Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganic Chemistry Communications 7 (2004) 510–512

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

A novel three-dimensional metal-organic interpenetrating framework constructed from mixed adipate and 4,4′-bipy ligands: $[Co(OOC(CH_2)_4COO)(4,4'\text{-bipy})]$ (adipate = $HOOC(CH_2)_4COOH$, 4,4′-bipy = 4,4′-bipyridine) ☆

Na Hao, Enhong Shen, Yangguang Li, Enbo Wang *, Changwen Hu, Lin Xu

Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P.R. China

Received 12 November 2003; accepted 7 February 2004

Abstract

A novel metal-organic hybrid compound $[Co(OOC(CH_2)_4COO)(4,4'\text{-bipy})]$ **1**, has been hydrothermally synthesized and structurally characterized. Compound **1** exhibits a novel three-dimensional interpenetrating network with mixed adipate and 4,4′-bipy ligands constructed by covalent bonds.

Keywords: Hydrothermal synthesis; Interpenetration; Metal-organic; Crystal structure

The investigation of novel metal-organic hybrid compounds have attracted considerable interest and importance in recent years, not only due to their intriguing structural motifs but also their potential applications in catalysis, medicine, host-guest chemistry and the promising photo-, electro- and magnetic materials [1–5]. In the various metal-organic frameworks, the entangled structure, in which two or more infinite networks interpenetrate each other has been widely researched [6]. In general, there are two important factors for the formation of interpenetrating structures: one is that infinite networks contain large pores or cavities for interpenetration; the other is that the individual two-dimensional networks should possess some appropriate elements of corrugation or undulation [7]. In this aspect, organic aromatic polycarboxylate ligands have been widely used in constructing such compounds [8]. However, complexes based on dicarboxylate ligand adipate have rarely reported hitherto, especially in the respect of the interpenetrating frameworks [9]. More recently, adipate has proved to be a good candidate for assembling high dimensional metal-organic architectures owing to its three interesting structural features. In the first place, it contains two bridging moieties, which leads to a variety of connection modes with transitional metal centers and provides abundant structural motifs. Also, it can act not only as hydrogen bond donors but as acceptors. At last, it has six carbon atoms which may construct high dimension and pore structures. On the other hand, so far most of the high dimensional networks are not purely bridged by one ligand. They usually employ two or more ligands in the construction of metal-organic complexes. It is noteworthy that 4,4′-bipyridine is an excellent rigid bridging ligand for the construction of novel metal-organic hybrid compounds due to its various coordinative modes with metal ions [10]. To date, there have been a lot of reports on various dimensional hybrid compounds assembled by 4,4′-bipy ligands [11]. Based on the above opinions, a motivation for design and synthesis of novel metal-organic interpenetrating frameworks containing adipate and 4,4′-bipy ligands under hydrothermal conditions has been

---

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2004.02.006.

* Corresponding author. Tel.: +86-431-5268787; fax: +86-431-5684009.

E-mail address: wangenbo@public.cc.jl.cn (E. Wang).

1387-7003/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2004.02.006

raised. In this communication, we report the hydrothermal synthesis and structural characterization of [Co(OOC(CH_2)$_4$COO)(4,4′-bipy)] **1,** which exhibits a novel three-dimensional interpenetrating network constructed by covalent bonds. To the best of our knowledge, **1** represents the first metal-organic interpenetrated framework composed of mixed adipate and rigid 4,4′-bipy ligands.

Compound **1** was prepared from a mixture of $Co(NO_3)_2 \cdot 2H_2O$, adipate, 4,4′-bipy, and H_2O with the molar ratio of 1:1:0.3:444, stirred for 1 h, sealed in a 15 ml Teflon-lined stainless steel bomb, and kept at 160 °C under autogenous pressure for 4 days [12].

The X-ray diffraction analysis [13,14] reveals that compound **1** exhibits a novel three-dimensional metal-organic interpenetrating framework based on dinuclear cobalt dimer building blocks with mixed adipate and 4,4′-bipy ligands. The fundamental unit is shown in Fig. 1. There is one crystallographically unique Co center in the symmetric unit. The Co(1) center coordinates to two oxygen atoms of one chelating bidentate adipate anion ligand and two oxygen atoms from different bridging bidentate adipate anions ligands, two nitrogen atoms (Co(1)–N(1) 2.169(2) and Co(1)–N(2) 2.160(2) Å) of two different 4,4′-bipy ligands. Four different carboxylate groups with Co(1)–$O_{(carboxyl)}$ distances in the range 2.021(2)–2.195(2) Å. The O–Co(1)–O bond angles vary from 59.59(8) to 151.58(9)°. Therefore, Co center displays a distorted octahedral coordination geometry. The two $\{CoN_2O_4\}$ octahedra are connected together to form a linear binuclear Co dimer via the edge-sharing mode. In addition, four carboxylate groups of the adipate anions ligand exhibit two kinds of coordination modes with Co centers. That is, two carboxylate groups act as a bidentate ligand to bridge two Co centers, while the other two exhibit chelating mode to link with two Co centers. Thus, four adipate ligands are connected with two Co centers by covalent bonds to form two-dimensional grid-like network with large pores parallel to the [0 1 1] direction. The size of the cavities is about 13.148 × 10.888 $Å^2$, as shown in Fig. S3. The most important structural feature of **1** is that two such individual two-dimensional grid-like networks are interconnected by 4,4′-bipy ligands each other to form an interesting three-dimensional twofold interpenetrating framework, illustrated in Fig. 2. To the best of our knowledge, it is the first interpenetrating composite network has hitherto been observed with mixed adipate and 4,4′-bipy ligands. It is noteworthy that both the individual two-dimensional grid-like network and twofold interpenetration of such three-dimensional framework provide the feasibility to the assembly of interpenetrating architectures. The bond valence calculations (Co, 1.90) suggest Co atom is in the +2 oxidation state. The O(1)–O(4) have bond valence sums of 1.70, 1.70, 1.86, and 1.85, respectively, [15]. These results indicate that all the oxygen atoms of adipate groups are deprotonated [16]. These results are consistent with the charge balance considerations of compound **1**.

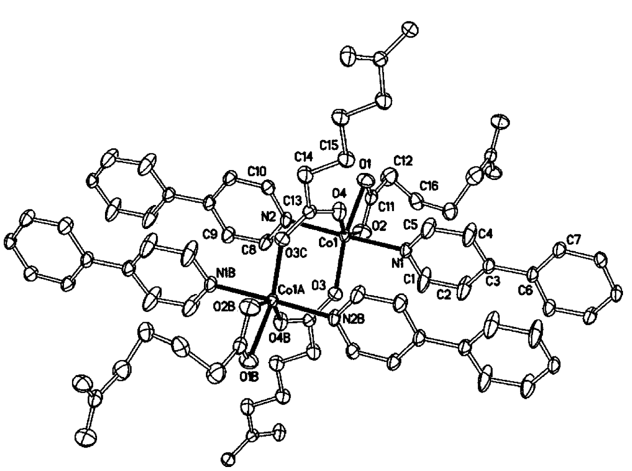

Fig. 1. The ORTEP drawing of **1** showing the local coordination environment of Co(II). Hydrogen atoms are omitted for clarity.

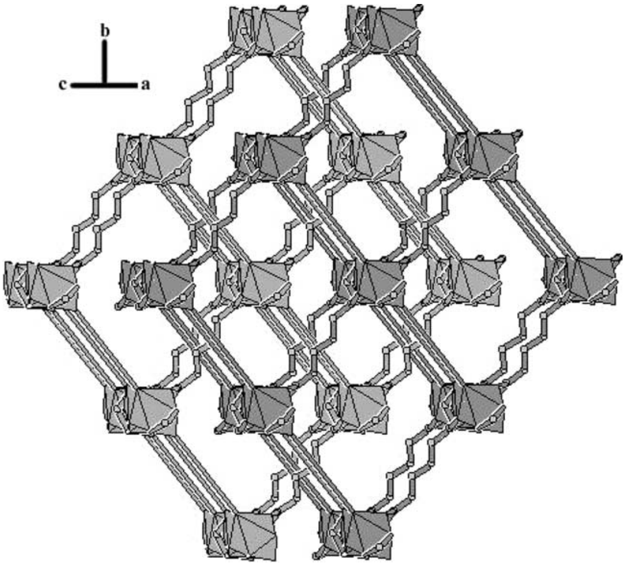

Fig. 2. Polyhedral representation of the three-dimensional metal-organic framework of compound **1**. The light and dark colors represent two interpenetrating layers with different extending directions, respectively.

In this communication, we report a novel metal-organic hybrid compound [Co(OOC(CH_2)$_4$COO)(4,4′-bipy)] **1** which features an interesting interpenetrated framework by covalent bonds.

Supplementary materials

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, the IR spectrum, the TG curve and TG analysis, and packing diagram of individual two-dimensional-like network of compound **1** were available from the authors on request. CCDC reference number: 221497.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (20171010).

References

[1] S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853–908.

[2] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem. Int. Ed. 38 (1999) 2638–2684.

[3] X.M. Zhang, M.L. Tong, X.M. Chen, Angew. Chem. Int. Ed. 41 (2002) 1029–1031.

[4] (a) X.H. Bu, W. Chen, S.L. Lu, R.H. Zhang, D.Z. Liao, W.M. Bu, M. Shionoya, F. Brisse, J. Ribas, Angew. Chem. Int. Ed. 40 (2001) 3201–3203;
(b) S.H. Feng, R.R. Xu, Acc. Chem. Res. J. 34 (2001) 239–247.

[5] (a) M. Yuan, Y.G. Li, E.B. Wang, Y. Lu, C.W. Hu, N.H. Hu, H.Q. Jia, J. Chem. Soc. Dalton Trans. (2002) 2916–2920;
(b) Y. Lu, E.B. Wang, M. Yuan, G.Y. Luan, Y.G. Li, H. Zhang, C.W. Hu, Y.G. Yao, Y.Y. Qin, Y.B. Chen, J. Chem. Soc. Dalton Trans. (2002) 3029–3031;
(c) Z.B. Han, E.B. Wang, G.Y. Luan, Y.G. Li, H. Zhang, Y.B. Duan, C.W. Hu, N.H. Hu, J. Mater. Chem. 12 (2002) 1169–1173.

[6] A web site has been set up by Prof. S.R. Batten containing known examples of interpenetrating nets: http://web.chem.monash.edu.au/Department/Staff/Batten/intptn.htm.

[7] (a) S.R. Batten, R. Robson, Angew. Chem. Int. Ed. 37 (1998) 1460–1494;
(b) Y.G. Li, N. Hao, E.B. Wang, Y. Lu, C.W. Hu, Eur. J. Inorg. Chem. (2003) 2567–2571.

[8] (a) H. Li, M. Eddaoudi, M. O'keeffe, O.M. Yaghi, Nature 402 (1999) 276–279;
(b) H.K. Fun, S.S.S. Raj, R.G. Xiong, J.L. Zuo, Z. Yu, X.Z. You, J. Chem. Soc. Dalton Trans. (1999) 1915–1916;
(c) S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, Science 283 (1999) 1148–1150.

[9] (a) M. Kurmoo, J. Mater. Chem. 9 (1999) 2595–2598;
(b) Y. Kim, D.Y. Jung, Inorg. Chem. 39 (2000) 1470–1475;
(c) E.G. Bakalbassis, M. Korabik, A. Michailides, J. Morzinski, et al., J. Chem. Soc. Dalton Trans. (2001) 850–857;
(d) Y.Z. Kim, E.W. Lee, D.Y. Jung, Chem. Mater. 13 (2001) 2684–2690;
(e) P.S. Mukherjee, S. Konar, E. Zangrando, et al., Inorg. Chem. 42 (2003) 2695–2703.

[10] J.K. Lu, M.A. Lawandy, J. Li, Inorg. Chem. 38 (1999) 2695–2704.

[11] (a) Y.H. Wang, L.Y. Feng, Y.G. Li, C.W. Hu, E.B. Wang, N.H. Hu, H.Q. Jia, Inorg. Chem. 41 (2002) 6351–6357;
(b) R.W. Gable, B.F. Hoskins, R.J. Robson, J. Chem. Soc. Chem. Commun. (1990) 1677–1678;
(c) M. Fujita, Y. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. 116 (1994) 1151–1152;
(d) O.M. Yaghi, H. Li, J. Am. Chem. Soc. 118 (1996) 295–296;
(e) J. Tao, M.L. Tong, X.M. Chen, J. Chem. Soc. Dalton Trans. (2000) 3669–3674.

[12] Elem. anal. found: C: 53.6; H: 3.8; N: 8.1; Co: 16.2. Calcd. for $C_{16}H_{14}CoN_2O_4$: C, 53.8; H, 4.0; N, 7.8; Co, 16.5 (%). Selected FTIR data (cm^{-1}): 3435(m), 2995(s), 1593(s), 1552(s), 1432(s), 1336(m), 1299(m), 1216(m), 1141(m), 1066(s), 922(w), 819(s), 761(w), 733(m), 630(s), 472(w).

[13] Crystal data for **1**: $C_{16}H_{14}CoN_2O_4$, triclinic, space group $P\bar{1}$, $a = 8.5735(17)$ Å, $b = 8.8559(18)$ Å, $c = 10.775(2)$ Å, $\alpha = 109.43(3)°$, $\beta = 95.20(3)°$, $\gamma = 102.70(3)°$, $V = 740.6(3)$ Å^3, $Z = 2$, $D_c = 1.602$ mg/m^3, $\mu = 1.181$ mm^{-1}, $F_{(000)} = 366$, λ(Mo Kα) = 0.71073 Å, $T = 293$ K. 5267 reflections measured ($2.47° < \theta < 27.48°$, $\lambda = 0.71073$ Å), 3336 unique ($R_{int} = 0.0457$). Structure solution and refinement based on 3336 independent reflections with $I > 2\alpha(I)$ and 219 parameters gave $R_1(wR_2) = 0.0433$ (0.1236) and $S = 0.996$.

[14] (a) G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997;
(b) G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.

[15] I.D. Brown, D. Altermatt, Acta. Crystallogr. Sect. B 41 (1985) 244–247.

[16] R.K. Chiang, C.C. Huang, C.S. Wur, Inorg. Chem. 40 (2001) 3237–3239.