

The first indium-organic two-dimensional layer network with rhombus grids

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Abstract

The indium(III)-organic compound $[\text{In}(\text{HBtc})_2(4,4'\text{-bpy})](4,4'\text{-Hbpy})(\text{H}_2\text{O})_{0.5}$ (Btc = 1,3,5-benzenetricarboxylate, 4,4'-bpy = 4,4'-bipyridine) has been synthesized under hydrothermal condition and characterized by IR, fluorescent spectroscopy, TGA and single-crystal X-ray diffraction analyses. The compound crystallizes in monoclinic, space group $P2(1)/c$, $a = 17.0884(2) \text{ \AA}$, $b = 12.28390(10) \text{ \AA}$, $c = 17.9456(4) \text{ \AA}$, $\beta = 104.1920(10)^\circ$, $V = 3652.03(10) \text{ \AA}^3$, $Z = 4$, $R_1 = 0.0572$ and $wR_2 = 0.1116$ [$I > 2\sigma(I)$]. All the indium atoms in the compound are hepta-coordinated and link 1,3,5-benzenetricarboxylate forming a 2-D layer structure with rhombus grids.

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1. Introduction

Coordination polymers with 1-D chains, 2-D sheets and 3-D network represent a fast growing area due to their potential application in the field of optics, electronics, catalyst and magnet [1–5]. Compared to the immense number of transition metal polymers, main group metal polymers are rare documented in spite of the well-known zeolites formed by aluminophosphates and aluminosilicates as well as the indium phosphates. Within indium polymers, most of the research to date has been focused on the indium phosphates. The coordination polymers assembled from indium and organic donors remain relatively undeveloped because indium is not inclined to coordinate with organic donors. Benzene-multicarboxylic acids and relative materials are chosen as bridging units because they are favorable to self-assembly with metal cations into 1-D materials [6], 2-D solids [7], 3-D compounds [8], interpenetrating [9] and open networks [10]. Here we report the hydrothermal synthesis and structure of a novel layer indium(III)-multicarboxylate polymer containing

rhombus grid network, $[\text{In}(\text{HBtc})_2(4,4'\text{-bpy})](4,4'\text{-Hbpy})(\text{H}_2\text{O})_{0.5}$ (**1**). This is the first case of polymer constructed from indium(III) and 1,3,5-benzenetricarboxylate.

2. Experimental

2.1. Synthesis of $[\text{In}(\text{HBtc})_2(4,4'\text{-bpy})](4,4'\text{-Hbpy})(\text{H}_2\text{O})_{0.5}$ (**1**)

1,3,5-benzenetricarboxylic acid (0.25 g, 1.2 mmol), 4,4'-bpy (0.19 g, 1.2 mmol) and $\text{In}_2(\text{SO}_4)_3$ (0.13 g, 0.24 mmol) were placed into a 23-mL Teflon-lined stainless-steel vessel, and then 8 mL KOH solution (3.7 mmol) was added until the pH of the resulting mixture was adjusted to about 5.0. The vessel was then sealed and heated at 170°C for 72 h. After cooling to room temperature at 0.1°/min, the orange-yellow block-shaped crystalline product of **1** was obtained. The yield based on $\text{In}_2(\text{SO}_4)_3$ was 51%. Anal. Calcd for $\text{C}_{38}\text{H}_{26}\text{InN}_4\text{O}_{12.5}$: C, 53.48; H, 3.07; N, 6.56%, (found) C, 53.65; H, 3.21%; N, 6.57%. IR (KBr, cm^{-1}): 3500 m, 3429 m, 3052 m, 2889 m, 1720 s, 1633 s, 1587 s, 1487 s,

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1417 s, 1360 s, 1248 s, 1188 m, 1072 m, 1022 m, 806 s, 760 s, 725 s, 694 m, 677 m, 636 m, 551 w, 509 m.

2.2. Characterization

The analysis of C, N and H contents were performed on an Elementar Vario EL III microanalyzer. The FT-IR spectrum was measured on a Nicolet FT-IR Magna 750 spectrophotometer using KBr pellets. The fluorescent spectrum was recorded with a Edinburgh Instrument F920 fluorescent spectrometer using Xe lamp. Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851e analyzer with a heating rate of 10°C/min in nitrogen atmosphere.

2.3. Determination of crystal structure

Single crystal of compound **1** with size of $0.30 \times 0.22 \times 0.20 \text{ mm}^3$ was mounted on a SMART CCD diffractometer equipped with a graphite monochromator and $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Intensity data were collected at 293(2) K. A total of 11,251 reflections were collected, of which 6364 were independent ($R_{\text{int}} = 0.046$) and 3935 were considered to be observed with $I > 2\sigma(I)$. Systematic absence and statistics of intensity distribution resulted in a space group of $P2(1)/c$. The structure was solved by direct method. Three hydrogen atoms from 4,4'-bpy and Hbtc units were located from E-maps, while the others were placed geometrically. All non-hydrogen atoms except oxygen atom of water were refined anisotropically by full-matrix least-square using SHELXTL program package [11]. Experimental X-ray data are listed in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1
Crystal data and structure refinement for the title compound

Empirical formula	$\text{C}_{38}\text{H}_{26}\text{InN}_4\text{O}_{12.5}$
Formula weight	853.44
Space group	$P2(1)/c$
a (Å)	17.0884(2)
b (Å)	12.28390(10)
c (Å)	17.9456(4)
β (°)	104.1920(10)
V (Å ³)	3652.03(10)
Z	4
ρ (calcd.) (g cm ⁻³)	1.550
μ (mm ⁻¹)	0.719
$F(000)$	1724
θ range (°)	4.06–45.00
Independent reflections	6362
Obs. refl [$I > 2\sigma(I)$]	3935
Parameters	512
Goodness-of-fit on F^2	1.089
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0572$, $wR_2 = 0.1116$
Largest diff. Peak and hole (e/Å ⁻³)	0.749/−0.527

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum (F_o^2 - F_c^2)^2] / [\sum (F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for the title compound

In–O(24)	2.134(5)	C(21)–O(21)	1.271(8)
In–O(35)	2.141(4)	C(22)–O(23)	1.240(8)
In–O(32)	2.208(4)	C(23)–O(25)	1.166(9)
In–O(21)	2.239(4)	C(31)–O(31)	1.249(8)
In–O(22)	2.320(5)	C(32)–O(33)	1.307(9)
In–O(31)	2.360(5)	C(33)–O(35)	1.270(8)
In–N(11)	2.287(5)		
O(24)–In–O(35)	163.43(18)	O(22)–C(21)–O(21)	120.3(6)
O(24)–In–O(21)	101.67(18)	O(23)–C(22)–O(24)	124.6(7)
O(32)–In–O(21)	80.56(17)	O(25)–C(23)–O(26)	123.2(8)
O(21)–In–O(22)	57.33(16)	O(31)–C(31)–O(32)	120.1(6)
O(35)–In–O(22)	92.51(18)	O(34)–C(32)–O(33)	123.6(8)
O(32)–In–N(11)	139.23(18)	O(36)–C(33)–O(35)	125.1(6)
O(24)–In–N(11)	80.4(2)		

3. Results and discussion

3.1. Synthesis

Hydrothermal reaction of 1,3,5-benzenetricarboxylic acid, 4,4'-bpy and $\text{In}_2(\text{SO}_4)_3$ in water gave rise to the orange-yellow block-shaped crystalline compound **1**. The IR data of **1** show that there are difference of $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ appearing in 1587, 1487 and 1360, 1417 cm^{-1} , respectively, which is currently utilized to determine the coordination mode of the carboxylate groups. The $\Delta\nu(\nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2))$ values (227 and 70 cm^{-1} , respectively) indicate the carboxylate groups coordinate to In(III) atoms both in monodentate ($227 \text{ cm}^{-1} > 95 \text{ cm}^{-1}$) and in bidentate ($70 \text{ cm}^{-1} < 95 \text{ cm}^{-1}$) mode [12,13], an characteristic absorption appearing at 1720 cm^{-1} suggests the presence of uncoordinated protonated carboxylate group. The presence of water is shown by the OH stretch at 3429 cm^{-1} while the absorption at 3500 cm^{-1} is assigned to $\nu_{\text{N-H}}$ concerning protonated 4,4'-Hbpy. The formula of $[\text{In}(\text{HBtc})_2(4,4'\text{-bpy})](4,4'\text{-Hbpy})(\text{H}_2\text{O})_{0.5}$ was confirmed by elemental analysis, IR results and X-ray single crystal diffraction analyses.

3.2. Structure description

The asymmetric unit of the compound **1** is shown in Fig. 1. Each indium(III) center is hepta-coordinated and bonded by six oxygen and one nitrogen atoms from four HBtc units and one 4,4'-bpy to form a pentagonal bipyramidal geometry. O(24) and O(35) occupy the axial vertexes of the pentagonal bipyramid. Three carboxylate groups of HBtc adopt three different coordination modes, one is uncoordinated, and the other two bond in a mono- and chelating bidentate fashion, respectively. Thus, HBtc units act as bridges and connect the indium(III) centers to form a 2-D network with rhombus grids. As shown in Fig. 2, each rhombus grid

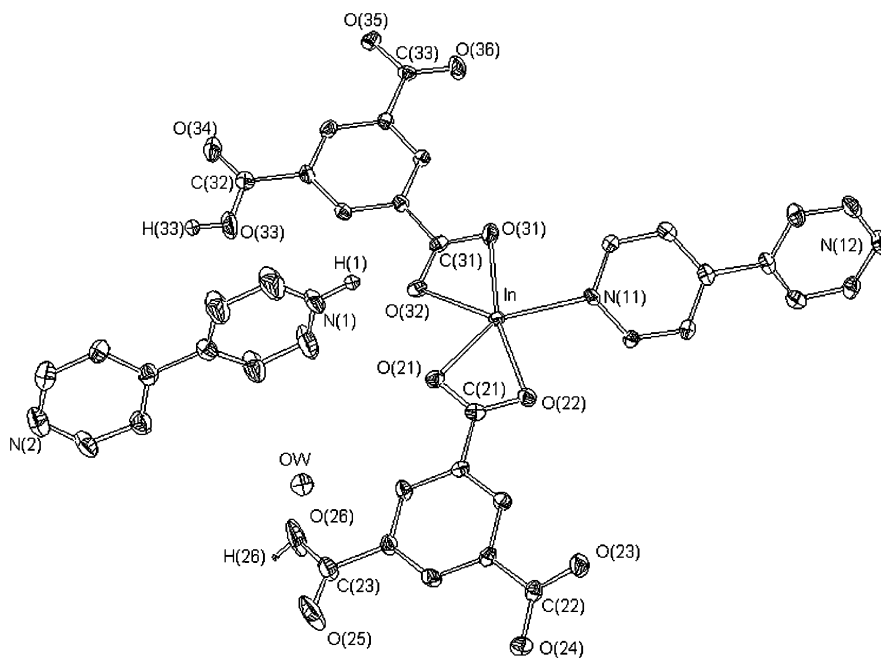


Fig. 1. Ortep drawing (at 30% probability level) of asymmetric unit in **1**.

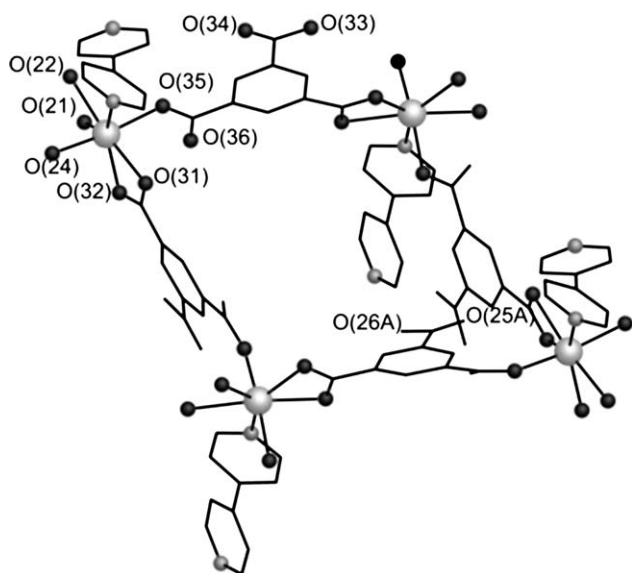


Fig. 2. View of a rhombus grid formed from four In(III) ions and four HBtc units.

unit is formed from four indium atoms and four HBtc units with the diagonal lengths of 12.284(1) and 17.088(1) Å. The grids are extended along [100] and [010] to generate a 2-D layer structure. The adjacent layers parallel each other and pack in a staggered way with the grids shift of $a/2$ and $b/2$, as shown in Fig. 3.

One kind of 4,4'-bpy molecules in **1** act as terminal groups and coordinate to indium vertices of grids, and each is trans to neighboring 4,4'-bpy ligands, which undulate 2-D layers slightly. The other kind of 4,4'-bpy

molecules act as counter-cations. Through E-maps, we can locate the H atoms attached on protonated O and N atoms (as shown in Fig. 1), which confirm the suggestion about charge assignment. The isolated 4,4'-Hbpy molecules fill in the void space of crystal with pyridyl ends being within the grids or within the layers region. The pyridyl rings of 4,4'-bpy molecules are twisted by 37.86° and 9.81° for the coordinated ones and solvate ones, respectively. The distance of neighboring layers amounts to approximately 8.7 Å and they are interacted by the hydrogen bonds. Two of them are the strongest, one is between the O atoms from uncoordinated carboxylate and N atoms from terminal 4,4'-bpy molecules (O(33)–H(33)⋯N(12), 2.59 Å, 170.2°), the other involves N atoms from protonated 4,4'-Hbpy and O atoms from monodentate carboxylate (N(1)–H(1)⋯O(36), 2.70 Å, 159.7°).

3.3. Thermogravimetric and luminescent analysis

Thermogravimetric analysis (TGA) results show that the loss between 30°C and 150°C is 1.0% and corresponds to 0.5 mol of H₂O per formula unit (calcd. 1.0%). The compound **1** is thermally stable until around 300°C, and then the weight loss is 80.7% in the temperature range of 307–500°C, the step corresponds to the removal of 4,4'-bpy and part of HBtc components (calcd. 82.7%). Because isolated 4,4'-bpy molecules take the role of counter-cations, the framework collapses during the removal of organic components. After decomposition at high temperature, the residues are indium oxides that constitute 18.3% (calcd. 16.7%). When illuminated with the wavelength of 396 nm, the

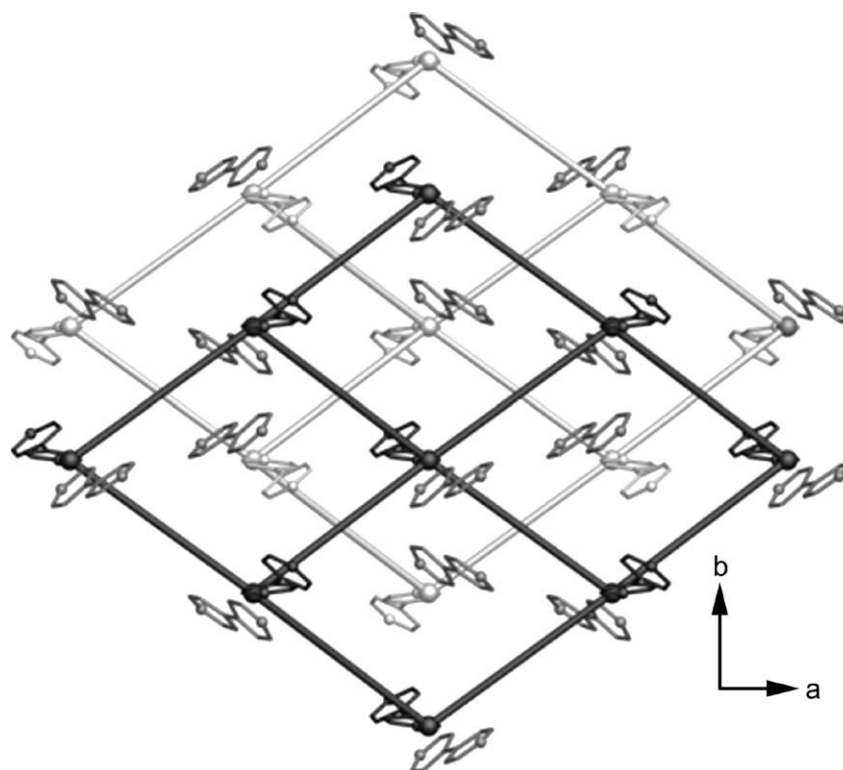


Fig. 3. Scheme diagram showing the staggered layers and the position of 4,4'-bpy molecules (isolated 4,4'-Hbpy molecules display at medium grey). The vertices of grids are In(III) and lines between In(III) atoms designate HBtc groups. The water molecules and hydrogen atoms are omitted for clarity.

solid state of compound **1** displays a strong broad fluorescent emission centred at 487 nm (FWHM = 50 nm), while solid state of 4,4'-bpy emits at 486 nm with almost the same intensity when excited at 301 nm. Thus, we regard the emission of the compound **1** is caused by intraligand transition of 4,4'-bpy.

4. Conclusion

This work shows that benzene-tricarboxylate groups can coordinate to indium(III) through monodentate and chelating bidentate modes to form 2-D layers with rhombus grids. The 4,4'-bpy ligands on adjacent layers are interdigitated, producing a slightly undulating effect. The layers are linked by hydrogen bonds between carboxylate groups and 4,4'-bpy ligands, giving rise to a 3-D network.

Supporting information

Additional information including atomic coordinates, thermal parameters and the complete bond lengths and bond angles had been deposited with the Cambridge Crystallographic Data Center (CCDC No. 214531).

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