



## ***In situ* hydrothermal synthesis of Co(III) formate coordination polymer**

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### **ABSTRACT**

One new Co(III) complex  $\{[\text{CoL}_3]_3(\text{CH}_3\text{OH})_3\}_8$  [HL = formate] was prepared by hydrothermal reaction and structurally characterized. Single crystal X-ray diffraction analysis revealed that the Co(III) is six-coordinate by six oxygen atoms of six L ligand. Crystal data: triclinic, space group R-3c,  $a = 8.2379(12) \text{ \AA}$ ,  $b = 8.2379(12) \text{ \AA}$ ,  $c = 22.353(5) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $V = 1313.7(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D = 1.684 \text{ Mg}\cdot\text{m}^{-3}$ .

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### **KEYWORDS**

Hydrothermal synthesis;  
Single crystal;  
Coordination polymer.

### **INTRODUCTION**

Recently, metal-organic frameworks (MOFs) have drawn much attention because of their intriguing variety of architectures and their potential applications<sup>[1-2]</sup>. The versatility of carboxylate anions as units for ligating and connecting metal centres has led to extensive research on the structures and properties of carboxylate complexes. Carboxylate linkers are the most important and widely used bridging ligands for constructing stable MOFs. Particularly, Yaghi and co-workers have reported highly porous IRMOFs built from linear dicarboxylate groups with varied structures<sup>[3]</sup>. Highly porous MOFs have also been built from tricarboxylate linkers, as well as tetracarboxylate linkers<sup>[4-5]</sup>. Recently, Schröder and co-workers have synthesized a series of highly porous MOFs utilizing different sizes of tetra carboxylate linkers (biphenyl-3,3',5,5'-tetracarboxylate, terphenyl-3,3'',5,5'''-tetracarboxylate, and quaterphenyl-3,3''',5,5''''-tetracarboxylate), all of which have shown high hydrogen adsorption capacity<sup>[6]</sup>. The formate anion is the simplest carboxylate, and its Mn(II), Co(II), Fe(II), Zn(II), and Cu(II) complexes and their properties have been reported<sup>[7-10]</sup>. However, to the best of our knowledge, *In situ* hydrothermal synthesis of metal formate coordination polymers is rare<sup>[11]</sup>. Herein, we report the hydrothermal synthesis of a new Co(III) complex *in situ*.

### **EXPERIMENTAL**

#### **1. Preparation of $\{[\text{CoL}_3]_3(\text{CH}_3\text{OH})_3\}_\infty$**

A mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1mmol), 3-Nitro-1,2-benzenedicarboxylic acid (0.5mmol), DMF (4mL),  $\text{CH}_3\text{OH}$  (4mL) and distilled water (4mL) was sealed in a 25mL stainless steel reactor with Teflon liner and directly heated to 140°C for two days, then cooled to room temperature during 12 h. Block single crystals were obtained in 30% yield.

#### **2. Structure determination**

X-ray single-crystal diffraction data for the cobalt complex was collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by  $\omega$  scan mode. The program SAINT<sup>[12]</sup> was used for integration of the diffraction profiles. Semiempirical absorption corrections were applied using SADABS program. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL<sup>[13]</sup>. Metal atoms in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on  $F^2$ . Hydrogen atoms of carbon were included in calculated positions and refined with fixed ther-

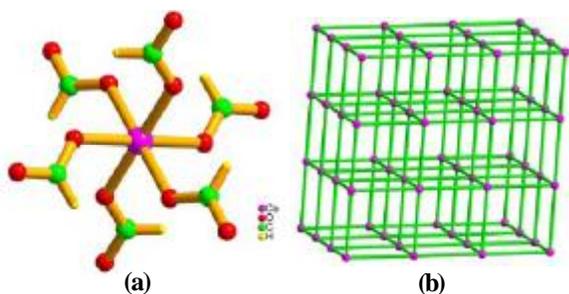
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**TABLE 1: Crystallographic data and structure refinement summary for the complex**

Chemical formula	$C_{12}H_9Co_3O_{21}$	$\gamma / \text{deg}$	120
Formula weight	665.98	$V / \text{\AA}^3$	1313.7(4)
Crystal system	Trigonal	Z	2
space group	R-3c	$D/g \text{ cm}^{-3}$	1.684
a (Å)	8.2379(12)	$\mu/\text{mm}^{-1}$	1.957
b (Å)	8.2379(12))	T / K	293(2)
c (Å)	22.353(5)	$R^a/wR^b$	0.0295/ 0.0986
$\alpha/\text{deg}$	90	Total/unique	3460/268/0.0240
$\beta/\text{deg}$	90	/ $R_{\text{int}}$	-

**TABLE 2: Selected bond distances (Å) and angles (deg) for the complex**

Co(1)-O(1)	2.121(2)	-	-
O(1) <sup>#1</sup> -Co(1)-O(1)	88.54(9)	O(1) <sup>#2</sup> -Co(1)-O(1)	91.46(9)
O(1) <sup>#3</sup> -Co(1)-O(1)	91.46(9)	O(1) <sup>#4</sup> -Co(1)-O(1)	180.00(13)
O(1)-Co(1)-O(1)#5	88.54(9)	-	-



**Figure 1: View of the coordination environment of Co(III) ions in the complex**

mal parameters riding on their parent atoms. Crystallographic data and experimental details for structural analysis are summarized in TABLE 1. Selected bond lengths and angles are listed in TABLES 2.

## RESULTS AND DISCUSSION

The application of the hydrothermal technique to synthetic crystal growth has been used for some time<sup>[14]</sup>. The title compound was obtained as an air-stable pink solid after heated to 140 °C for two days, and Co(II) has a process of oxidation changing to Co(III), while the L come from decomposed of molecular of DMF. The complex crystallizes in the Trigonal symmetry with space group of R-3c. X-ray single-crystal diffraction analysis reveals that it has a structure constructed from two independent  $CoL_3$  units with methanol molecules. As shown in figure 1a, the Co(III) locates in a distorted octahedron geometry, being coordinated with six O donors of six L ligands with the Co–O bond distances being 2.121(2) Å (TABLE 2). Each L Ligand bridges two Co(III) centers and each metal center can be re-

garded as a six-connected nod, the whole molecular forms a neutral three dimensional framework (see figure 1b). In conclusion, a new three dimensional metal-organic framework has been synthesized in situ.

## REFERENCES

- [1] (a) O.M.Yaghi, M.O'Keeffe, N.W.Ockwig, H.K. Chae, M.Eddaoudi, J.Kim; *Nature*, **423**, 705 (2003). (b) S.Kitagawa, R.Kitaura, S.Noro; *Angew.Chem. Int.Ed.*, **43**, 2334 (2004).
- [2] (a) S.J.Lee, A.G.Hu, W.B.Lin; *J.Am.Chem.Soc.*, **124**, 12948 (2002). (b) J.S.Seo, D.Whang, H.Lee, S.I.Jun, J.Oh, Y.J.Jeon, K.Kim; *Nature*, **404**, 982 (2000).
- [3] M.Eddaoudi, J.Kim, N.Rosi, D.Vodak, J.Wachter, M.O'Keefe, O.M.Yaghi; *Science*, **295**, 469 (2002).
- [4] D.Sun, S.Ma, Y.Ke, D.J.Collins, H.Zhou; *J.Am. Chem.Soc.*, **128**, 3896 (2006).
- [5] Y.Liu, J.F.Eubank, A.J.Cairns, J.Eckert, V.C. Kravtsov, R.Luebke, M.Eddaoudi; *Angew.Chem. Int.Ed.*, **46**, 3278 (2007).
- [6] X.Lin, J.Jia, X.Zhao, K.M.Thomas, A.J.Blake, G.S. Walker, N.R.Champness, P.Hubberstey, M. Schroder; *Angew.Chem.Int.Ed.*, **45**, 7358 (2006).
- [7] (a) Z.Wang, B.Zhang, T.Otsuka, K.Inoue, H.Kobayashi, M.Kurmoo; *J.Chem.Soc., Dalton Trans.*, 2209 (2004). (b) Z.Wang, B.Zhang, H.Fujiwara, H.Kobayashi, M.Kurmoo; *Chem.Commun.*, 416 (2004).
- [8] (a) M.Viertelhaus, P.Adler, R.Clerac, C.F.Anson, A.K.Powell; *Eur.J.Inorg.Chem.*, 692 (2005). (b) Y.L.Fu, M.Ji, X.L.Shen, S.W.Ng; *Acta.Cryst.*, **E61**, m688 (2005). (c) Z.Wang, B.Zhang, M.Kurmoo, M.A.Green, H.Fujiwara, T.Otsuka, H.Kobayashi, *Inorg.Chem.*, **44**, 1230 (2005).
- [9] T.Arii, A.Kishi, Y.Kobayashi, *Thermochim.Acta*, **325**, 151 (1999).
- [10] F.Sapina, M.Brugos, E.Escriva, J.Folgado, D. Marcos, A.Beltran, D.Beltran; *Inorg.Chem.*, **32**, 4337 (1993).
- [11] Y.L.Fu, J.L.Ren, Z.W.Xu, S.W.Ng; *Acta.Cryst.*, **E61**, m2395 (2005).
- [12] SAINT Software Reference Manual; Bruker AXS: Madison, WI, (1998).
- [13] G.M.Sheldrick; SHELXTL NT, Version 5.1.Program for Solution and Refinement of Crystal Structures: University of Gottingen, Germany, (1997).
- [14] S.H.Feng, R.R.Xu; *Acc.Chem.Res.*, **34**, 239 (2004).