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A chiral twofold interpenetrated diamond-like 3D In(III) coordination network with 4,4',4"-phosphoryltribenzoate

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ABSTRACT

A novel In(III) coordination complex, $[In(ptc)(H_2O)]_n (H_3ptc = 4,4',4''-phosphoryltribenzoic acid) (1)$, was synthesized under hydrothermal condition and characterized by single-crystal X-ray analysis, IR, X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and solid-state photoluminescence. Complex 1 crystallizes in a chiral $P2_1$ space group, In(III) ions are eight-coordinated and the ligand exhibits a novel and unique tetrahedral coordination mode. The complex shows intense blue emission at 435 nm with the excitation of 330 nm.

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The design and construction of metal-organic frameworks (MOFs) are under intensive investigations in recent years due to their potential applications in various research fields, such as gas adsorption and separation, catalysis, magnetism, and luminescence [1]. In order to obtain MOFs with desirable topologies and properties, different metal ions were tested, and most concentrations were focused on transition divalent metal ions [2]. We and some other groups, however, are interested in the research of one IIIA group metal ion, In(III) [3]. Compared to divalent transition metal ions, which are usually four- or six-coordinated, In(III) ions have the ability to adopt MO₆, MO₇, or even MO₈ coordination modes. Moreover, the increased valence charge of In(III) may also show some influence on the resulting structure as it is postulated that the incorporation of trivalent metal ions might create diverse structures different from those containing divalent metal ions.

On the other hand, multifunctional organic ligands are well exploited. Many carboxylate ligands with high symmetry have been synthesized and studied [4]. The results indicate that they have great advantages over those ligands with low symmetry in constructing geometrically consummate polyhedra with large pore sizes. Among them trigonal carboxylate ligands bearing C_3 symmetry are intensively investigated. For example, Yaghi's group and Zhou's group have independently designed several threefold symmetric tricarboxylates such as 1,3,5-benzenetribenzoate (BTB) and 1,3,5-tris[4'-carboxy(1,1'-biphenyl-4-yl)]-benzene (TCBPB) and plenty of porous MOFs with excellent gas adsorption properties have been obtained by utilizing these ligands. Inspired by these re-

search results, we intended to exploit another ligand, 4,4',4''-phosphoryltribenzoic acid (H₃ptc) [7], which can be regarded as a derivative of these ligands. Except for the three C_3 -related carboxylic groups, there is one more coordination atom O of the P=O bond, which may impose great influence on the final framework. Up to now, only a few results have been documented on the coordination research of this ligand [5]. And the research was all focused on divalent traditional metal ions, such as Co(II), Mn(II) and Zn(II). However, to the best of our knowledge, the investigation with main group metal ions and trivalent metal ions is still unprecedented.

Hydrothermal reaction of H₃ptc and indium(III) chloride at 150 °C results in the formation of colorless block crystals of 1 [6]. A single-crystal X-ray diffraction study [8] reveals complex 1 crystallizes in a chiral P21 space group and In(III) ion exhibits an unusual high coordination number of eight [3a]. As shown in Fig. 1, the center metal ion is coordinated by six oxygen atoms from three carboxylate groups of three individual ptc ligands, as well as one oxygen atom from the P=O of the fourth ligand and one water molecule, forming a dodecahedron motif. The In-O bond lengths range from 2.103 (4) Å to 2.550 (8) Å, which are comparable with those reported [3]. The ligand uses all seven coordinating oxygen atoms available in a $\kappa^2 - \kappa^2 - \kappa^2 - \kappa^1 - \mu_4$ coordination mode, with all three carboxylate groups in chelating coordination mode and the oxygen atom (O₇) from P=O bond in monodentate coordination mode (Scheme 1). As far as we know, such a coordination mode is unprecedented. There are in all four types of coordination modes of H₃ptc ligand (Scheme S1), and none of them uses all of the seven oxygen atoms to engage in the coordination. The difference may be attributed to the abundant coordination modes and increased valence charge of In(III).

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Fig. 1. The coordination environment around In(III) in 1 with the thermal ellipsoid at the 30% probability level. Symmetry code: (A) x, y, z - 1; (B) x, 1 + y, z; (C) x - 1, y, z.



Scheme 1. Coordination mode of H₃ptc ligand in the article.

In this way, the ligand joints four metal centers in four directions that resemble a tetrahedron. This coordination motif is dominated by the conformation of the ligand. Moreover, the metal centers share similar coordination motif with the ligands, which

give rise to the final 3D framework. The structure can be better understood from topological perspective. The metal centers and the ligands both serve as distorted tetrahedral 4-connected nodes and the distances are 3.538 Å, 8.665 Å, 8.693 Å and 8.722 Å, respectively. The connection between these nodes produces a well constructed 3D diamond-like network (Fig. 2). There are large channels in the framework along the three axes due to the rigid conformation of the ligand. In order to fill the large void space, another diamond net interpenetrates with this one, thus forming a twofold interpenetrating structure (Fig. 3). As a self-dual net, interpenetrating diamond-like nets have been well studied and examples are known of degrees of interpenetration ranging from twoto tenfold [10]. According to the classification of interpenetration topology by Blatov et al., the complex belongs to class IIa, that is, the individual nets are related by means of a full interpenetration symmetry element. In this case, the twofold dia nets are generated by a 2_1 screw axis and the nonetranslational degree $Z_n = 2$. Up to now, there are only two examples of this type [10]. The whole framework is thus chiral. These two nets are interacted through two groups of hydrogen bonds between the coordination water molecules (O8) and two oxygen atoms (O2 and O6) of two carbox-



Fig. 2. (a) Schematic representation of the diamond-like net along *c*-axis. Hydrogen atoms are omitted for clarity. (b) Topological representation of **1**. Color code: green, In; pink, P; red, O; gray, C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. (a) Schematic representation of the twofold interpenetration of 1 along *b*-axis. Hydrogen bonds are shown in dashed lines. Topological representation of interpenetration along *b*-axis (b) and *c*-axis (c).

ylate groups. The $08\cdots02$ and $08\cdots06$ distances are 2.803(7) Å and 2.871(8) Å, the angles of $08-H8A\cdots02$ and $08-H8B\cdots06$ are 150.9° and 140.9° , respectively.

The FT-infrared (IR) spectrum of **1** shows a broad absorption at 3448 cm⁻¹ which can be attributed to the presence of water molecules. The absorption range from 1396 to 1703 cm⁻¹ is consistent with that of the carboxylate groups. Furthermore, the strong peaks at 1268 cm⁻¹, 1166 cm⁻¹, 1106 cm⁻¹, 707 cm⁻¹ and 576(m) cm⁻¹ justify the presence of P=O bond. The X-ray powder diffraction (XRD) of **1** was measured at room temperature. The peak positions of simulated XRD pattern matches with the observed, indicating that the complex is obtained in pure phase (Fig. S1). The thermal stability of 1 was investigated. As illustrated in Fig. S2, the loss of coordination water molecules occurred in the range of 60-150 °C (calcd 3.33%, found 3.34%), then the complex underwent decomposition in two steps. The first step corresponds to a weight loss of 42.3%, indicating the partial decomposition of the ligand, the second step suggests a weight loss of 15.56%, implying the total decomposition of the ligand, which yields the final residual of the mixture of In_2O_3 and P_2O_5 (calcd 38.70%, found 38.81%).

The photoluminescence property of **1** was recorded at room temperature and 10 K in the solid state. As shown in Fig. 4, Complex **1** exhibits intense pure blue photoluminescence with an emission maximum at ca. 435 nm upon excitation at 330 nm, and the blue emission could even be observed by naked eyes under irradiation of ultraviolet light with the wavelength of 365 nm. At 10 K, the emission spectrum displays a sharp peak at ca. 441 nm with upon excitation at 330 nm, which shows a negligible shift of 6 nm in comparison with that at room temperature. The free H₃ptc ligand exhibits a similar emission at ca. 450 nm upon excita



Fig. 4. Solid-state photoluminescent spectrum of 1 at room temperature and 10 K.

tion at 330 nm (Fig. S3). So the emission of **1** can be attributed to intraligand charge transfer.

Conclusion

In summary, a chiral twofold interpenetrated diamond-like 3D In(III) coordination network with 4,4',4''-phosphoryltribenzoate was hydrothermally synthesized. The results indicate that H₃ptc li-

gand is a good candidate for the construction of such 4-connected diamond-like networks. The intensive blue emission suggests that 1 may be potential fluorescent material.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.09.031.

References

 (a) M. Eddaoudi, J. Kim, N. Rosi, D. vodka, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science 295 (2002) 469;

(b) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R.V. Belosludov, T.C. Kobayashi, H. Salamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, Nature 436 (2005) 238;

(c) C.-D. Wu, W.-B. Lin, Angew. Chem., Int. Ed. 44 (2005) 1958;

(d) D.-F. Sun, S.-Q. Ma, Y.-X. Ke, D.J. Collins, H.-C. Zhou, J. Am. Chem. Soc. 128 (2006) 3896;

(e) M. Yoshizawa, M. Tamura, M. Fujita, Science 312 (2006) 251;

(f) S.-C. Xiang, X.-T. Wu, J.-J. Zhang, R.-B. Fu, S.-M. Hu, X.-D. Zhang, J. Am. Chem. Soc. 127 (2005) 16352;

(g) L.-H. Gao, M. Guan, K.-Z. Wang, L.-P. Jin, C.-H. Huang, Eur. J. Inorg. Chem. (2006) 3731.

[2] (a) R.K. Feller, A.K. Cheetham, Dalton Trans. (2008) 2034;

(b) H.-W. Wang, S. Gao, L.-H. Huo, S.-W. Ng, J.G. Zhao, Cryst. Growth Des. 8 (2008) 665;

(c) J.-L. Du, T.-L. Hu, J.-R. Li, S.-M. Zhang, X.-H. Bu, Eur. J. Inorg. Chem. (2008) 1059.

[3] (a) Z.-Z. Lin, F.-L. Jiang, L. Chen, D.-Q. Yuan, Y.-F. Zhou, M.-C. Hong, Eur. J. Inorg. Chem. (2005) 77;

(b) Z.-Z. Lin, F.-L. Jiang, L. Chen, D.-Q. Yuan, M.-C. Hong, Inorg. Chem. 44 (2005) 73;

(c) Z.-Z. Lin, F.-L. Jiang, L. Chen, C.-Y. Yue, D.-Q. Yuan, A.-J. Lan, M.-C. Hong, Cryst. Growth Des. 7 (2007) 1712;

(d) Z.-Z. Lin, J.-H. Luo, M.-C. Hong, R.-H. Wang, L. Han, R. Cao, J. Solid State Chem. 177 (2004) 2494;

(e) Z.-Z. Lin, L. Chen, F.-L. Jiang, M.-C. Hong, Inorg. Chem. Commun. 8 (2005) 199; (f) Y.-L. Liu, J.F. Eubank, A.J. Cairns, J. Eckert, V. Ch. Kravtsov, R. Luebke, M. Eddaoudi, Angew. Chem., Int. Ed. 46 (2007) 3278;

(g) J.L. Belof, A.C. Stern, M. Eddaoudi, B. Space, J. Am. Chem. Soc. 129 (2007) 15202;

(h) B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M.A. Monge, C. Ruiz-Valero, N. Snejko, Inorg. Chem. 41 (2002) 2429;

(i) Z.-G. Guo, Y.-F. Li, W.-B. Yuan, X.-D. Zhu, X.-F. Li, R. Cao, Eur. J. Inorg. Chem. (2008) 1326;

(j) C. Chen, Y.-L. Liu, S.-H. Wang, G.-H. Li, M.-H. Bi, Z. Yi, W.-Q. Pang, Chem. Mater. 18 (2006) 2950.

[4] (a) H.K. Chae1, D.Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, O.M. Yaghi, Nature 427 (2004) 523;

(b) D.-F. Sun, Y.X. Ke, T.M. Mattox, S. Parkin, H.-C. Zhou, Inorg. Chem. 45 (2006) 7566;

(c) J. Kim, B.-L. Chen, T.M. Reineke, H.-L. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 123 (2001) 8239;

(d) T.K. Ronson, J.L. Fisher, L.P. Harding, M.J. Hardie, Angew. Chem., Int. Ed. 46 (2007) 9086;

(e) S.J. Garibay, J.R. Stork, Z.-Q. Wang, S.M. Cohen, S.G. Telfer, Chem. Commun. (2007) 4881;

(f) S.B. Choi, M.J. Seo, M. Cho, Y. Kim, M.K. Jin, D.-Y. Jung, J.-S. Choi, W.-S. Ahn, J.L.C. Rowsell, Jaheon Kim, Cryst. Growth Des. 7 (2007) 2290;

(g) R. Sun, S.-N. Wang, H. Xing, J.-F. Bai, Y.-Z. Li, Yi. Pan, X.-Z. You, Inorg. Chem. 46 (2007) 8451;

(h) R. Sun, Y.-Z. Li, J. -F Bai, Y. Pan, Cryst. Growth Des. 7 (2007) 890.

[5] (a) S.M. Humphrey, S.E. Oungoulian, J.W. Yoon, Y.K. Hwang, E.R. Wisea, J.-S. Chang, Chem. Commun. (2008) 2891;

(b) M.J. Plater, M.R.St.J. Foreman, E. Coronado, C.J. Gomez-Garcia, A.M.Z. Slawin, J. Chem. Soc., Dalton Trans. (1999) 4209;
(c) M.J. Plater, M.R.St.J. Foreman, T. Gelbrich, M.B. Hursthouse, J. Chem. Cryst. 30 (2000) 155;

(d) M.J. Plater, M.R.St.J. Foreman, J.M.S. Skakle, J. Chem. Cryst. 30 (2000) 449.

- [6] Synthesis of 1: The ligand H₃ptc was synthesized according to the literature [7]. A aqueous mixture of $InCl_3H_2O$ (74.0 mg, 0.25 mmol), H₃ptc (102 mg, 0.25 mmol), NaOH (10 mg, 0.25 mmol) and H₂O (8.0 ml) in 30-ml Teflon-lined stainless steel vessel was heated at 150 °C for 96 h, and then the reaction system was cooled to room temperature at a rate of 6 °C h⁻¹. Colorless block crystals of 1 were obtained (yield 60% based on $InCl_3$). Anal. Calcd for $C_{21}H_{14}InO_8P$ (%): C, 46.70; H, 2.61; found (%): C, 46.78; H, 2.53. IR (KBr): 3448(br. s), 1703(s), 1604(w), 1564(w), 1396(s), 1268(s), 1166(m), 1106(s), 707(m), 576(m) cm⁻¹.
- [7] W.N. Chou, M. Pomerantz, J. Org. Chem. 56 (1991) 2762.
- [8] Crystal data of 1: $C_{21}H_{14}InO_8P$, Mr = 540.11, monoclinic system, space group $P2_1$, a = 10.527 (2) Å, b = 9.3735 (17) Å, c = 10.527 (2) Å, $\beta = 92.29$, V = 1037.9 (3) Å³, Z = 4, $D_c = 1.728$ g/cm³, $\mu = 2.267$ mm⁻¹, $F_{000} = 536$, Flack's parameter $\chi = -0.04(3)$, Rigaku Mercury CCD area-detector, Mo K α radiation, $\lambda = 0.71073$ Å, T = 293(2) K, $2\theta_{max} = 55.0^\circ$, 7877 reflections collected, 4175 unique ($R_{int} = 0.0578$). Final GooF = 0.934, $R_1 = 0.0468$, $wR_2 = 0.0794$. *R* indices based on 3420 reflections with $I > 2\sigma(I)$ (refinement on F^2). The structure was solved with direct methods and refined on F^2 with full-matrix least-squares methods using SHELXS-97 and SHELXL-97 programs, respectively [9]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms belonging to the water molecule O8 were found in the electron-density map. The other hydrogen atoms were generated geometrically.
- [9] G. M. Sheldrick, SHELXTL: Structure Determination Software Programs, Bruker Analytical X-ray System Inc., Madison, WI, USA, 1997.
- [10] V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, CrystEngComm 6 (2004) 377.