

水熱合成含銦(III)-苯-1,2-二甲酸配位錯合物及結構分析

Hydrothermal Synthesis, Crystal Structure of a Indium(III) Complex with Benzene-1,2-dicarboxylate

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摘要：將 $\text{In}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ 及苯-1,2-二甲酸加水混合，在溫度 423 K 下，利用水熱合成反應，得到含銦(III)的配位化合物，其化學式為 $[\text{In}(1,2\text{-BDC})(\mu_2\text{-OH})(\text{H}_2\text{O})]_n$ (**1**)，(1,2-BDC= 苯-1,2-二甲酸根)。利用元素分析儀、FT-IR 光譜儀及 X-Ray 晶體繞射儀測定產物晶體結構及性質。化合物 **1** 以銦(III)離子為配位中心，配位六個氧原子，三個來自 1,2-BDC 的羧酸氧原子及一個配位水分子和兩個氫氧離子配位基，配位構成六配位且些微扭曲的正八面體型幾何結構，每個 1,2-BDC 配位基同時鄰接三個銦金屬。配位中心銦(III)離子經由 1,2-BDC 配位基的連結形成二維的結構。晶體結構中含有傳統性的氫鍵作用力($\text{O}-\text{H} \cdots \text{O}$)，以及芳香環之間的 $\pi \cdots \pi$ 吸引力，使的晶體結構更穩定。其中鄰近互相平行芳香環的雙面角為 $1.1(2)^\circ$ ，兩個 1,2-BDC 的中心距離為 $3.671(3)\text{\AA}$ 。研究指出化合物 **1** 具有對掌異構物 [弗萊克(Flack)參數為： $0.48(3)$]。

關鍵詞：水熱合成、苯-1,2-二甲酸、銦金屬、氫鍵

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Abstract : The title polymer compound, $[\text{In}(\text{1,2-BDC})(\mu_2\text{-OH})(\text{H}_2\text{O})]_n$ (**1**), (1,2-BDC= benzene-1,2- dicarboxylate) has been synthesized by a hydrothermal reaction using $\text{In}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, benzene-1,2- dicarboxylic acid and water at 423 K. The structure of **1** was characterized by elemental analysis, FT-IR and single-crystal X-ray diffraction. The asymmetric unit of compound **1** contains a six-coordinate In(III) ion with a slightly distorted octahedral geometry, defined by six O atoms from one water molecules, three 1,2-BDC ligands and two hydroxyl ligands. Each 1,2-BDC ligand affords a three-connecting node. The In(III) centers are interconnected through 1,2-BDC ligands to generate a two-dimensional layered structure. Classical O—H \cdots O hydrogen bonding is observed in the crystal structure. The crystal structure is further consolidated by $\pi\cdots\pi$ stacking between nearly parallel aryl ring systems [dihedral angle = $1.1(2)^\circ$], the centroid \cdots centroid distance between aromatic rings of adjacent 1,2-BDC ligands being 3.671(3)Å. The crystal was found to be a racemic twin, and the flack parameter is 0.48(3).

Key words : Hydrothermal Synthesis, Benzene-1,2-dicarboxylic acid, Indium, Hydrogen bonding.

I . Introduction

Recently, a huge number of metal-organic compounds have been prepared because of the fascinating structural and topological features of these compounds and their potential applications as functional materials, such as catalysts, gas storage and optical materials^{1,2}. In this field, many organic bridging ligands, such as aromatic polycarboxylates and their related species, are often selected to coordinate to metal centres to obtain various types of polymeric structures, including one-, two- and three-dimensional network structures. Benzene-1,2-dicarboxylic acid, a polydentate organic ligand containing two carboxyl group, can be used as a bridging and/or terminal ligand when it coordinates to various metallic ions³⁻⁸. In recent years, transition metal compounds are most studied, and the research of main group metal compound is significantly less explored⁹⁻¹³. At present, the research field has been extended to using main group metal as framework polyhedral node. In this paper, we report the hydrothermal synthesis and structural characterization of the title compound $[\text{In}(\text{C}_8\text{H}_4\text{O}_4)(\mu_2\text{-OH})(\text{H}_2\text{O})]_n$ (**1**), which exhibits a three-dimensional network structure through bridging by the benzene-1,2-dicarboxylate anion.

II . Experimental Section

Materials and methods

All chemicals purchased were reagent grade and used without further purification. Elemental analysis (C, H and N) was performed on a Heraeus CHN-O-Rapid elemental analyzer. The content of Indium was determined by Perkin Elmer Optima 2100 inductively coupled plasma (ICP-OES) Emission Spectrometer. FT-IR spectra were recorded in the range 400-4000 cm^{-1} on a **JASCO 6200**



Micro-FT-IR spectrophotometer using a KBr pellet. All measurements were performed at room temperature.

X-ray Crystallographic Analysis

Diffraction data of the title compound were collected on a Bruker SMART CCD area detector diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) in ψ and ω scan modes. All the structures were solved by direct methods using the program SHELXS 97 and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97^{14, 15}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths for the title compound are listed in Table 2.

Table 1. Crystal data of compound **1**.

Chemical formula	[C ₈ H ₇ InO ₆]
Molecular weight	313.96
Temperature, K	297
Wavelength, \AA	0.71073
Crystal system	orthorhombic
Crystal description color	Parallelepiped, colorless
Space group	Fdd2
Unit cell parameters, a, b, c, \AA	11.9181(7), 42.277(3), 7.3127(4)
Volume, \AA^3	3684.3(4)
Z	16
dx, g/cm ³	1.691
Extinction coefficient, mm ⁻¹	2.57
F(000)	2432
Crystal size, mm	0.38 x 0.28 x 0.10
h, k, l limits	-14 \leq h \leq 10, -51 \leq k \leq 51, -8 \leq l \leq 8
Data completeness on θ , %	3.3-26.0, 99.8%
Measured/independent reflections	5099/ 1703 [R(int) = 0.022]
Reflections with $I > 2\sigma(I)$	1699
Number of parameters	4747



Transmission	0.98517-1.00000
Refinement	Full-matrix least squares against F^2
GOOF against F^2	0.051
Final R factor [$I > 2\sigma(I)$]	$R1 = 0.0217$, $wR2 = 0.0171$
R factor (all data)	$R1 = 0.0027$, $wR2 = 0.0511$
Residual electron density, e. \AA^{-3}	-0.68 and 0.75
Absolute structure	Flack (1983), 519 Friedel pair
Flack parameter	0.48(3)

Table 2. selected geometric parameters (\AA , $^\circ$)

Bond	$d(\text{\AA})$	Angle	Deg($^\circ$)
In—O1	2.159(3)	O5 ⁱ —In—O5	161.17(11)
In—O5	2.095(3)	O5 ⁱ —In—O2 ⁱ	100.04(11)
In—O6	2.245(4)	O5—In—O2 ⁱ	89.87(11)
In—O3 ⁱ	2.138(3)	O5 ⁱ —In—O3 ⁱⁱ	106.44(11)
In—O2 ⁱⁱ	2.136(3)	O5—In—O3 ⁱⁱ	89.93(11)
In—O5 ⁱⁱ	2.074(3)	O2 ⁱ —In—O3 ⁱ	86.88(12)
O1—C1	1.247(5)	O5 ⁱ —In—O1	83.81(11)
O5—In ⁱⁱⁱ	2.074(3)	O5—In—O1	87.95(11)
C1—O2	1.268(5)	O2 ⁱ —In—O1	173.44(12)
C8—O4	1.237(5)	O3 ⁱⁱ —In—O1	86.92(12)
C8—O3	1.283(5)	O5 ⁱ —In—O6	82.73(10)
O3—In ⁱⁱ	2.138(3)	O5—In—O6	80.64(10)

Symmetry code: (i) $-x+1, -y, z$ (ii) $-x+0.5, -y, z+0.5$ (iii) $x-0.5, y, z-0.5$

Synthesis

A mixture of $\text{In}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (0.1695g, 0.25 mmole), benzene-1,2-dicarboxylic acid (0.0836g, 0.50mmole) and distilled water (10 mL) sealed in a 23 mL Teflon-lined stainless autoclave was heated to 423 K under autogenously pressure for 99 h, then allowed to cool slowly to room temperature, the resulting reaction mixture was washed with 5 mL of acetone and colorless single crystals, were isolated by suction filtration (yield 50.83 % based on Indium). IR(KBr) (cm^{-1}) : 3443(m) \cdot 1661(s) \cdot 1581(s) \cdot 1553(s) \cdot 1495(m) \cdot 1432(s) \cdot 1362(s) \cdot 1148(m) \cdot 1090(w) \cdot 760(s) \cdot 691(m) \cdot 651(w) \cdot 565(w).



Elemental analysis calcd. for $\text{InC}_8\text{H}_7\text{O}_6$ ($M_w = 313.96$) : In, 36.57; C, 30.58; H, 2.25 %. Found : In, 37.27; C, 30.65; H, 2.28 %.

Results and discussion

Title compound has been prepared by hydrothermal reactions under nearly neutral conditions (the pH value adjusted to 6.8~7.0). Indium(III) sulfate nona hydrate reacts with benzene-1,2-dicarboxylic acid at 423 K to give benzene-1,2-dicarboxylate-In(III) compound. The product is stable in air and insoluble in water and common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, 1,2-dichloroethane, acetone and DMF.

Title compound was obtained as colorless crystals in relatively high isolation yield (50.83 %). The FT-IR spectrum of title compound exhibits peaks at 1611, 1581, and 1553 cm^{-1} that can be assigned to the asymmetric and symmetric C=O stretches (Fig. 1), respectively. The absence of the characteristic bands at around 1703 cm^{-1} , which is attributed to the protonated carboxylic group, indicates the full de-protonation of 1,2-BDCH₂ ligand upon reaction with In ions. The absorption peaks at 3443 cm^{-1} is assigned to $\nu_{\text{O-H}}$ of coordinated water molecule¹⁶.

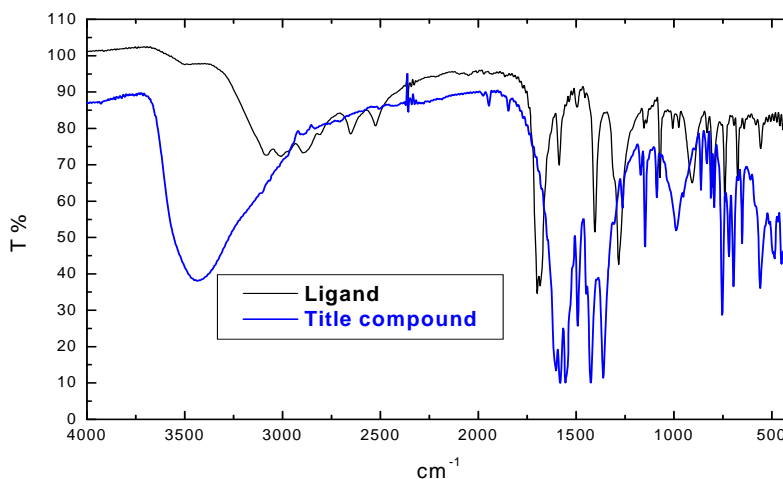


Fig. 1. The FT-IR spectrum of ligand and compound **1**

The valence sum calculations give the average value of 3.177 for Indium atom¹⁷⁻¹⁸, suggesting that all indium centers are in the +3 oxidation state ($[\text{Kr}]4d^{10}5s^05p^0$). The octahedral structure around the In(III) metal center of compound **1** is shown in Fig. 2. Each In(III) atom displays a slightly distorted octahedron geometry with six oxygen atoms of two bridging hydroxyl group, one water molecules and three different bridging carboxylate group of 1,2-BDC ligands. Each 1,2-BDC ligand affords a three-connecting node (Chart 1). The selected bond distances and bond angles are



listed in Table 2. The average bond distances of In---O are 2.074(3) and 2.254(4) Å, respectively. The 1,2-BDC ligand adopts a tridentate bridging coordination mode through its monodentate and bidentate carboxylate groups. The equatorial carboxylate O atoms crosslink the polymeric chains structure into a two-dimensional layered structure. The adjacent In(III) atoms are connected by two μ_2 -OH groups and two deprotonated carboxylate groups of two 1,2-BDC ligands in a syn-syn coordination mode to form a two-dimensional plane structure (0 1 0).

The O-H...O hydrogen bonds stabilize the crystal structure (Table 3, Fig. 3). A π ... π stacking interaction is also observed, the centroid...centroid distance between the parallel [dihedral angle = 1.1(2)°] aryl rings being 3.671(3)Å [Cg1^{vi}...Cg1(C2-C7)] (symmetry code: (vi) -1/4+X, -1/4-Y, 1/4+Z)¹⁹. The title compound as two-dimensional complex was assembled into 3-D networks via O-H...O hydrogen bond and π ... π stacking interaction (Fig. 4)²⁰. The crystal is racemic mixtures compound **1**, and the flack parameter is 0.48(3).

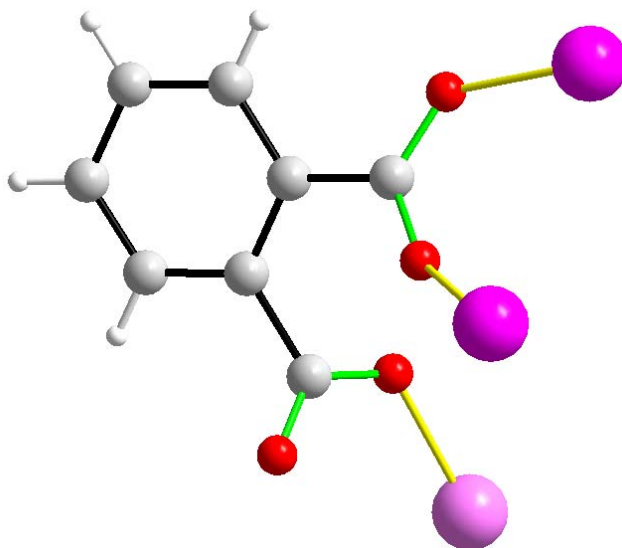


Chart 1



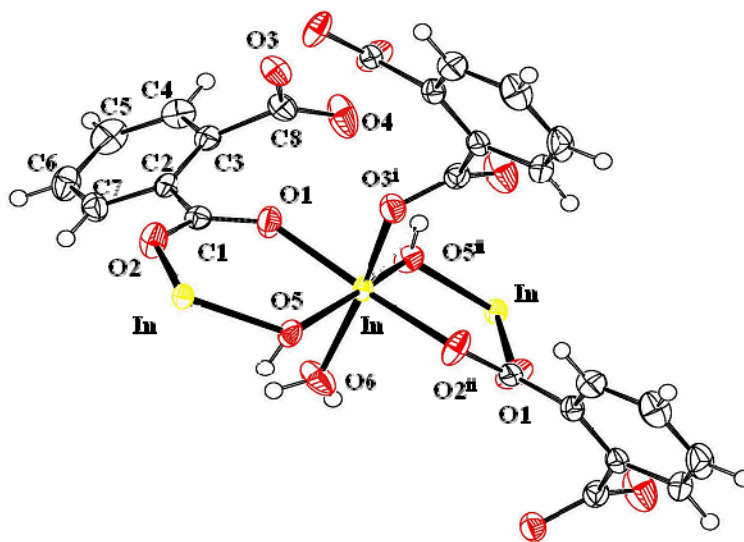


Fig. 2. View of the compound **1** with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Symmetry codes: (i) $-x+1, -y, z$, (ii) $-x+1/2, -y, z+1/2$.

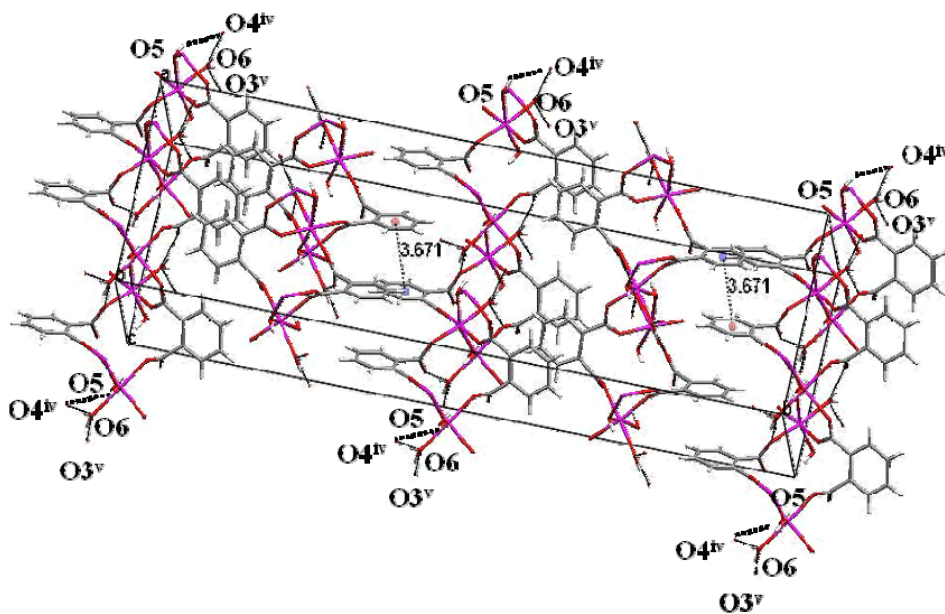


Fig. 3. The molecular packing for the compound **1**. Hydrogen bonds are shown as dashed lines.



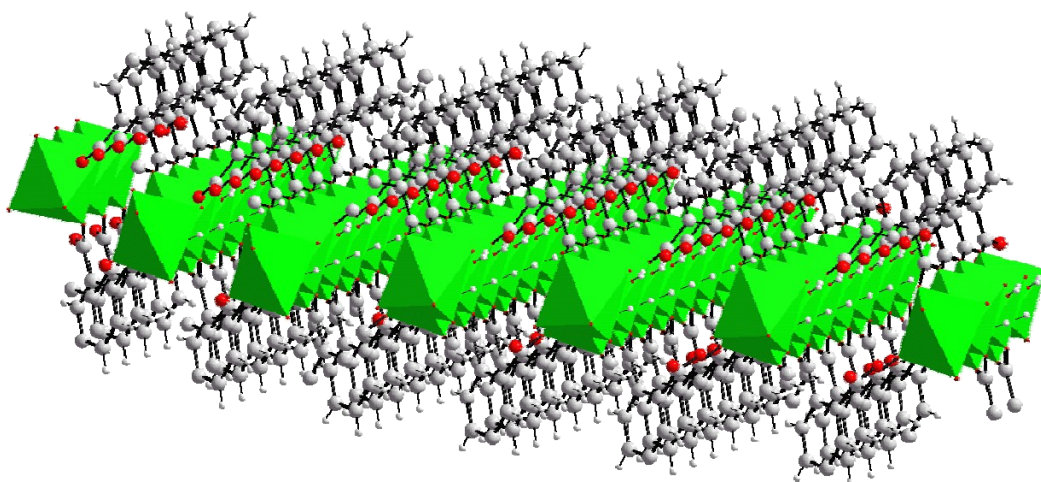


Fig. 4. View of the stacking arrangement of compound **1**, showing strong Hydrogen-bonding and $\pi\cdots\pi$ stacking interactions.

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D-H \cdots A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{D-H}\cdots\text{A}$
O5-H5B \cdots O4 ⁱⁱⁱ	0.8200	2.5100	3.220(5)	145.00
O6-H6A \cdots O3 ^{iv}	0.8200	2.1800	2.857(4)	140.00
O6-H6C \cdots O4 ⁱⁱⁱ	0.8200	2.0400	2.849(5)	169.00

Symmetry code: (iii) $x-0.5, y, z-0.5$ (iv) $-0.5+x, y, 0.5+z$

III. Conclusions

In this study, an In(III) polymer has been synthesized and structurally characterized. The synthesis of compound **1** not only proves that the hydrothermal reaction in preparing new metal-organic hybrid materials is successful but also shows that strong intermolecular interactions (O–H \cdots O hydrogen-bonding) and weak $\pi\cdots\pi$ stacking interactions contribute to the formation of higher-dimensional network.

IV. Acknowledgments

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