

Poly[aqua(μ_3 -benzene-1,2-dicarboxylato)(μ_2 -hydroxo)indium(III)]Yu-Ling Wang,^{a*} Qing-Yan Liu^b and Sheng-Liang Zhong^a^aCollege of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, People's Republic of China, and ^bState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China
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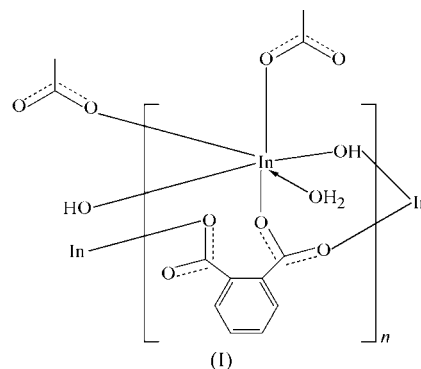
In the title compound, $[\text{In}(\text{C}_8\text{H}_4\text{O}_4)(\text{OH})(\text{H}_2\text{O})]_n$, the coordination of the In^{III} ion is composed of six O atoms from three dianionic benzene-1,2-dicarboxylate ligands, two hydroxyl groups and one coordinated water molecule in a distorted octahedral geometry. The In^{3+} ions are linked by the hydroxyl groups to form zigzag $\text{In}-\text{OH}-\text{In}$ chains, which are further bridged by the benzene-1,2-dicarboxylic acid ligands to generate a two-dimensional layered structure featuring three types of rings (six-, 14- and 20-membered). Hydrogen bonds between the water molecule and a carboxylate O atom, and between the hydroxyl group and a carboxylate O atom, are observed within the layers. In the crystal packing, there are $\pi-\pi$ stacking interactions between the benzene rings of adjacent layers, with a centroid-to-centroid distance of 3.668 (3) Å and a dihedral angle of 4.8 (2)°.

Comment

The construction of coordination polymers is one of the most active areas of materials research in recent years. The intense interest in these materials is driven by their potential applications as functional materials (catalysis, magnetism, electric conductivity, gas storage and non-linear optics), as well as their intriguing structural topologies (Janiak, 2003; Kitagawa *et al.*, 2004; O'Keeffe *et al.*, 2000). Among linker molecules, rigid aromatic carboxylic acids, such as benzene-1,3,5-tricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid and benzene-1,4-dicarboxylic acid, have been extensively studied because of their versatile coordinating modes (Yaghi *et al.*, 1997; Dai *et al.*, 2002; Karanović *et al.*, 2002). Benzene-1,2-dicarboxylic acid (H_2BDC) is an important dicarboxylate ligand as it has multiple coordinating modes, which together with the varied coordination geometry of metal ions has led to the generation of products containing one-dimensional chains, two-dimensional layers and three-dimensional frameworks (Ma *et al.*, 2004; Thirumurugan & Natarajan, 2004).

Much effort has so far been devoted to the study of transition metal-based coordination polymers. However, relatively

little attention has been paid to the coordination polymers of main group metal ions, despite their important applications in ion exchange or electroluminescent devices (Lin *et al.*, 2005; Liu & Xu, 2006). It has been postulated that the incorporation



of main group metal ions might create diverse structures different from those containing transition metal ions. In the search for a further class of materials, we have introduced a trivalent metal, namely indium(III), in order to investigate the influence of the change of the metal centre on the coordination architecture during the course of the assembly of the metal centres with H_2BDC . The In^{III} ion is liable to hydrolyse, which limits its use in the construction of coordination polymers. However, by adding an appropriate basic reagent to deprotonate H_2BDC and by carefully controlling the reaction conditions, we have found that In^{III} ions can be used to construct new frameworks. The hydrothermal reaction of InCl_3 with H_2BDC in the presence of 2-picoline yields the title complex, (I), and we present its structure here. To the best of our knowledge, no $\text{In}-\text{BDC}$ species have been reported previously.

The asymmetric unit of (I) consists of one In^{III} ion, one BDC^{2-} dianion, one hydroxyl group and one coordinated water molecule. As depicted in Fig. 1, the In^{III} atom is six-coordinated by four O atoms from three BDC^{2-} ligands and one coordinated water molecule in a distorted square-planar

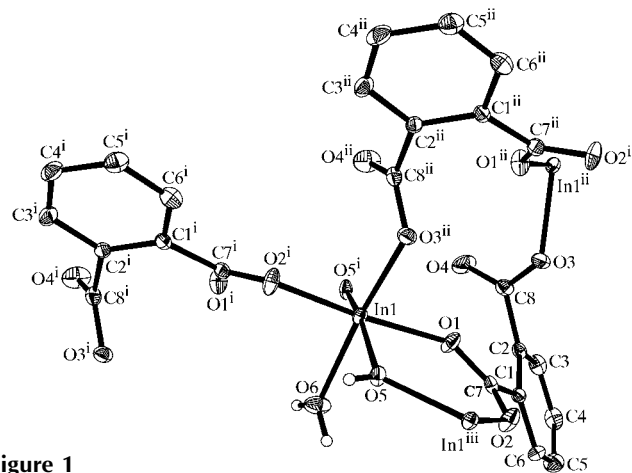


Figure 1
A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x - \frac{1}{2}, -y + \frac{1}{2}, z$; (iii) $-x, -y + \frac{1}{2}, z + \frac{1}{2}$.]

geometry, and two O atoms from two hydroxyl groups in the apical positions. The In–O octahedron is slightly compressed, with axial In–O bond lengths of 2.071 (3) and 2.093 (3) Å, and equatorial In–O bond lengths of 2.133 (3)–2.244 (4) Å, and with O–In–O bond angles varying from 80.4 (1) to 173.5 (2)° (Table 1). The bond dimensions involving In are normal, and are comparable with the values in related indium(III) complexes (Sun *et al.*, 2002).

The axial O-atom corners are shared by neighbouring octahedra to form a zigzag $\cdots\text{OH}-\text{In}-\text{OH}-\text{In}\cdots$ chain propagating along the *c* axis, with an In–OH–In angle of 126.4 (1)°, as illustrated in Fig. 2. The In–OH–In angle in (I) is considerably larger than corresponding angles of 118.6 (2)–120.6 (2)° in the three-dimensional framework of $\{[\text{In}(\text{OH})(p\text{-BDC})]_4[p\text{-H}_2\text{BDC}]_3\}_n$ (*p*-H₂BDC is benzene-1,4-dicarboxylic acid), where *p*-H₂BDC guest molecules are observed within the framework (Anokhina *et al.*, 2005). The In \cdots In separation is 3.72 Å, similar to the values of 3.63 Å in $\{[\text{In}(\text{OH})(p\text{-BDC})]_4[p\text{-H}_2\text{BDC}]_3\}_n$ and 3.77 Å in $\{[\text{In}_2(\text{OH})_3(p\text{-BDC})_{1.5}]\}_n$ (Gomez-Lor *et al.*, 2002). Those values are longer, as expected, but comparable with those of purely inorganic structures, such as the corundum-like In₂O₃ structure or indium metal (*d* = 3.34 Å in both cases) (Prewitt *et al.*, 1969). Neighbouring In^{III} ions in the zigzag chain are also bridged by a bidentate carboxylate group to form a six-membered ring, denoted *A* (Fig. 2). The chain is repeated by translation about every 7.3 Å along the *c* direction, comparable with the length of the *c* axis.

The BDC²⁻ ligand adopts a tridentate bridging coordination mode through its bidentate and monodentate carboxylate groups. The equatorial carboxylate O atoms are shared with

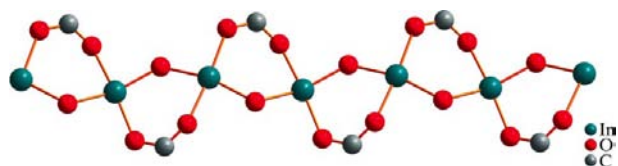


Figure 2
A view of the zigzag $\cdots\text{OH}-\text{In}-\text{OH}-\text{In}\cdots$ chain and the six-membered ring *A*.

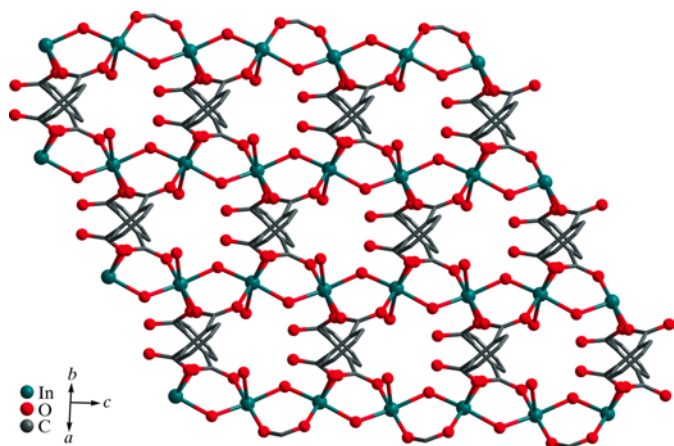


Figure 3
A perspective view of the two-dimensional layered structure of (I).

the BDC²⁻ anions that crosslink the octahedral chains into a two-dimensional layered structure (Fig. 3). Two other types of rings are observed in the two-dimensional layer. Ring *B* is a 14-membered ring, which consists of two BDC²⁻ anions and two In^{III} atoms, and ring *C* is a 20-membered ring containing two BDC²⁻ anions, five In^{III} atoms and three hydroxyl O atoms, as shown in Fig. 4. In the two-dimensional layered structure, all benzene rings are located on both sides of the plane formed by the In–OH–In chains. It is interesting that the benzene rings on one side are parallel and are twisted with respect to the benzene rings on the other side, with a dihedral angle of 86.1 (1)°.

Hydrogen bonds between the coordinated water molecule and a carboxylate O atom, and between the hydroxyl group and a carboxylate O atom, are observed within the two-dimensional layer, with O \cdots O distances in the range

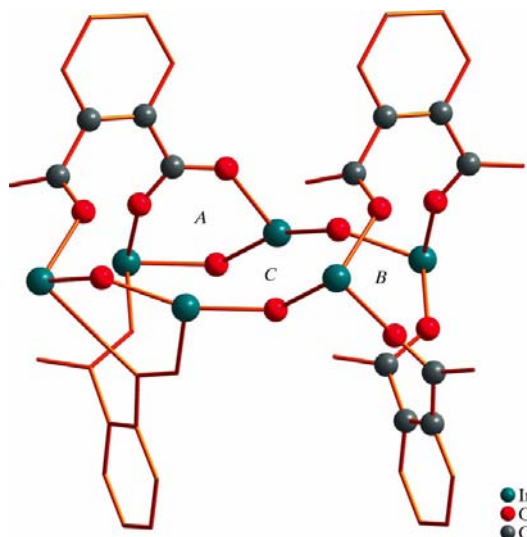


Figure 4
A perspective view of the six-, 14- and 20-membered rings *A*, *B* and *C*; atoms forming the rings are represented as spheres.

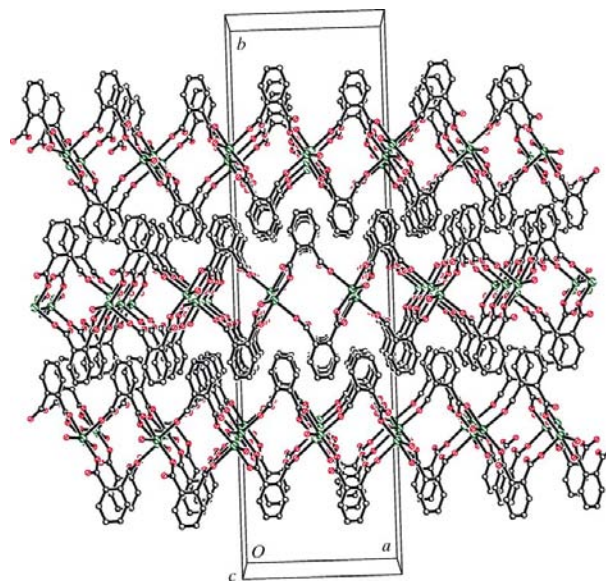


Figure 5
A view of the packing of (I), viewed down the *c* axis.

2.838 (5)–3.149 (5) Å (Table 2). There are π – π stacking interactions between the benzene rings of adjacent layers, with a centroid-to-centroid distance of 3.668 (3) Å and a dihedral angle of 4.8 (2)°, and these are responsible for the three-dimensional supramolecular framework structure (Fig. 5).

Experimental

The title compound was synthesized by the hydrothermal method under autogenous pressure. A mixture of InCl₃ (221 mg, 1 mmol), benzene-1,2-dicarboxylic acid (166 mg, 1 mmol) and distilled water (15 ml) was stirred under ambient conditions. 2-Picoline (0.35 ml) was then added slowly to the suspension. The final mixture was sealed in a 25 ml Teflon-lined steel autoclave and heated at 433 K for 4 d, and then cooled to room temperature. Colourless plate-like crystals of (I) were obtained, and these were recovered by filtration, washed with distilled water and dried in air (yield 59%). Analysis calculated for C₈H₇InO₆: C 30.58, H 2.25%; found: C 30.55, H 2.21%.

Crystal data

[In(C ₈ H ₄ O ₄)(OH)(H ₂ O)]	Z = 16
<i>M_r</i> = 313.96	<i>D_x</i> = 2.270 Mg m ⁻³
Orthorhombic, <i>Fdd</i> 2	Mo <i>K</i> α radiation
<i>a</i> = 11.915 (1) Å	μ = 2.58 mm ⁻¹
<i>b</i> = 42.205 (5) Å	<i>T</i> = 295 (2) K
<i>c</i> = 7.3069 (9) Å	Plate, colourless
<i>V</i> = 3674.4 (7) Å ³	0.25 × 0.18 × 0.01 mm

Data collection

Rigaku Mercury70 diffractometer	6877 measured reflections
ω scans	1888 independent reflections
Absorption correction: multi-scan	1822 reflections with <i>I</i> > 2σ(<i>I</i>)
(<i>CrystalClear</i> ; Rigaku & Molecular Structure Corporation, 2000)	<i>R</i> _{int} = 0.033
<i>T</i> _{min} = 0.589, <i>T</i> _{max} = 0.976	θ_{max} = 27.5°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 12.2335P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.01	$\Delta\rho_{\text{max}} = 1.11 \text{ e \AA}^{-3}$
1888 reflections	$\Delta\rho_{\text{min}} = -0.94 \text{ e \AA}^{-3}$
145 parameters	Absolute structure: Flack (1983),
H atoms refined by a mixture of constrained and independent refinement	with 755 Friedel pairs
	Flack parameter: -0.02 (4)

Table 1

Selected geometric parameters (Å, °).

In1–O5 ⁱ	2.071 (3)	In1–O6	2.244 (4)
In1–O5	2.093 (3)	O1–C7	1.252 (6)
In1–O3 ⁱⁱ	2.133 (3)	O2–C7	1.250 (6)
In1–O2 ⁱ	2.140 (3)	O3–C8	1.297 (5)
In1–O1	2.159 (3)	O4–C8	1.237 (6)
O5 ⁱ –In1–O3 ⁱⁱ	106.74 (13)	O2 ⁱ –In1–O1	173.51 (15)
O5–In1–O3 ⁱⁱ	89.60 (13)	O5 ⁱ –In1–O6	83.02 (13)
O5–In1–O2 ⁱ	89.92 (12)	O5–In1–O6	80.40 (13)
O3 ⁱⁱ –In1–O2 ⁱ	86.85 (14)	O2 ⁱ –In1–O6	93.79 (16)
O5 ⁱ –In1–O1	83.70 (13)	O1–In1–O6	91.93 (16)
O5–In1–O1	88.01 (12)	In1 ⁱⁱⁱ –O5–In1	126.35 (13)
O3 ⁱⁱ –In1–O1	86.99 (15)		

Symmetry codes: (i) $-x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x - \frac{1}{2}, -y + \frac{1}{2}, z$; (iii) $-x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O5–H5A...O4 ⁱⁱⁱ	0.89 (4)	2.28 (2)	3.149 (5)	166 (5)
O6–H6A...O4 ^{iv}	0.89 (5)	1.96 (3)	2.838 (5)	169 (7)
O6–H6B...O3 ^v	0.90 (5)	2.01 (3)	2.854 (5)	156 (6)

Symmetry codes: (iii) $-x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, y, z + \frac{1}{2}$; (v) $x + \frac{1}{2}, y, z - \frac{1}{2}$.

Aromatic H atoms were placed in calculated positions and treated using a riding-model approximation, with C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). H atoms bonded to O atoms were visible in a difference map and were refined with a DFIX (*SHELXTL*; Sheldrick, 1997) restraint of O–H = 0.90 Å and with *U*_{iso}(H) = 1.5*U*_{eq}(O).

Data collection: *CrystalClear* (Rigaku & Molecular Structure Corporation, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3026). Services for accessing these data are described at the back of the journal.

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