

Hydrothermal synthesis of indium tartrates: Structures of the chiral polymer $[\text{In}(\text{L-TAR})^{3-}\text{H}_2\text{O}] \cdot 0.5\text{H}_2\text{O}$ containing the tartrate trianion, and a microporous hybrid solid $[\text{In}(\text{OH})(\text{D/L-TAR})^{2-}] \cdot 2\text{H}_2\text{O}$

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Received 10 October 2005; accepted 10 January 2006

Available online 31 March 2006

Abstract

Hydrothermal reaction of indium hydroxide with L-tartaric acid or racemic D/L-tartaric acid at 110 °C for 3 days affords, respectively **1** $[\text{In}(\text{L-TAR})\text{H}_2\text{O}] \cdot 0.5\text{H}_2\text{O}$ which contains tartrate trianions and has a 2D structure, and **2** $[\text{In}(\text{OH})(\text{D/L-TAR})] \cdot 2\text{H}_2\text{O}$, with a microporous 3D framework that undergoes phase transformation at ca. 150 °C.

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Keywords: Hydrothermal synthesis; Indium; Microporous solids; Chiral polymers

Recently the hydrothermal synthesis of the enantiopure microporous lanthanide polymers $[\text{Ln}_2(\text{L-TAR})_3(\text{H}_2\text{O})_2]$ was reported [1]. These were prepared using the commonly available chiral ligand L-tartrate, which was shown to be capable of surviving hydrothermal conditions of 160 °C for several days. In attempting to extend these studies to the preparation of other stable chiral frameworks using trivalent metals, we have studied the parallel reactions of indium and found quite different resultant coordination chemistry which we report herein. Indium³⁺ typically has 6-coordination rather than the 8 or 9-coordination found for lanthanide tri-cations. Hydrothermal reaction of either indium hydroxide $[\text{In}(\text{OH})_3]$ or indium acetate hydrate $[\text{In}(\text{OAc})_3 \cdot x\text{H}_2\text{O}]$ with L-tartaric acid at 110 °C for 3 days, affords a crystalline phase **1**, whilst use of racemic D/L-tartaric acid crystals give a second phase type **2** [2]. Thermal gravimetric analyses of both product phases were inconsistent with the originally expected $[\text{In}_2(\text{TAR})_3] \cdot x\text{H}_2\text{O}$ formulations, so individual crystal specimens were subjected

to single crystal X-ray structure determination to characterize the products [3].

In the case of **1** the crystal structure revealed the formula to be $[\text{In}(\text{L-TAR})^{3-}\text{H}_2\text{O}] \cdot 0.5\text{H}_2\text{O}$ which has a 2D sheet structure. Charge balance for this 1:1 In:TAR ratio is achieved through partial deprotonation of the tartrate alcohol groups and the formation of tartrate trianions $[\text{C}_4\text{H}_3\text{O}_6]$. The asymmetric unit is complex and contains two independent In ions, one 6- and other 7-coordinate and two $[\text{L-TAR}]^{3-}$ ligands, in which the chiral centers C(12), C(13), C(22) and C(23) are all of R-stereochemistry. The deprotonated alkoxy oxygens sit in bridging environment between adjacent In centers forming dimeric units with $[\text{In}_2\text{O}_2]$ rings, as found in alkoxides such as $[\text{In}_2(\text{O-Bu}^t)_6]$, [4] a frequently observed structural motif for In³⁺ [5].

The 7-coordinate indium In(1) forms 1,2,3-tris chelate and 1,2-chelate rings to the tartrate trianions. The 6-coordinate In center In(2) has severely distorted octahedral geometry, with the trans angles ranging from 156° to 163° and forms 1,2-chelate and 1,3-chelate rings. Overall each In connects to three tartrate neighbors and vice versa;

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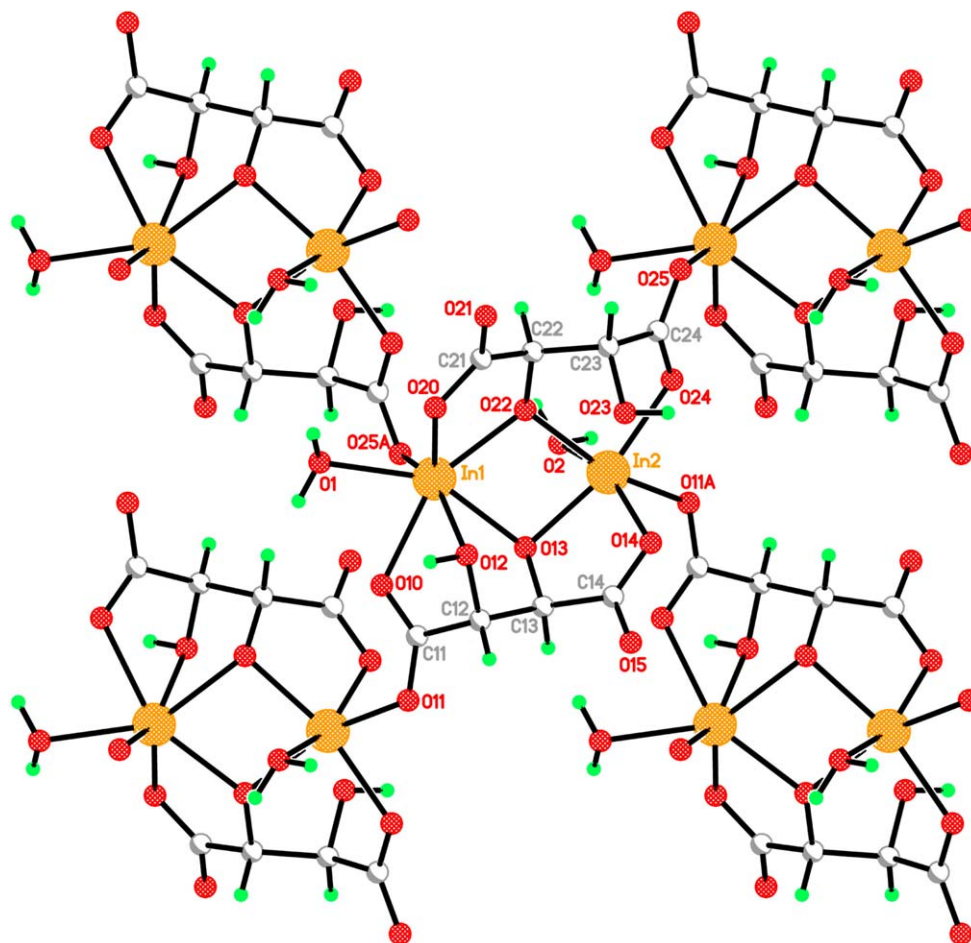


Fig. 1. Structure of **1** showing labelling scheme and connectivity of dimer units to neighbours within the 2D sheet. 7-coord. In(1)–O 2.145(3)–2.329(3) Å; 6-coord. In(2)–O 2.117(3)–2.235(3) Å.

through this 3:3 connectivity a corrugated layer sheet structure is formed, as shown in Fig. 1. The two tartrates have chemically different environments and may be described as (μ_3, κ^5-) and (μ_3, κ^4-), respectively [6]. The dimeric structural core of **1** shown in Fig. 1 is reminiscent of the dimeric structures with $[\text{Ti}_2\text{O}_2]$ rings found for the important fam-

ily of titanium tartrate epoxidation catalysts developed by Sharpless, in which the tartrate alcohols are also deprotonated [7,8] (see Tables 1 and 2).

Although the $(\text{TAR})^{3-}\text{C}_4\text{H}_3\text{O}_6^{3-}$ has not been definitively characterized before, the deprotonation of tartrate alcohol groups in their metal complexation chemistry is well-prece-

Table 1
Crystallographic data for compounds **1** and **2**

Compound	1 $[\text{In}(\text{L-TAR})\text{H}_2\text{O}] \cdot 0.5\text{H}_2\text{O}$	2 $[\text{In}(\text{OH})(\text{D/L-TAR})] \cdot 2\text{H}_2\text{O}$
CSD deposition number	286,082	286,083
Formula, Fw, Z	$\text{C}_8\text{H}_{12}\text{In}_2\text{O}_{15}$, 577.82, 2	$\text{C}_4\text{H}_9\text{InO}_9$, 315.93, 4
Temperature (K), λ (Å)	298, 0.71073	298, 0.71073
Crystal system, space group	Monoclinic, P2(1)	Orthorhombic, Pnna
Unit cell parameters	$a = 7.2584(12)$ Å $b = 10.5946(17)$ Å $c = 9.1061(15)$ Å $\beta = 93.986(3)^\circ$ $V = 698.6(2)$ Å ³	$a = 7.2642(7)$ Å $b = 15.0204(14)$ Å $c = 8.8286(8)$ Å $\beta = 90^\circ$ $V = 963.30(16)$ Å ³
D_c Mg/m ³ , μ mm ⁻¹	2.747, 3.392	2.178, 2.481
$2\theta_{\text{max}}$, GoF, η	56, 1.019, -0.01(2)	50, 1.008, N/A
Data/restraints/parameters	2854/1/226	815/0/67
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0197$, $wR2 = 0.0436$	$R1 = 0.0293$, $wR2 = 0.0507$
R indices (all data)	$R1 = 0.0205$, $wR2 = 0.0440$	$R1 = 0.0365$, $wR2 = 0.0534$
Residual electron density	0.610 and -0.465 e Å ⁻³	0.305 and -0.518 e Å ⁻³

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