:1.5:3:1100 was fully stirred until homogeneous, then heated at 160 °C for 5 days to give purple needle crystals of **2**. Yield: ca. 57% based on Co. IR (KBr, cm⁻¹) v: 1677 (s), 1612 (s), 1540 (m), 1442 (m), 1359 (m), 1318 (m), 1260 (m), 1142 (m), 1094 (m), 1068 (s), 945 (m), 830 (m), 797 (s), 751 (s), 662 (s) 619 (s). Anal. Calcd. for $Co_{0.5}C_4H_4N_2O_2$: C, 33.94; H, 2.85; N, 19.79%. Found: C, 34.07; H, 2.66; N, 20.01%.

[Mn(2,2'-bpy)(ox)] 3. The yellow block crystals of **3** were produced from a simple hydrothermal reaction of CrCl₃ · 6H₂O (530 mg, 2.0 mmol), MnCl₂ · 4H₂O (400 mg, 2.0 mmol), H₂(ox) · 2H₂O (250 mg, 2.0 mmol), bpy (320 mg, 2.0 mmol), NaOH (160 mg, 4.0 mmol) and H₂O (20 ml) in a molar ratio of 1:1:1:1:2:740 at 160 °C for 3 days with a yield ca. 15% based on Mn. IR (KBr, cm⁻¹) *v*: 1673 (s), 1612 (s), 1473 (w), 1443 (m), 1311 (m), 1164 (w), 1017 (m), 795 (m), 769 (m), 738 (w) 649 (w). Anal. Calcd. for MnC₁₂H₈N₂O₄: C, 48.18; H, 2.70; N, 9.37%. Found: C, 47.99; H, 2.45; N, 9.31%.

 $[Fe(H_2O)_2(ox)]$ 4. The yellow columnar crystals of 4 were grown from identical hydrothermal reaction as for 1 except that Hna (250 mg, 2.0 mmol) replaced im. Yield: ca. 50% based on Fe. IR (KBr, cm⁻¹) v: 3434 (b), 1714 (s), 1682 (s), 1644 (s), 1392 (s), 1274 (m), 891 (w), 805 (m), 532 (w). Anal. Calcd. for

Table 2

Crystal data and structure refinement for the title compounds

	1	2	3	4
Empirical formula	Co ₂ C ₁₆ H ₁₆ N ₈ O ₈	$Co_{0.5}C_4H_4N_2O_2$	MnC ₁₂ H ₈ N ₂ O ₄	Fe _{0.5} CH ₂ O ₃
Formula weight	566.23	141.56	299.14	89.95
Crystal	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/c	P na 2_1	<i>C</i> 2/c
a (Å)	8.463 (2)	13.372 (2)	9.674 (2)	12.016 (2)
b (Å)	11.494 (2)	10.296 (2)	9.2890 (2)	5.558 (1)
c (Å)	13.020 (3)	9.080 (3)	13.921 (3)	9.705 (2)
α (°)	81.92 (3)			
β (°)	72.55 (3)	97.67 (2)		126.93 (3)
γ (°)	83.16(3)			
$V(Å^3)$	1192.2 (4)	1239.0 (5)	1250.9 (4)	518.1 (2)
Z	2	8	4	8
$\mu ({\rm mm}^{-1})$	1.577	1.518	1.588	2.307
$D (g \cdot cm^{-3})$	1.448	1.393	1.066	2.865
Reflections collected	8289	1439	11490	1060
Unique reflections	5314	1083	2827	575
R _{int}	0.0740	0.0220	0.0377	0.0675
S	0.808	1.093	1.058	1.128
Final R_1 , $wR_2 [I \ge 2\sigma (I)]$	0.0498, 0.0715	0.0427, 0.1170	0.0307, 0.0661	0.0328, 0.0828
(All data)	0.1639, 0.0926	0.0488, 0.1203	0.0412, 0.0712	0.0400, 0.0852

 $Fe_{0.5}CH_2O_3:$ C, 13.35; H, 2.24%. Found: C, 13.22; H, 2.13%.

2.2. Physical measurement

C, H and N analyses were performed with a Perkin-Elmer 2400LS II elemental analyzer. Infrared spectra were recorded with Perkin-Elmer Spectrum *I* spectrophotometer in the 4000–400 cm⁻¹ region using a powdered sample on a KBr plate.

2.3. X-ray structure determination

Data were collected with Mo K α radiation ($\lambda = 0.71073$ Å) on a Siemens P4 diffractometer for **2** and **4** and on a Rigaku R-AXIS RAPID IP diffractometer for **1** and **3**. The structures were solved using weight-atom methods except **4** using direct methods with SHELXTL program, and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement and the hydrogen atoms of aromatic rings were treated using a riding model. The structure was then refined on F^2 with SHEL-XL-97. The structure of **3** can be obtained in a centered space group *P* nma, but both ox and bpy encounter serious

disorder. Basic information pertaining to the crystal parameters and structure refinement of the title compounds is summarized in Table 2. CCDC numbers for compounds 1–4 are 296310–296313.

3. Results and discussion

From Table 1, some viewpoints can be realized: (i) transition metal salts in reaction with ox tend to form the chain compounds with the common formulas of $[M(L')_2(ox)]$ or [M(L'')(ox)] (L', monodentate ligand, L'', bidentate ligand) as displayed by Entries 6-11 and correlative literatures [6– 8], whereas Zn and Cd may be self-assembled into the novel frameworks according to Entries 1–5 and correlative literatures [9]; (ii) according to Entry 2 the in situ reaction between ox and bda can give a novel aromatic N-donor ligand bbim, which can be used to assemble new compounds; (iii) although sometimes ox or L did not appear in the resulting framework, at least they adjusted the pH level of synthetic system. For instance, im in Entry 1 provided the OH source.

With aromatic monodentate N-donor ligands (L') as the ancillary ligands, the ML_2^{2+} units generally adopt *cis*-configuration, held together by tetradentate oxalate ligands into an infinite zigzag chain. The reported compounds



Fig. 1. 2-D supramolecular sheets of $[Co_2(im)_4(ox)_2] \mathbf{1}$ (a) and $[Co(im)_2(ox)] \mathbf{2}$ (b).

 $[Zn(py)_2(ox)]$ (py, pyridine) [8b], $[Zn(py)_2(ox) \cdot H_2O]$ [8a], $[Cu(3-OHpy)_2(ox)]$ [8g] and $[Fe_2(im)_4(ox)_2]$ [6] are the typical examples. Im can act as bridging ligand in nature, but in compounds $[Co_2(im)_4(ox)_2] \mathbf{1}$ and $[Co(im)_2(ox)] \mathbf{2}$, it bonds to the metal center only via the monodentate mode. As shown in Fig. 1, compounds 1 and 2 are isomorphous with each other. The unique structural difference is the packing mode amongst interchain im molecules. In 2 im molecules just adopt the offset face-to-face packing, whereas in 1 there exists another edge-to-face packing with a dihedral angle of 76.8 °C besides the face-to-face packing. Interestingly, in two compounds the protonated N atoms of cis-Co(im)₂²⁺ units hydrogen bond to the O atoms of adjacent oxalate chains, extending the 1-D oxalate chains along two directions into 3-D supramolecular networks (1: $N6 \cdots O7 = 2.792 \text{ Å} N6 - H \cdots O7 = 159^{\circ}$ $N2 \cdots O5 = 2.780 \text{ Å}$ $N2 - H \cdots O5 = 164^{\circ}$, $N8 \cdots O2 =$ 2.760 Å N8–H···O2 = 164°, N4···O3 = 2.792 Å N4–H $\cdots O3 = 166^{\circ}$; **2**: N2 $\cdots O1 = 2.770$ Å N2-H $\cdots O1 =$ 169°).

With aromatic chelate ligands (L'') as the auxiliary ligands, the oxalate chains still take on the zigzag type.

In general, in these compounds as the reported $[M_2(2,2'$ $bpy_{2}(ox)_{2} \cdot 2H_{2}O(M, Cu [8f], Cd [8c]), [M(2,2'-dpa)(ox)]$ (M. Fe, Ni [8d], Co [8e]; dpa, dipyridylamine), various C(or N)-H···O hydrogen-bonded interactions together with the π - π packing interactions amongst L' molecules play a rather important role in propagating the 1-D oxalate chains into 2-D or 3-D supramolecular networks. Compound [Mn(2,2'-bpy)(ox)] 3 is another example of this family. Fig. 2 shows the interchain supramolecular interactions. In [001] direction, the bipyridine rings array parallel to each other characterized by a distance of 3.9 Å along the *a* axis, meanwhile, C8 of pyridine molecule forms the hydrogen bond with O1 of oxalate of neighboring chain $(C8 \cdots O1 = 3.159 \text{ Å } C8 - H \cdots O1 = 122.5^{\circ})$. Through these weak interactions, the 1-D oxalate chains are self-assembled into a 2-D supramolecular layer [see Fig. 2(a)]. In [100] direction, via the C2-H···O4 hydrogen bonds, the 2-D supramolecular layers are interconnected finally into a 3-D supramolecular network along the c axis $(C2 \cdot \cdot \cdot O4 = 3.319 \text{ Å } C2 - H \cdot \cdot \cdot O4 = 154.5^{\circ})$ [see Fig. 2(b)].

Once the N-donor ligands are the bridging ones, the ML_2^{2+} units will adopt the *trans*-configuration, and the



Fig. 2. Supramolecular interactions in [Mn(2,2'-bpy)(ox)] 3.



Fig. 3. Hydrogen-bonded network in $[Fe(H_2O)_2(ox)]$ 4.

oxalate chains will show the linear type, extended further by the N-donor bridging ligands into a 2-D planar layer with regular macrocycle rings. The typical example is a family with the general formula of [M(4,4'-bpy)(ox)] [10]. H₂O is a special ligand. In the reported compound $[Co(H_2O)_2(ox)] \cdot H_2O$ [11], although H₂O coordinates to the metal center just through the monodentate mode, the $Co(H_2O)_2^{2+}$ unit adopts a *trans*-configuration and the oxalate chain shows the linear type, which can be attributed to the presence of stronger O ··· O hydrogen-bonded interactions. Compound $[Fe(H_2O)_2(ox)]$ 4 is another example that H₂O acts as the ancillary ligand. As shown in Fig. 3, each terminal H₂O (Ow3) molecule hydrogen bonds to two O atoms coming, respectively, from adjacent two oxalate chains, on the other hand, each O (O1 and O2) atom of oxalate molecules hydrogen bonds to the H₂O molecules from adjacent oxalate chains, producing finally a 3-D supramolecular network $(O1 \cdots Ow = 2.767 \text{ Å}, O1 - H)$ $\cdots Ow = 153.73^{\circ}; O2 \cdots Ow = 2.746 \text{ Å}, O2 - H \cdots Ow =$ 158.87°).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc. 2006.03.079.

References

- [1] (a) D.P. Cheng, M.A. Khan, R.P. Houser, Cryst. Growth Des. 2 (2002) 415;
 - (b) P.A. Prasad, S. Neeraj, S. Natarajan, C.N.R. Rao, Chem. Commun. (2000) 1251.
- [2] (a) A.M. Beatty, Coord. Chem. Rev. 246 (2003) 131;
 (b) J. Lu, J.H. Yu, X.Y. Chen, P. Cheng, X. Zhang, J.Q. Xu, Inorg. Chem. 44 (2005) 5978;
 (c) J.H. Yu, J.Q. Xu, L. Ye, H. Ding, W.J. Jing, T.G. Wang, J.N. Xu,
- H.B. Jia, Z.C. Mu, G.D. Yang, Inorg. Chem. Commun. 5 (2002) 572.
 [3] (a) X.X. Hu, J.Q. Xu, P. Cheng, X.Y. Chen, X.B. Cui, J.F. Song, G.D. Yang, T.G. Wang, Inorg. Chem. 43 (2004) 2261;
- (b) Y.P. Tong, S.L. Zheng, X.M. Chen, Eur. J. Inorg. Chem. (2005) 3734.
- [4] J. Lu, K. Zhao, Q.R. Fang, J.Q. Xu, J.H. Yu, X. Zhang, H.Y. Bie, T.G. Wang, Cryst. Growth Des. 5 (2005) 1091.
- [5] J. Lu, J.Q. Xu, J.H. Yu, X. Zhang, Q.F. Yang, X.Y. Yu, 9th Conference on Solid State Chemistry and Inorganic Synthesis, China, 2005 p. 124.
- [6] J.H. Yu, J.Q. Xu, L.J. Zhang, J. Lu, X. Zhang, H.Y. Bie, J. Mol. Struct. 743 (2005) 243.
- [7] H.B. Jia, J.H. Yu, J.Q. Xu, H. Ding, W.J. Jing, Y.J. Liu, Y.Z. Li, Y. Xu, L. Ye, T.G. Wang, J.N. Xu, Z.C. Li, Collect. Czech. Chem. Commun. 67 (2002) 1609.
- [8] (a) S.K. Ghost, G. Savitha, P.K. Bharadwaj, Inorg. Chem. 43 (2004) 5495;
 - (b) O.R. Evens, W.B. Lin, Cryst. Growth Des. 1 (2001) 9;
 - (c) S.Q. Xia, S.M. Hu, J.C. Dai, X.T. Wu, Z.Y. Fu, J.J. Zhang, W.X. Du, Polyhedron 23 (2004) 1003;
 - (d) J.Y. Lu, T.J. Schroeder, A.M. Babb, M. Olmstead, Polyhedron 20 (2001) 2445;
 - (e) J.Y. Lu, A. Babb, Inorg. Chim. Acta 318 (2001) 186;
 - (f) H. Oshio, U. Nagashima, Inorg. Chem. 31 (1992) 3295;
 - (g) O. Castillo, A. Luque, M. Julve, F. Lloret, P. Román, Inorg. Chim. Acta 315 (2001) 9.
- [9] P. Orioli, B. Bruni, M.D. Vaira, L. Messori, F. Piccioli, Inorg. Chem. 41 (2002) 4312.
- [10] J.Y. Lu, M.A. Lawandy, J. Li, T. Yuen, C.L. Lin, Inorg. Chem. 38 (1999) 2695.
- [11] U. García-Couceiro, O. Castillo, A. Luque, G. Beobide, P. Román, Inorg. Chim. Acta 357 (2004) 339.