Synthesis, Structure and Characterization of a 3D Chiral Indium Carboxylate Metal-organic Framework Based on 1,1 -Biphenol Ligand (Post-print)

Authors: MENG Chun-Long, LI Zi-Jian, LIU Yan, LIU Bai-Zhan, CUI Yong

Date: 2017-11-05T00:00:00+00:00

Abstract

A novel indium-based chiral metal organic-framework 1 {In2L(2-O)(H2O)3}n was synthesized from C2-symmetric 1,1 -biphenol-based ligand H4L and structurally characterized by single-crystal and powder X-ray diffraction, Fourier-transform infrared spectra (FTIR), solid-state circular dichroism (CD) and thermal gravimetric analysis (TGA). 1 crystallizes in monoclinic space group P21 with a = 10.1861(5), b = 18.5632(9), c = 16.5153(8) Å, V = 3077.1(3) Å3, Z = 2, Mr = 944.29 g/mol, Dc = 1.019 g/cm3, F(000) = 944, GOOF = 0.932, the final R = 0.0577 and wR = 0.1091 for 22090 observed reflections with I > 2 (I). Each In2 cluster in 1 is linked by four ligands and each ligand is coordinated to four In2 clusters to generate a 3D network. Additionally, the photoluminescence of 1 and H4L were also investigated.

Full Text

Preamble

Synthesis, Structure and Characterization of a 3D Chiral Indium Carboxylate Metal-organic Framework Based on 1,1 -Biphenol Ligand

MENG Chun-Long, LI Zi-Jian, LIU Yan, LIU Bai-Zhan, CUI Yong

1State Key Laboratory of Metal Matrix Composites; School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China
2China Tobacco, Shanghai 200240, China

Abstract

A novel indium-based chiral metal-organic framework 1, {In L(-O)(H O) } , was synthesized from a C -symmetric 1,1 -biphenol-based ligand H L and structurally characterized by single-crystal and powder X-ray diffraction, Fourier-transform infrared spectroscopy (FTIR), solid-state circular dichroism (CD), and thermogravimetric analysis (TGA). Compound 1 crystallizes in the monoclinic space group P2 with a = 10.1861(5), b = 18.5632(9), c = 16.5153(8) Å, V = 3077.1(3) Å³, Z = 2, M = 944.29 g/mol, Dc = 1.019 g/cm³, F(000) = 944, GOOF = 0.932, and final R = 0.0577 and wR = 0.1091 for 22090 observed reflections with I > 2 (I). Each In cluster in 1 is linked by four ligands, and each ligand is coordinated to four In clusters to generate a 3D network. Additionally, the photoluminescence properties of 1 and H L were investigated.

Keywords: 1,1 -biphenol; indium; chiral metal-organic framework; photoluminescence

1. Introduction

Metal-organic frameworks (MOFs) and porous coordination polymers (CPs) have attracted considerable attention not only for their diverse structural topologies and chemical tunability but also for their promising applications in gas storage, gas separation, catalysis, drug delivery, sensing, and recognition [**?**].

While significant effort has been devoted to studying the reactivity of first-row divalent transition metals (e.g., Cu^2 , Zn^2), less work has focused on MOF-type compounds incorporating trivalent metals, particularly p-block elements such as aluminum, gallium, or indium [**?**]. As heterogeneous Lewis acid catalysts, these materials offer advantages of low toxicity and high selectivity, enabling various organic reactions to proceed smoothly under mild conditions—consistent with the principles of green chemistry and demonstrating excellent prospects. On the other hand, 1,1 -biphenol derivatives with intrinsic C symmetry have long been recognized as privileged chiral ligands [**?**]. Herein, we report the synthesis, structure, thermal stability, and photoluminescence of a 1,1 -biphenol-based indium framework.

2. Experimental

2.1 Materials and Apparatus

All chemicals were commercially available and used without further purification. IR spectra (KBr pellet, 400–4000 cm ^{1} region) were recorded on a Nicolet Magna 750 FT-IR spectrometer. TGA was performed under N atmosphere at a heating rate of 10 °C·min ^{1} using a STA449C integration thermal analyzer. Fluorescence spectra were measured on an LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan).

2.2 Synthesis of 1

A mixture of InCl (13.2 mg, 0.06 mmol), H L (19.6 mg, 0.03 mmol), DMF (0.5 mL), DMSO (1.4 mL), THF (5.6 mL), H O (2.8 mL), and HOAc (0.2 mL) in a capped vial was heated at 100 °C for 24 h. Colorless crystals of 1 were filtered, washed with THF and Et O, and dried at room temperature. Yield: 23.6 mg (72%). FTIR (KBr pellet, /cm ^{1}): 509 (w), 586 (w), 640 (w), 663 (w), 679 (w), 711 (m), 719 (m), 732 (m), 760 (m), 780 (s), 838 (w), 880 (w), 896 (w), 951 (m), 994 (w), 1025 (s), 1091 (w), 1127 (w), 1171 (m), 1213 (w), 1254 (w), 1305 (w), 1366 (s), 1435 (s), 1458 (s), 1467 (s), 1497 (w), 1507 (w), 1582 (s), 1627 (s), 1654 (w), 1663 (w), 1692 (w), 1697 (w), 1753 (w), 1769 (w), 1867 (w), 2189 (w), 2461 (w), 2786 (w), 2869 (s), 2921 (s), 2961 (s), 2992 (w), 3406 (s), 3508 (s), 3741 (w), 3883 (w).

2.3 Crystallographic Measurements and Structure Determination

Single-crystal XRD data for 1 were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated MoK radiation (= 0.71073 Å) at 173.15 K. The structure was solved by direct methods using SHELXS-2014 and refined with SHELXL-2014 [**?**] through OLEX 2.0 [**?**]. All non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters. Hydrogen atoms were geometrically fixed at calculated positions attached to their parent atoms and treated as riding atoms, while guest water molecules were refined isotropically without hydrogen atoms. For 1, the final R = 0.0577 and wR = 0.1091 (w = 1/[^{2}(F ^{2}) + (0.1117P)^{2}], where P = (F ^{2} + 2F_c^{2})/3), S = 0.932, (Δ/) = 0.001, (Δ) = 0.981 and (Δ) = -0.520 e/Å^{3}.

2.4 Structure Determination

Selected bond lengths and angles are given in Table 1 .

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond Lengths	
In(1)-O(2)#1	2.094(9)
In(1)-O(1W)	2.147(11)
In(1)-O(5)	2.061(8)
In(1)-O(7)#2	2.168(9)
In(1)-O(2W)	2.170(11)
In(1)-O(8)	2.087(10)
In(2)-O(1)	2.183(9)
In(2)-O(3W)	2.396(6)
In(2)-O(3)#3	2.228(6)
In(2)-O(4)#3	2.213(7)
In(2)-O(5)	2.101(8)

Bond Lengths	
In(2)-O(6)#2	2.134(8)

Bond Angles	
O(2)#1-In(1)-O(1W)	83.0(3)
O(2)#1-In(1)-O(7)#2	88.9(4)
O(2)#1-In(1)-O(2W)	91.9(4)
O(1W)-In(1)-O(7)#2	89.7(5)
O(1W)-In(1)-O(2W)	90.2(5)
O(5)-In(1)-O(2)#1	102.3(4)
O(5)-In(1)-O(1W)	174.7(4)
O(5)-In(1)-O(7)#2	90.1(4)
O(5)-In(1)-O(2W)	89.9(4)
O(5)-In(1)-O(8)	89.8(4)
O(7)#2-In(1)-O(2W)	179.2(5)
O(8)-In(1)-O(2)#1	167.9(4)
O(8)-In(1)-O(1W)	84.9(4)
O(8)-In(1)-O(7)#2	90.0(4)
O(8)-In(1)-O(2W)	89.2(5)
O(1)-In(2)-O(3W)	175.5(3)
O(1)-In(2)-O(3)#3	82.4(4)
O(1)-In(2)-O(4)#3	82.1(3)
O(3)#3-In(2)-O(3W)	95.4(3)
O(4)#3-In(2)-O(3W)	93.4(3)
O(4)#3-In(2)-O(3)#3	58.0(3)
O(5)-In(2)-O(1)	89.8(4)
O(5)-In(2)-O(3W)	94.5(3)
O(5)-In(2)-O(3)#3	102.7(3)
O(5)-In(2)-O(4)#3	159.9(3)
O(5)-In(2)-O(6)#2	102.4(3)
O(6)#2-In(2)-O(1)	86.9(4)
O(6)#2-In(2)-O(3W)	93.3(3)
O(6)#2-In(2)-O(3)#3	152.6(3)
O(6)#2-In(2)-O(4)#3	95.6(3)

Symmetry transformations: #1: -x-3, y+1/2, -z+2; #2: -x-3, y+1/2, -z+1; #3: -x-2, y+1/2, -z+1; #4: -x-3, y-1/2, -z+2; #5: -x-2, y-1/2, -z+1; #6: -x-3, y-1/2, -z+1

3. Results and Discussion

3.1 Synthesis and Characterization of 1

As shown in Scheme 1, MOF 1 was synthesized via hydro/solvothermal reaction between InCl and the tetracarboxyl-functionalized 1,1 -biphenol ligand H L. The IR spectrum of 1 shows an absorption peak at 3406 cm [1] assignable to (-OH) stretching vibrations, while characteristic C–O stretching vibrations appear in the lower frequency region (1171 cm [1]). Phase purity was confirmed by the good agreement between experimental and simulated X-ray powder diffraction patterns (Fig. 1 [Figure 1: see original paper]). CD spectra of 1 prepared from R and S enantiomers of the H L ligand are mirror images, confirming its enantiomeric nature (Fig. 2 [Figure 2: see original paper]). Thermogravimetric analysis of 1 under N atmosphere from 50 to 800 °C indicates thermal stability up to 300 °C (Fig. 3 [Figure 3: see original paper]).

3.2 Structural Description

Single-crystal X-ray diffraction reveals that 1 crystallizes in the chiral monoclinic space group P2 . The basic building block is a near-linear dimeric [In (O C) (-O)(H O)] unit with a C axis passing through one metal center, clustered by one monodentate and three carboxylate groups from four different 1,1 -biphenol units. As illustrated in Fig. 4(a) [Figure 4: see original paper], the asymmetric unit contains two In^{3} ions, one L ligand, three coordinated water molecules, and one -O atom. In1 is six-coordinated to six oxygen atoms: three from three different carboxylate groups, one from -O, and two from coordinated water molecules. In2 is also six-coordinated to oxygen atoms: four from three different ligands (carboxylate), one from -O, and one from coordinated water. The In–O bond lengths range from 2.061(8) to 2.396(6) Å, which are typical for six-coordinate In(III) ions [**?**]. Each dinuclear In cluster is linked by four 1,1 -biphenol ligands, and each ligand connects to four In clusters to form a chiral 3D network (Fig. 5(a) [Figure 5: see original paper]). This 3D network can be simplified by considering the dimeric In clusters as four-connecting nodes and the H L ligands as tetradentate linkers (Fig. 5(b) [Figure 5: see original paper]). PLATON calculations indicate that 1 contains approximately 50% void space available for guest inclusion.

3.3 Photoluminescence

Upon excitation at 346 nm, the free H L ligand exhibits fluorescent emission at 435 nm, while compound 1 excited at 423 nm shows a blue shift of about 12 nm (Fig. 6 [Figure 6: see original paper]). Due to the d^{1} closed-shell electronic configuration, the In atom is difficult to oxidize or reduce. Therefore, the most plausible explanation for the blue shift in 1 is intraligand charge transfer rather than metal-to-ligand or ligand-to-metal charge transfer [**?**].

4. Conclusion

In summary, we have synthesized and characterized a 1,1 -biphenol-based chiral metal-organic framework with indium. The structure has been determined by single-crystal and powder X-ray diffraction, CD spectroscopy, and TGA. Furthermore, the photoluminescence properties of both 1 and the free ligand have been investigated.

References

(1) Xuan, W.; Zhu, C.; Liu, Y.; Cui, Y. Mesoporous metal-organic framework materials. *Chem. Soc. Rev.* **2012**, *41*, 1677–1695.

(2) Stock, N.; Biswas, S. Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites. *Chem. Rev.* **2011**, *112*, 933–969.

(3) Vande, B.; Bueken, B.; Denayer, J.; Devos, D. Adsorptive separation on metal-organic frameworks in the liquid phase. *Chem. Soc. Rev.* **2014**, *43*,

(4) Nagarkar, S.; Desai, A.; Ghosh, S. A nitro-functionalized metal-organic framework as a reaction-based fluorescence turn-on probe for rapid and selective H S detection. *Chem. Eur. J.* **2015**, *21*, 9994–9997.

(5) Yoon, M.; Srirambalaji, R.; Kim, K. Homochiral metal-organic frameworks for asymmetric heterogeneous catalysis. *Chem. Rev.* **2012**, *112*,

(6) Zhu, C.; Yuan, G.; Chen, X.; Yang, Z.; Cui, Y. Chiral nanoporous metal-metallosalen frameworks for hydrolytic kinetic resolution of epoxides. *J. Am. Chem. Soc.* **2012**, *134*, 8058–8061.

(7) Furukawa, H.; Cordova, K.; O' Keeffe, M.; Yaghi, O. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*, 1230444.

(8) Sumida, K.; Rogow, D.; Mason, J.; McDonald, T.; Bloch, E.; Herm, Z.; Bae, T.; Long, J. Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* **2012**, *112*, 724–781.

(9) Horcajada, P.; Gref, R.; Baati, T.; Allan, P.; Maurin, G.; Couvreur, P.; Ferey, G.; Morris, R.; Serre, C. Metal-organic frameworks in biomedicine. *Chem. Rev.* **2012**, *112*, 1232–1268.

(10) Ye, C.; Zhu, C.; Gong, T.; Shen, E.; Xuan, W.; Cui, Y.; Liu, B. A novel Cu-based metallosalan complex: synthesis, structure and chiral sensor study. *Chin. J. Struct. Chem.* **2013**, *32*, 1076–1082.

(11) Wang, X.; Li, Z.; Gong, W.; Liu, Y.; Liu, B.; Cui, Y. A novel TADDOL-based chiral metal-organic framework: synthesis, structure and photoluminescence study. *Chin. J. Struct. Chem.* **2016**, *35*, 1399–1405.

(12) Lu, K.; He, C.; Lin, W. A chlorin-based nanoscale metal-organic framework for photodynamic therapy of colon cancers. *J. Am. Chem. Soc.* **2015**, *137*, 7600–7603.

(13) Zhang, F.; Zhou, Y.; Dong, J.; Liu, B.; Zheng, S.; Cui, Y. Synthesis and crystal structure of a novel chiral 3D metal-organic framework based on an N-methyl substituted salan ligand. *Chin. J. Struct. Chem.* **2014**, *33*, 1154–1158.

(14) Crespo, P.; Veen, M.; Gobechiya, E.; Houthoofd, K.; Filinchuk, Y.; Kirschhock, C.; Martens, J.; Sels, B.; Vos, D.; Kapteijn, F.; Gascon, J. NH -MIL-53(Al): a high-contrast reversible solid-state nonlinear optical switch. *J. Am. Chem. Soc.* **2012**, *134*, 8314–8317.

(15) An, Y.; Liu, Y.; An, P.; Dong, J.; Xu, B.; Dai, Y.; Qin, X.; Zhang, X.; Whangbo, M.; Huang, B. NiII coordination to Al-based metal-organic framework made from 2-aminoterephthalate for photocatalytic overall water splitting. *Angew. Chem. Int. Ed.* **2017**, *56*, 1–6.

(16) Hajjar, R.; Volkringer, C.; Loiseau, T.; Guillou, N.; Marrot, J.; Ferey, G.; Margiolaki, I.; Fink, G.; Morais, C.; Taulelle, F. ^{1}Ga slow-CTMAS NMR and crystal structures of MOF-type gallium carboxylates with infinite edge-sharing octahedra chains (MIL-120 and MIL-124). *Chem. Mater.* **2011**, *23*, 39–47.

(17) Banerjee, D.; Kim, S.; Wu, H.; Xu, W.; Borkowski, L.; Li, J.; Parise, J. Anionic gallium-based metal-organic framework and its sorption and ion-exchange properties. *Inorg. Chem.* **2011**, *50*, 208–212.

(18) Ortiz, G.; Chaplais, G.; Paillaud, J.; Nouali, H.; Patarin, J.; Raya, J.; Marichal, C. New insights into the hydrogen bond network in Al-MIL-53 and Ga-MIL-53. *J. Phys. Chem. C* **2014**, *118*, 22021–22029.

(19) Rhauderwiek, T.; Waitschat, S.; Wuttke, S.; Reinsch, H.; Bein, T.; Stock, N. Nanoscale synthesis of two porphyrin-based MOFs with gallium and indium. *Inorg. Chem.* **2016**, *55*, 5312–5319.

(20) Volkringer, C.; Meddouri, M.; Loiseau, T.; Guillou, N.; Marrot, J.; Ferey, G.; Haouas, M.; Taulelle, F.; Audebrand, N.; Latroche, M. The kagome topology of the gallium and indium metal-organic framework types with a MIL-68 structure: synthesis, XRD, solid-state NMR characterizations, and hydrogen adsorption. *Inorg. Chem.* **2008**, *47*, 11892–11901.

(21) Sun, J.; Weng, L.; Zhou, Y.; Chen, J.; Chen, Z.; Liu, Z.; Zhao, D. QMOF-1 and QMOF-2: three-dimensional metal-organic open frameworks with a quartzlike topology. *Angew. Chem. Int. Ed.* **2002**, *41*, 4471–4473.

(22) Gomez-lor, B.; Gutierrez-puebla, E.; Iglesias, M.; Monge, M.; Ruiz-valero, C.; Snejko, N. In (OH) (BDC) . (BDC = 1,4-benzendicarboxylate): an In(III) supramolecular 3D framework with catalytic activity. *Inorg. Chem.* **2002**, *41*, 2429–2432.

(23) Peng, Y.; Gong, T.; Zhang, K.; Lin, X.; Liu, Y.; Jiang, J.; Cui, Y. Engineering chiral porous metal-organic frameworks for enantioselective adsorption and separation. *Nat. Commun.* **2014**, *5*, 1–9.

(24) Xie, Z.; Wurthner, F. Perylene bisimides with rigid 2,2 -biphenol bridges at bay area as conjugated chiral platforms. *Org. Lett.* **2010**, *12*, 3204.

(25) Mo, K.; Yang, Y.; Cui, Y. A homochiral metal-organic framework as an effective asymmetric catalyst for cyanohydrin synthesis. *J. Am. Chem. Soc.* **2014**, *136*, 1746–1749.

(26) Fabris, F.; DeLucchi, O. Central to axial transfer of chirality in menthone or camphor-derived 2,2 -biphenols. *J. Org. Chem.* **1997**, *62*, 7156.

(27) Peng, Y.; Gong, T.; Cui, Y. A homochiral porous metal-organic framework for enantioselective adsorption of mandelates and photocyclization of tropolone ethers. *Chem. Commun.* **2013**, *49*, 8253–8255.

(28) Sheldrick, G. M. SHELXT-2014, 2013.

(29) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(30) Wu, X.; Pan, Y.; Sun, X.; Zhu, Y. Synthesis and crystal structure of tetraethyl-bis[10-hydroxybenzo[h]quinolinato]-diindium(III). *Chin. J. Struct. Chem.* **1999**, *18*, 421–422.

(31) Yang, J.; Qin, Y.; Ye, R.; Zhang, X.; Yao, Y. Employing mixed-ligand strategy to construct a series of luminescent Cd(II) compounds with structural diversities. *CrystEngComm.* **2016**, *18*, 8309–8320.

Note: Figure translations are in progress. See original paper for figures.