An anionic two-dimensional indium carboxylate framework derived from a pseudo C_3 -symmetric semi-flexible tricarboxylic acid

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Abstract. Hydrothermal treatment of indium(III) nitrate with a flexible pseudo C_3 -symmetric tricarboxylic acid at 115°C for 5 days in DMF yields a new layered anionic indium carboxylate framework, $[(CH_3)_2NH_2][In(L)(HCOO)(DMF)]_n$ (**1**) ($L = 2,4,6$ -tris[(4'-carboxyphenoxy)methyl]-1,3,5-trimethylbenzene), existing as two-dimensional sheets. The framework solid has been characterized by elemental analysis, FT-IR spectroscopy, TGA, PXRD and single crystal X-ray diffraction studies. DMF undergoes cleavage to dimethyl ammonium and formate ions, which are incorporated in the framework. A slipped stacking of the two dimensional sheets along a -axis in **1** results in a drastic decrease in the anticipated large porosity of the framework.

Keywords. Indium carboxylate; trivalent metals; flexible ligand; 2-D framework; anionic framework; hydrogen bonding.

1. Introduction

Development of new one- to three-dimensional metal carboxylate framework architectures to meet enhanced functional applications such as gas storage, separation, catalysis, magnetism, and drug delivery has been an extensively investigated theme in inorganic synthesis over the last two decades.^{1–3} The growth in this area is attributable to the ability of building blocks, viz. metal-connecting nodes and organic bridging ligands, to connect in multiple binding modes while maintaining the structural integrity throughout synthetic process, by which the structure topology of the final framework can be understood in advance. In this regard, large number of porous/non-porous metal-organic frameworks (MOFs)⁴ are documented with divalent transition metals to enhance their usefulness for various applications. However, barring a few exceptions, MOFs incorporating heavier main group trivalent metals have been largely overlooked^{5–9} compared to the divalent transition metal counterparts. Depending on the reaction conditions and the dimensionality the ligand can impose on the final product, these large trivalent ions such as In(III) can form structurally interesting 1D to 3D MOFs, showing applicability in gaseous absorption and heterogeneous catalysis.^{10–12}

In view of the importance of In(III) carboxylates for a variety of applications described above, an attempt has been made in the present study to synthesize

framework indium carboxylates employing a semi-flexible polydentate ligand in view of the well-demonstrated ability of such conformationally flexible poly-carboxylic acids^{13–15} and poly-pyridine ligands' ability to yield diverse framework structures. These investigations resulted in the isolation of a new 2-D In(III) carboxylate framework and the details are presented in this contribution.

2. Experimental

2.1 Methods, materials and instruments

The starting materials such as methyl 4-hydroxybenzoate (Merck, India), DMF (Merck, India), mesitylene (Alfa Aesar) and $In(NO_3)_3 \cdot 5H_2O$ (Alfa Aesar) were procured from commercial sources.

The melting points were measured in glass capillaries and are reported uncorrected. Elemental analyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. FT-IR spectra were recorded on a Perkin Elmer Spectrum One Infrared Spectrometer as KBr diluted disks. The 1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. The ESI mass spectra were recorded on Water Micromass Q-Tof mass spectrometer. Thermogravimetric analyses were performed on PerkinElmer Pyris Diamond TGA instrument under continuous flow of nitrogen gas. Single crystal X-ray diffraction measurements were performed using Mo- $K\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$) on

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a Rigaku AFC10K Satrun 724HG based diffractometer. PXRD data were collected on a Philips X'pert Pro (PANAnalytical) diffractometer using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). N₂ and H₂ adsorption/desorption experiments were performed isothermally at 77 K on Quantachrome autosorb-1.

2.2 Synthesis of H₃L

Ligand H₃L was synthesized in a different route by reacting a mixture of methyl 4-hydroxybenzoate and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene in DMSO and NaOH.¹⁶ A mixture of methyl 4-hydroxybenzoate (7.6 g, 50.0 mmol), NaOH (4.0 g, 100 mmol) and DMSO (100 mL) was stirred at 75°C for 1 h. To this hot mixture, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (5.98 g, 15.0 mmol) was added and the resulting mixture was heated for another 24 h at 75°C. The mixture was cooled to room temperature and poured into 200 mL of distilled water. To this, 50 mL aqueous solution of NaOH (20.0 g, 250 mmol) was added and heated for another 12 h at 75°C. The mixture was again cooled to room temperature and acidified with diluted HCl (final pH $\sim$ 2). A white precipitate formed immediately upon acidification was filtered under suction and washed repeatedly with water and then diethyl ether and dried under vacuum to obtain analytically pure acid H₃L. Yield; 5.65 g, 73%. M.p. 270–275°C. Anal. calcd for C₃₃H₃₀O₉: C, 69.46; H, 5.30. Found: C, 69.34; H, 5.37. ¹H NMR (400 MHz, DMSO-*d*₆, 295 K): δ 12.69 (s, 3 H, COOH), 7.93 (d, ³*J*_{HH} = 8.72 Hz, 6 H, ArH), 7.17 (d, ³*J*_{HH} = 7.76 Hz, 6 H, ArH), 5.21 (s, 6 H, BzCH₂), 2.36 (s, 9 H, ArCH₃) ppm. ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆, 295 K): δ 167.0, 162.4, 139.2, 131.4, 131.2, 123.3, 114.5, 65.1, 15.6 ppm. LR-MS(ESI); *m/z* calcd for C₃₃H₃₁O₉⁺ 571.19, found 571.14 [M + H]⁺. FT-IR (KBr diluted disc): 3400–2600, 1682, 1603, 1510, 1428, 1244, 1168 cm^{−1}.

2.3 Synthesis of [(CH₃)₂NH₂][In(L)(HCOO)(DMF)]_n (I)

A mixture of H₃L (0.057 g, 0.10 mmol), In(NO₃)₃·5H₂O (0.078 g, 0.20 mmol), DMF (2.7 g) and H₂O (0.5 g) was stirred for half an hour in a 20 mL glass vial. The homogeneous mixture was transferred to a 15 mL Teflon vial and closed tightly in a stainless steel solvothermal autoclave, and heated at 115°C for 5 days and then cooled to room temperature at a cooling rate of 2°C/h. Colourless crystals, suitable for single crystal X-ray measurements, were obtained from the bottom

of the vial. Yield; 0.06 g (51 % based on H₃L). M.p. > 250°C. Anal. calcd for C₃₉H₄₃InN₂O₁₂: C, 55.33; H, 5.12; N, 3.31. Found: C, 54.84; H, 5.48; N, 4.57. FT-IR (KBr diluted disc): 3200, 3122, 2924, 1602, 1418, 1243 (s) cm^{−1}.

2.4 X-ray crystallography

The single crystal X-ray data were collected on a Rigaku Saturn 724 CCD diffractometer with a Mo-K α radiation source ($\lambda = 0.71075 \text{ \AA}$) at 150 K under continuous flow of nitrogen. The data integration and indexing were performed using Rigaku Crystal Clear software and a multi-scan method was employed to correct for absorption. The structure was solved by direct methods using *SIR* 92¹⁷ and refined by full-matrix least-squares fitting on F² using *SHELX*-97 programs.¹⁸ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to C atoms were refined isotropically as rigid atoms in their idealized locations. The [(Me)₂NH₂]⁺H-atoms were located from difference Fourier maps and were refined independently. The solvent accessible volumes were calculated using *CALC SOLV* utility of *PLATON*. The data refinement details are been given in table 1.

Table 1. Crystal data and structure refinement details for 1.

formula	C ₃₉ H ₄₃ InN ₂ O ₁₂
formula wt	846.57
temperature [K]	150(2)
wavelength [Å]	0.71075
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> [Å]	9.08(3)
<i>b</i> [Å]	12.01(4)
<i>c</i> [Å]	18.10(10)
α [deg]	82.90(3)
β [deg]	86.40(3)
γ [deg]	70.90(2)
volume (Å) ³	1850(13)
<i>Z</i>	2
density (calcd) [g/cm ³]	1.519
absorption coeff (mm ^{−1})	0.706
<i>F</i> (000)	872
crystal size [mm ³]	0.09 x 0.08 x 0.03
θ range [deg]	2.61 to 25.00
reflection collected	14024
data (Rint)	6479 (0.0642)
completeness to θ [%]	99.1
restraints/parameters	0/487
GoF on F ²	1.132
R1 [<i>I</i> > 2 σ (<i>I</i>)]/all data	0.0754/0.0951
wR2 [<i>I</i> > 2 σ (<i>I</i>)]/all data	0.1292/0.1401
Largest peak and hole (e, Å ^{−3})	0.564, −0.708

3. Results and Discussion

3.1 Synthesis and characterization

The semi-flexible ligand H_3L itself has been synthesized through a one-pot reaction between tris-(bromomethyl)-2,4,6-trimethylbenzene¹⁹ and methyl 4-hydroxybenzoate in DMSO followed by de-esterification by NaOH and neutralization with HCl (scheme 1). The anionic indium carboxylate framework $[(CH_3)_2NH_2][In(L)(HCOO)(DMF)]_n$ (**1**) has been obtained as colourless crystals through hydrothermal synthesis.

Ligand H_3L is characterized by elemental analysis, and mass, NMR and FT-IR spectroscopy while the framework **1** is characterized by elemental analysis, TGA, FT-IR spectroscopy, and powder and single crystal X-ray diffraction studies (see SI for details). The DMF used in the synthesis of **1** not only serves as the reaction medium but also source of cationic $[(Me)_2NH_2]^+$ and formate anion through decomposition under solvo/hydrothermal conditions.

1H NMR spectrum of H_3L (figure S1) in $DMSO-d_6$ exhibits two doublets in the aromatic region at δ 8.04 and 7.05 ppm indicating the presence of *p*-phenylene

Scheme 1. Synthesis of H_3L and **1**.

Figure 1. (a) A portion of the crystal structure of **1** showing bonding environment around In(III) and L^{3-} . (b) Ball and stick representation of the InO_7 polyhedron (H-atoms are omitted for clarity). Selected bond distances (Å): In(1)-O(6), 2.104(7); In(1)-O(11), 2.134(7); In(1)-O(10), 2.220(7); In(1)-O(4), 2.223(10); In(1)-O(9), 2.279(8); In(1)-O(8), 2.289(11); In(1)-O(5), 2.334(10). Selected bond angles ($^\circ$): O(6)-In(1)-O(11), 172.67(2); O(6)-In(1)-O(10), 87.7(3); O(11)-In(1)-O(10), 87.3(3); O(6)-In(1)-O(4), 100.8(3); O(11)-In(1)-O(4), 83.9(2); O(10)-In(1)-O(4), O(6)-In(1)-O(9), 92.0(2); O(11)-In(1)-O(9), 88.4(2); O(10)-In(1)-O(9), 140.2(2); O(4)-In(1)-O(9), 135.77(16); O(6)-In(1)-O(8), 85.3(3); O(4)-In(1)-O(8), 164.13(17); O(10)-In(1)-O(5), 139.73(15).

rings ($-\text{C}_6\text{H}_4-$). Benzylic methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-\text{O}-$) protons appear as two singlets at δ 2.44 and 5.15 ppm, respectively.²⁰ The ethereal ($-\text{CH}_2-\text{O}-$) linkages between peripheral *p*-phenylene rings and central mesitylene ring impart flexibility to the ligand system. A broad singlet at δ 12.69 ppm is assigned to the $-\text{COOH}$ groups. ^{13}C NMR (figure S2) and mass spectra (figure S3) further prove the formation of H_3L .

3.2 Crystal structure of **1**

Compound **1** crystallizes in triclinic *P*-1 space group. The structure solution from single crystal x-ray diffraction data reveals that compound **1** is an anionic lamellar 2-D framework ($Z = 2$). The repeating unit of each 2-D sheet contains one In(III) center coordinated to one L^{3-} ligand, one formate, and one molecule of DMF, while one $[(\text{Me})_2\text{NH}_2]^+$ cation stays outside the metal coordination sphere. The detailed coordination environment behaviour of L^{3-} is shown in figure 1a while the coordination polyhedron of In(III) centre is depicted in figure 1b; the bond lengths and bond angles are listed in table TS1.

The In(III) center in **1** exhibits a pentagonal bipyramidal geometry through coordination to five O atoms from three different L^{3-} ligands (O(4), O(5), O(6), O(7) and O(9)), one formate oxygen (O(11)) and one DMF oxygen (O(10)), thus resulting in an all oxygen coordinated InO_7 polyhedron (figure 1b).²¹ In the InO_7 polyhedra, axial positions are occupied by η^1 coordinated arm of L^{3-} and formate anions, whereas the equatorial positions are occupied by η^2 modes of L^{3-} ligands and the DMF molecule (figure 1a). The axial bonds are slightly compressed with In-O bond distances (2.104 and 2.134 Å) compared to the longer equatorial bonds (2.220–2.334 Å); the average In-O distance is comparable to those reported for similar In-O distances in other indium based framework solids.^{22,23} The O–In–O bond angles vary over a large range of 57.5(3) to 172.67(18)°, where the largest value is associated with the axial O–In–O angle while small angles are found in the chelate rings.

Of the three carboxylate groups at the end of the three arms of L^{3-} , two exhibit bidentate chelating mode of coordination and bind to two different In(III) centres: the third carboxylate group coordinates to a

Figure 2. Crystal structure of **1** (a) a 2-D sheet with hexagonal voids and (b) two centrosymmetry related 2-D sheets (green and orange) connected by H-bonds through InO_7 polyhedron (H-atoms and non-oxygen portions of the coordinated DMF molecules have been omitted for clarity).

third In(III) centre in a terminal unidentate coordination mode. Thus, L^{3-} can be defined as a 3-connecting node. The fact that each L^{3-} connects three metals (or each indium ion is surrounded by three such ligands) results in the formation of a two-dimensional honeycomb sheet-like structure with huge hexagonal voids as shown in figure 2a. *TOPOS*²⁴ analysis indicates that this two-dimensional sheet features a uninodal 6-connected sql/Shubnikov plane net (3,6) with $(3^6.4^6.5^3)$ topology.²⁵ Centrosymmetry related adjacent 2-D sheets are stacked over each other in the lattice in a staggered fashion as shown in figure 2b, thus blocking the voids originally present in each of these sheets. The $[(Me)_2NH_2]^+$ cations present in the lattice form H-bonds (table 2) with carboxylate groups of L^{3-} and hence bridge the adjacent 2-D sheets (by

connecting the adjacent InO_7 polyhedra across centre of inversion) as shown in figure 2b. The layered nature of the final architectures is depicted in figure 3. A schematic representation of the packing diagram is shown in figure 4.

The powder x-ray diffraction (PXRD) pattern (figure S5) obtained for the bulk sample of **1** matches well with the simulated pattern from the single crystal X-ray diffraction data. The thermal decomposition behaviour of **1** (figure S6) as examined by TGA exhibits a two-stage weight loss. The first weight loss of $\sim 15\%$ (calculated: 14%) in the temperature range of 125–210°C corresponds to the loss of DMF and $[(Me)_2NH_2]^+$ moieties. The second weight loss observed from 210 to 480°C is due to the decomposition of the organic ligand.

Table 2. Hydrogen bond parameters (distances in Å and angles in °) of **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2WA)...O(7) ^a	0.995(7)	1.974(10)	2.800(15)	138.8(4)
N(2)-H(1WB)...O(5) ^b	0.945(6)	2.383(8)	2.954(12)	118.6(4)
N(2)-H(1WB)...O(9) ^c	0.945(6)	2.167(10)	2.925(13)	136.4(4)

Symmetry transformations used to generate equivalent atoms:

^a $-x+1, -y, -z+2$ ^b $x, y, z-1$ ^c $x+1, y, z$

Figure 3. (a) Ball and stick model and (b) space fill model (the atoms are represented by spheres of van der Waals radii) views of crystal structure of **1**. Green and pink nets are two centrosymmetry related networks.

Figure 4. Schematic representation of the 2-fold interpenetration in **1**.

3.3 Surface area measurements of **1**

N₂ adsorption isotherm measurements at 77 K reveals almost no N₂ uptake (figure S7) indicating densely packed crystal lattice mainly resulting from the slipped packing of the adjacent layers blocking the possible pores as well as the presence of dimethylammonium cations. The calculated BET and Langmuir surface areas based on N₂ adsorption are just 2.92 m²/g and 7.78 m²/g, respectively. In contrast, a BET surface area of 6.85 m²/g and a relatively higher uptake (0.034 wt %) of H₂ gas has been observed at 77 K (figure S8).

4. Conclusions

An anionic new 2-D In(III) carboxylate using a flexible tri-carboxylic acid has been synthesized and characterized by elemental analysis, TGA, PXRD, FT-IR spectroscopy and single crystal X-ray diffraction. The cationic [(Me)₂NH₂]⁺ species, generated from the decomposition of DMF molecules under solvothermal conditions, play a major role in packing of the 2-D sheets through H-bonds with InO₇ polyhedron across centre of symmetry. The complex features an anionic uninodal 6-connected sql/Shubnikov plane net (3,6) with (3⁶.4⁶.5³) topology. Since the solvent used in the present study has directed the final structure through its decomposition to ionic constituents, we are currently exploring the possibilities of isolating other types of heavier main group metal by employing H₃L as ligand system.

Supplementary Information

CCDC 966488 contains supplementary crystallographic data in CIF format that can be obtained free of

charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html. ¹H and ¹³C NMR, ESI-MS, and FT-IR spectra, PXRD patterns, TGA curve, N₂ and H₂ adsorption/desorption curves.

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