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# Hydrothermal synthesis of two layered indium oxalates with 12-membered apertures

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**Abstract**

Two layered indium oxalates, $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$, I, and $In(C_2O_4)_{1.5}(H_2O)_3$, II, have been hydrothermally synthesized. In I, the linkage between indium and oxalate units gives rise to a sheet with a rectangular 12-membered aperture (six indium atoms and six oxalate units). Indium atom of II has an unusual pentagonal bipyramidal coordination arrangement. The connectivity between indium and oxalate units forms a neutral puckered layer with 12- (along *a*-axis) and eight-membered (along *b*-axis) apertures. Crystal data for these two indium oxalates are as follows: I, triclinic, space group: *P*-1 (No. 2), $a = 8.725(3)$ Å, $b = 9.170(3)$ Å, $c = 9.901(3)$ Å, $\alpha = 98.101(4)^\circ$, $\beta = 97.068(4)^\circ$, $\gamma = 102.403(4)^\circ$, $V = 756.3(4)$ Å$^3$, $Z = 2$, $M = 463.0(5)$, $\rho_{calc} = 2.042$ g/cm$^3$, $R_1 = 0.0377$, w$R_2 = 0.0834$. II, monoclinic, space group: $P2_1/c$ (No. 14), $a = 10.203(5)$ Å, $b = 6.638(1)$ Å, $c = 11.152(7)$ Å, $\beta = 95.649(4)^\circ$, $V = 751.7(4)$Å$^3$, $Z = 4$, $M = 300.9(0)$, $\rho_{calc} = 2.659$ g/cm$^3$, $R_1 = 0.0229$, w$R_2 = 0.0488$. TG analyses indicate the water molecules of I can be removed at 150°C. The dehydrated product retains structural integrity.


*Keywords:* Hydrothermal synthesis; Indium oxalate; Crystal structure; Open framework

## 1. Introduction

The synthesis of open-framework materials has emerged as an important area of research because of their potential applications in separation processes, ion exchange and catalysis. Aluminosilicate represents the predominant class of open-framework materials [1,2]. A large number of metal phosphates have been synthesized since 1982 [3]. The synthesis of other chemistry composition open-framework materials such as germanate, chalcogenides, halides, nitrides and oxides, phosphonates, carboxylates has also been accomplished [4,5]. In the past few years, there has been considerable effort in designing open-framework structures formed by metal organic carboxylates because of its interesting structural features and the quality for apt design [6,7]. Open-framework metal oxalate is a new family of metal organic materials. Some divalent metals such as tin(II) [8–10], zinc [11–13] and cadmium [14–19] oxalates have been reported in the last 3–4 years. Some of these structures are monomers, some are layered oxalates with honeycomb networks. Three-dimensional structures are formed if oxalate units link the layers. Recently, rare earth [20–22] or yttrium(III) [23–25] oxalate structures were reported, which showed more interesting structural features because of its high coordination. Similar to rare earth metal, the heavy group 13 element, indium has a high coordinated number and can construct novel open frameworks. But unfortunately, to the best of our knowledge [26,27], only a few indium oxalate open frameworks have been reported. In this paper, we report the hydrothermal synthesis of two open-framework two-dimensional indium oxalates, $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$, I, and $In(C_2O_4)_{1.5}(H_2O)_3$, II. I is synthesized by using 1,3-diaminopropane as structure-directing agent, while II is prepared without using any organic amines. Both of the indium oxalates contain large 12-membered apertures. The indium atom of structure I is coordinationed with eight oxalate oxygens, the linkage between indium and oxalate units forms a sheet with a rectangular 12-membered aperture. The organic amine and water molecules are located between two sheets, interacting with the sheets by hydrogen bonds. Form II

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is isostructural with the indium oxalate dihydrate reported by Bulc et al. [26]. In II, indium atom is seven coordinated with two water molecules and two and a half oxalate units, resulting in a neutral puckered layer with 12- (along *a*-axis) and eight-membered (along *b*-axis) apertures.

## 2. Experimental section

### 2.1. Hydrothermal synthesis

The indium oxalates I and II were hydrothermally synthesized under autogenous pressure. In a typical reaction mixture of composition of I, 0.40 g $In(NO_3)_3 \cdot 4.5H_2O$ was dissolved in 10.03 g of deionized water, then 0.507 g oxalic acid and 0.262 g 1,3-diaminopropane were added with constant stirring. Phosphoric acid was added until the pH of the final mixture was 1.7 with the molar ratio $In(NO_3)_3 \cdot 4.5H_2O$:$3.8H_2C_2O_4$:$1.1H_3PO_4$:$3.4C_3N_2H_{10}$:$531 \cdot 8H_2O$. The gel was then transferred into a 23-mL PTFE bottle, and sealed in a stainless-steel autoclave. The sealed pressure bomb was heated at 100°C for 48 h. For II, the initial mixture contained a mixture of 0.37 g $In(NO_3)_3 \cdot 4.5H_2O$, 0.510 g oxalic acid, 0.127 g phosphoric acid (85 wt%), and 10.48 g water, which has a pH of 1.1 in the molar ratio $In(NO_3)_3 \cdot 4.5H_2O$: $4.2H_2C_2O_4$:$1.1H_3PO_4$:$600 \cdot 4H_2O$. The starting mixture was stirred at room temperature for 24 h, then heated in the autoclave at 100°C for 72 h. The products of I and II were filtered and washed thoroughly with deionized water. Product I of transparent quadrate single crystal was obtained in 81% yield. A large octahedron crystal of product II was separated in 45% yield.

### 2.2. Characterization

Powder X-ray diffraction (XRD) data were obtained from a Brucker D4 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The $2\theta$ angles are in the range 3–45°. The step size was 0.1 s and the increment was 0.01°. Thermogravimetric analysis was performed on a Perkin–Elmer TEC 7/DX analyzer in $N_2$ atmosphere with a heating rate of 5°C/min, from 25°C to 700°C.

### 2.3. Single-crystal structure determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with adhesive. Single-crystal structure determination by XRD was performed on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. A hemisphere of intensity data was collected at room temperature with a scan width of 0.30° in $\omega$ and exposure time of 10 s per frame. An empirical absorption corrections based on the SADABS program was applied for both compounds. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. The structure was solved by direct method followed by successive difference Fourier methods. All calculations were performed using SHELXS and SHELXTL-97, and final full-matrix refinements were against $F^2$. Details of the final refinements are given in Table 1. The final atomic coordinates, and selected bond distances and angles are presented in Tables 2–4 for I; Tables 5 and 6 for II.

Table 1
Crystal data and structure refinement parameters for I $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$ and II $In(C_2O_4)_{1.5}(H_2O)_3$

| | I | II |
|---|---|---|
| Empirical formula | $InO_{13}C_8N_2H_{16}$ | $InO_9C_3H_6$ |
| Formula weight | 463.05 | 300.90 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P*-1 | *P*2(1)*c* |
| *a* (Å) | 8.725(3) | 10.203(3) |
| *b* (Å) | 9.170(3) | 6.638(2) |
| *c* (Å) | 9.901(3) | 11.153(3) |
| $\alpha$ (deg) | 98.101(4) | 90 |
| $\beta$ (deg) | 97.068(4) | 95.649(4) |
| $\gamma$ (deg) | 102.403(4) | 90 |
| Volume (Å$^3$) | 756.3(4) | 751.7(4) |
| *Z* | 2 | 4 |
| $\rho_{calcu}$ (g/cm$^3$) | 2.042 | 2.659 |
| $\mu$ (mm$^{-1}$) | 1.638 | 3.172 |
| *F*(000) | 466 | 580 |
| Crystal size (mm) | $0.20 \times 0.05 \times 0.02$ | $0.50 \times 0.20 \times 0.20$ |
| $2\theta$ range (deg) | 2.10 to 25.01 | 2.01 to 27.14 |
| Index ranges | $-10 \leqslant h \leqslant 6$, $-10 \leqslant k \leqslant 10$ $-8 \leqslant l \leqslant 11$ | $13 \leqslant h \leqslant 7$, $-8 \leqslant k \leqslant 7$ $-14 \leqslant l \leqslant 12$ |
| Reflections collected | 3179 | 3372 |
| Independent reflections | 2621 [$R_{int} = 0.0254$] | 1626 [$R_{int} = 0.0190$] |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data with [$I > 2\sigma(I)$]/ parameter | 2621/243 | 1626/142 |
| Goodness-of-fit on $F^2$ | 1.034 | 1.152 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0379$ | $R_1 = 0.0229$ |
| | $wR_2 = 0.0840$ | $wR_2 = 0.0488$ |
| *R* indices (all data) | $R_1 = 0.0443$ $wR_2 = 0.0864$ | $R_1 = 0.0262$ $wR_2 = 0.0499$ |
| Largest difference map peak and hole (e Å$^{-3}$) | 0.688 and −0.777 | 0.512 and −0.421 |

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

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for I $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| In(1) | 2800(1) | 1909(1) | 9171(1) | 18(1) |
| O(1) | −21(5) | 3860(4) | 6524(4) | 35(1) |
| O(2) | 1140(5) | 1783(4) | 4953(3) | 34(1) |
| O(3) | 1193(4) | 3279(4) | 8421(4) | 29(1) |
| O(4) | 2289(4) | 1245(4) | 6881(3) | 26(1) |
| O(5) | 4538(4) | 3879(4) | 8386(4) | 27(1) |
| O(6) | 3885(4) | 3793(4) | 10920(3) | 26(1) |
| O(7) | 3737(4) | 736(4) | 10968(4) | 28(1) |
| O(8) | 4771(4) | 891(4) | 8574(3) | 26(1) |
| O(9) | 962(4) | 1879(4) | 10657(4) | 26(1) |
| O(10) | 1183(4) | -436(4) | 8778(3) | 25(1) |
| O(11) | 8138(8) | 3625(7) | 103(8) | 80(2) |
| O(12) | 2739(7) | 4026(6) | 3511(6) | 55(1) |
| O(13) | 2016(6) | −348(6) | 3041(6) | 50(1) |
| C(1) | 794(6) | 3129(5) | 7115(5) | 24(1) |
| C(2) | 1455(6) | 1947(6) | 6235(5) | 24(1) |
| C(3) | 5200(6) | 5027(5) | 9276(5) | 22(1) |
| C(4) | 5307(6) | 44(5) | 9312(5) | 22(1) |
| C(5) | −53(6) | 663(5) | 10542(5) | 21(1) |
| C(6) | 4461(7) | 7684(7) | 4647(6) | 40(1) |
| C(7) | 3587(8) | 8083(7) | 5799(6) | 46(2) |
| C(8) | 2600(7) | 6719(7) | 6247(6) | 39(1) |
| N(1) | 3375(6) | 7190(5) | 3301(5) | 36(1) |
| N(2) | 1110(6) | 7009(5) | 6656(5) | 33(1) |

$U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 3
Selected bond lengths (Å) and Angles (deg) for I $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$

| | | | |
|---|---|---|---|
| In(1)–O(3) | 2.204(3) | O(4)–C(2) | 1.247(6) |
| In(1)–O(6) | 2.221(3) | O(5)–C(3) | 1.253(6) |
| In(1)–O(4) | 2.226(3) | O(6)–C(3)#1 | 1.254(6) |
| In(1)–O(8) | 2.227(3) | O(7)–C(4)#2 | 1.242(6) |
| In(1)–O(10) | 2.256(3) | O(8)–C(4) | 1.261(6) |
| In(1)–O(9) | 2.304(3) | O(9)–C(5) | 1.247(6) |
| In(1)–O(7) | 2.356(3) | O(10)–C(5)#3 | 1.258(6) |
| In(1)–O(5) | 2.383(3) | C(1)–C(2) | 1.547(7) |
| O(1)–C(1) | 1.228(6) | C(3)–C(3)#1 | 1.522(10) |
| O(2)–C(2) | 1.246(6) | C(4)–C(4)#2 | 1.530(10) |
| O(3)–C(1) | 1.277(6) | C(5)–C(5)#3 | 1.532(9) |
| Organic moiety | | | |
| C(6)–N(1) | 1.488(8) | C(7)–C(8) | 1.513(8) |
| C(6)–C(7) | 1.495(9) | C(8)–N(2) | 1.474(7) |
| O(3)–In(1)–O(4) | 73.59(12) | C(3)–O(5)–In(1) | 116.0(3) |
| O(3)–In(1)–O(10) | 102.23(14) | C(3)#1–O(6)–In(1) | 120.4(3) |
| O(6)–In(1)–O(10) | 139.32(12) | C(4)#2–O(7)–In(1) | 115.5(3) |
| O(10)–In(1)–O(9) | 71.82(12) | C(4)–O(8)–In(1) | 119.6(3) |
| O(8)–In(1)–O(7) | 70.57(12) | C(5)–O(9)–In(1) | 116.1(3) |
| O(3)–In(1)–O(5) | 76.96(13) | C(5)#3–O(10)–In(1) | 117.7(3) |
| O(6)–In(1)–O(5) | 70.13(12) | O(1)–C(1)–O(3) | 125.6(5) |
| O(4)–In(1)–O(5) | 76.40(12) | O(1)–C(1)–C(2) | 118.9(4) |
| O(8)–In(1)–O(5) | 75.34(13) | O(2)–C(2)–O(4) | 125.2(5) |
| O(10)–In(1)–O(5) | 150.36(12) | O(2)–C(2)–C(1) | 118.3(4) |
| O(9)–In(1)–O(5) | 133.80(12) | O(5)–C(3)–C(3)#1 | 115.6(5) |
| O(7)–In(1)–O(5) | 120.83(13) | O(8)–C(4)–C(4)#2 | 116.3(5) |
| C(1)–O(3)–In(1) | 117.2(3) | O(9)–C(5)–C(5)#3 | 117.5(5) |
| C(2)–O(4)–In(1) | 117.0(3) | | |
| Organic moiety | | | |
| N(1)–C(6)–C(7) | 111.5(5) | N(2)–C(8)–C(7) | 112.0(5) |
| C(6)–C(7)–C(8) | 113.7(5) | | |

Symmetry transformations used to generate equivalent atoms: #1 $-x+1,-y+1,-z+2$; #2 $-x+1,-y,-z+2$; #3 $-x,-y,-z+2$.

## 3. Results

### 3.1. Synthesis and initial characterization

New open-framework indium oxalate $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$ I can be hydrothermally synthesized by using 1,3-diaminopropane as structure directing-agent and $In(NO_3)_3$ as an indium source. Product I can be obtained at a wide temperature range of room temperature to 150°C. The crystallization temperature affects the size of the crystals. The optimum condition is at 100°C for 72 h, the resultant crystals are well-proportioned, transparent and quadrate. Powder X-ray diffraction (PXRD) pattern showed that product I was pure phase. If the initial gel does not include 1,3-diaminopropane, product II is formed. Obtained product II consists of a small quantity of large octahedron crystals accompanied with white powders. Powder X-ray diffraction (PXRD) pattern showed that the powdered crystals were identified purities.

### 3.2. Structure of indium oxalate I

The asymmetric unit of I contains 24 non-hydrogen atoms, of which 16 belong to the framework (Fig. 1a). Each In atom is coordinated with four oxalate units or eight oxalate oxygens, forming a distorted square-antiprismatic arrangement (Fig. 1b). Two oxygen atoms of the oxalate units (O1 and O2) are not coordinated with any In atoms. The indium atoms are linked by the rest of the oxalate oxygens, giving rising to a rectangular network sheet (Fig. 2a). The structure consists of those macroanion sheets of formula $[In(C_2O_4)_{2.5}]^{2-}$ with interlamellar protonated amine $[H_3N(CH_2)_3NH_3]^{2+}$ ions. The 12-membered apertures exist within the sheets, which stack one over the other, yielding a unidimensional channel along the $c$-axis. The longest atom–atom contact distance of channel size is calculated to be $7.8 \times 10.8$ Å, if the van der Waals radii is considered. Two protonated organic amine and six water molecules interacting with the framework by hydrogen bonds can be observed along the 12-membered aperture (Fig. 2b). The important hydrogen-bond interactions are listed in Table 4. Along $c$-axis, the sheets stack one over the other with the water molecules situated between the layers as shown in Fig. 3.

Of the eight oxygens that are bound to indium, four In–O distances are in the range 2.204–2.256 Å, the remaining four have a longer distance of range

Table 4
Hydrogen bonds for I $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$ (Å and deg)

| D–H···A | d(D–H) (Å) | d(H···A) (Å) | d(D···A) (Å) | Angel D–H···A (deg) |
|---|---|---|---|---|
| O(11)–H(11A)···O(9)#1 | 0.80(2) | 2.55(8) | 3.247(8) | 147(13) |
| O(13)–H(13A)···O(2) | 0.80(6) | 2.04(6) | 2.818(6) | 167(6) |
| O(12)–H(12A)···O(2) | 0.79(6) | 2.10(6) | 2.882(7) | 170(6) |
| N(2)–H(2C)···O(1)#3 | 0.89 | 2.47 | 3.112(6) | 129.2 |
| N(2)–H(2B)···O(1) | 0.89 | 2.04 | 2.823(6) | 145.9 |
| N(2)–H(2A)···O(10)#4 | 0.89 | 2.04 | 2.902(5) | 162.1 |
| N(1)–H(1B)···O(8)#2 | 0.89 | 2.59 | 3.098(6) | 117.0 |
| N(1)–H(1C)···O(13)#4 | 0.89 | 1.91 | 2.794(7) | 169.8 |
| N(1)–H(1A)···O(12) | 0.89 | 2.22 | 2.876(7) | 130.6 |

Symmetry transformations used to generate equivalent atoms: #1 $x+1, y, z-1$; #2 $-x+1, -y+1, -z+1$; #3 $-x, -y+1, -z+1$; #4 $x, y+1, z$.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for II $In(C_2O_4)_{1.5}(H_2O)_3$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| In(1) | 2621(1) | 1526(1) | 4748(1) | 15(1) |
| O(1) | 552(2) | 1536(4) | 3896(2) | 22(1) |
| O(2) | 3882(2) | 1189(4) | 6466(2) | 19(1) |
| O(3) | 4627(2) | 2813(4) | 4514(2) | 20(1) |
| O(4) | 1475(2) | −484(4) | 5863(2) | 22(1) |
| O(5) | 2629(2) | 2578(4) | 2838(2) | 21(1) |
| O(6) | 2039(3) | 4472(4) | 5319(2) | 24(1) |
| O(7) | 3302(2) | −1286(4) | 4062(2) | 21(1) |
| O(8) | 5949(2) | 3942(4) | 3192(2) | 24(1) |
| O(9) | 9884(4) | 1491(6) | 1378(3) | 43(1) |
| C(1) | −273(3) | 579(5) | 4433(3) | 18(1) |
| C(2) | 3676(3) | 1748(5) | 7501(3) | 16(1) |
| C(3) | 4871(3) | 3361(5) | 3475(3) | 16(1) |

$U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 6
Selected bond lengths (Å) and angles (deg) for II $In(C_2O_4)_{1.5}(H_2O)_3$

| | | | |
|---|---|---|---|
| In(1)–O(1) | 2.228(2) | O(2)–C(2) | 1.249(4) |
| In(1)–O(2) | 2.212(2) | O(3)–C(3) | 1.263(4) |
| In(1)–O(3) | 2.257(2) | O(4)–C(1)#1 | 1.240(3) |
| In(1)–O(4) | 2.231(2) | O(5)–C(2)#2 | 1.251(4) |
| In(1)–O(5) | 2.243(2) | O(8)–C(3) | 1.236(4) |
| In(1)–O(6) | 2.158(3) | C(1)–C(1)#1 | 1.535(6) |
| In(1)–O(7) | 2.158(2) | C(3)–C(2)#2 | 1.551(4) |
| O(1)–C(1) | 1.254(4) | | |
| | | | |
| O(6)–In(1)–O(7) | 174.83(10) | O(7)–In(1)–O(3) | 87.62(9) |
| O(6)–In(1)–O(2) | 89.42(9) | O(2)–In(1)–O(3) | 71.42(8) |
| O(7)–In(1)–O(2) | 92.25(9) | O(5)–In(1)–O(3) | 71.59(7) |
| O(6)–In(1)–O(1) | 81.17(10) | C(1)–O(1)–In(1) | 116.53(19) |
| O(7)–In(1)–O(1) | 100.16(9) | C(2)–O(2)–In(1) | 129.38(19) |
| O(6)–In(1)–O(4) | 101.73(10) | C(3)–O(3)–In(1) | 118.55(18) |
| O(7)–In(1)–O(4) | 83.43(9) | C(1)#1–O(4)–In(1) | 116.2(2) |
| O(2)–In(1)–O(4) | 75.48(8) | C(2)#2–O(5)–In(1) | 118.68(18) |
| O(1)–In(1)–O(4) | 73.32(8) | O(2)–C(2)–O(5)#3 | 127.5(3) |
| O(6)–In(1)–O(5) | 91.41(9) | O(8)–C(3)–O(3) | 125.8(3) |
| O(7)–In(1)–O(5) | 84.31(9) | O(8)–C(3)–C(2)#2 | 119.5(3) |
| O(1)–In(1)–O(5) | 71.68(8) | O(3)–C(3)–C(2)#2 | 114.7(2) |
| O(6)–In(1)–O(3) | 88.28(10) | O(1)–C(1)–C(1)#1 | 116.2(3) |

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z+1$; #2 $x, -y+1/2, z-1/2$; #3 $x, -y+1/2, z+1/2$.

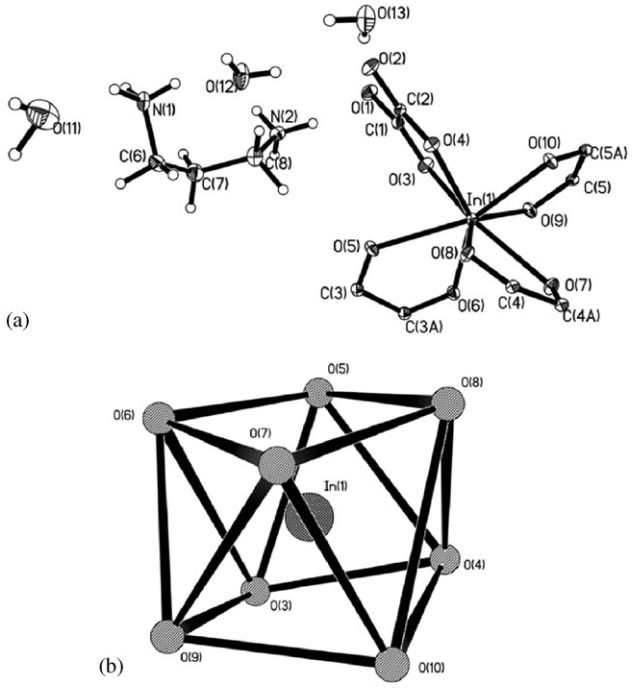


Fig. 1. (a) ORTEP plot of indium oxalate open framework I, thermal ellipsoids are given at 30% probability, and (b) distorted square antiprismtic coordination environment around indium.

2.226–2.383 Å, because the two types of oxygens are single and double bonded to carbon atoms, respectively. The distances of C–O bonds confirmed this difference. The O–In–O bond angles are in the range 70.13–139.32° (Table 3).

### 3.3. Structure of II

The asymmetric unit of indium oxalate II contains 13 non-hydrogen atoms, including 12 framework atoms and one free oxygen atom corresponding to guest water molecule (Fig. 4a). The hydrogen atoms of water molecules are located and refined with isotropic thermal parameters. Unlike I, the In atom in II is bonded to two

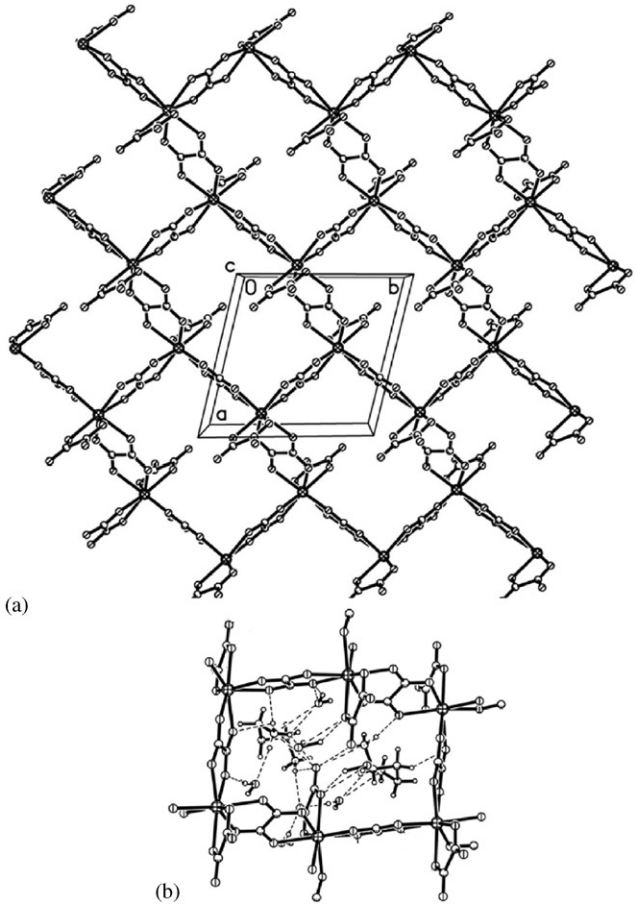


Fig. 2. (a) Structure of indium oxalate open framework I, along the *c*-axis, showing the square sheet, and (b) structure showing a single 12-membered aperture with 1,3-diaminopropane and water molecules. Dotted lines: hydrogen bond.

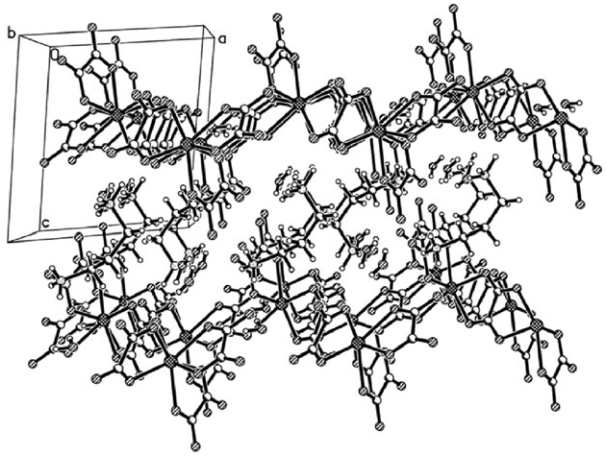


Fig. 3. Structure of indium oxalate open framework I, along *b*-axis, showing the layer arrangement.

water molecules and three oxalate units, one of which is monocoordinated with indium, showing an unusual seven coordinated. The five oxygens (O1–O5) of the oxalates lie in a plane and form a pentagon, while the

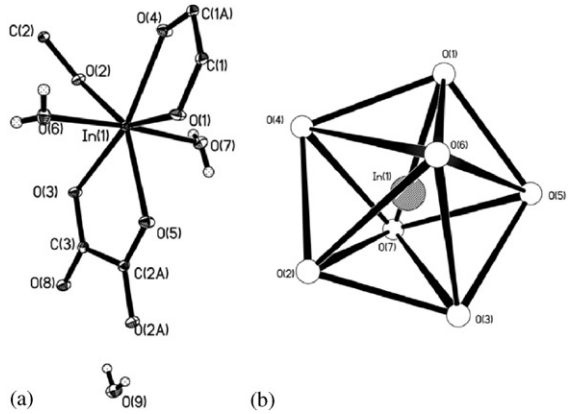


Fig. 4. (a) ORTEP plot of indium oxalate open framework II, thermal ellipsoids are given at 30% probability, and (b) pentagonal bipyramidal stereochemistry around indium.

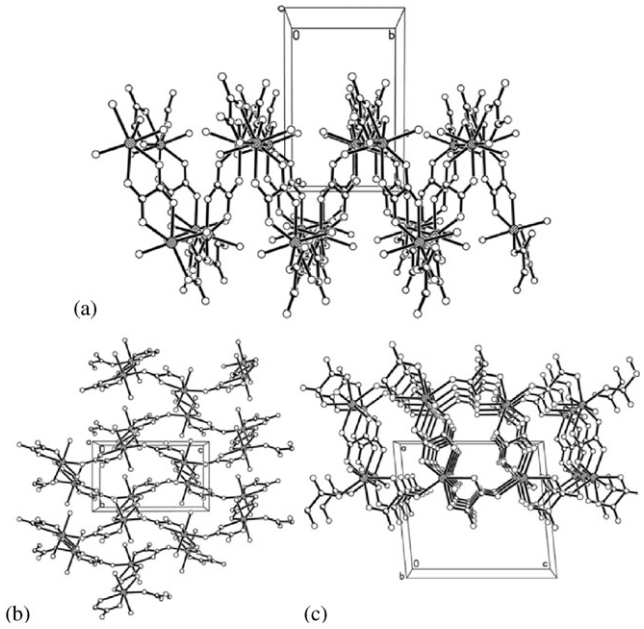


Fig. 5. (a) Structure of indium oxalate open framework II, a single puckered layer like a zigzag chain, (b) 12-membered aperture along *a*-axis of one layer, and (c) eight-membered aperture along *b*-axis of one layer.

other two oxygen atoms (O6, O7) form two vertices above and below the pentagon, respectively (Fig. 4b). It can be described as a pentagonal bibyramidal unit. The connectivity of such unit results in a puckered layer, the individual layer showing a zigzag structure along *c*-axis (Fig. 5a). These layers are neutral with formula $In(C_2O_4)_{1.5}(H_2O)_2$ and the structure consists of a circular 12-membered aperture with the calculated size of $6.5 \times 9.6$ Å along *a*-axis (Fig. 5b) and an eight-membered aperture with the small size of $5.3 \times 8.5$ Å along *b*-axis (Fig. 5c). The water molecules between the layers are not protonated and interact with the layers through the hydrogen bonds (Fig. 6).

The In–O distances are in the range of 2.158–2.257 Å (average 2.212 Å), similar to structure I and other metal oxalates reported previously [9,10]. The long distances are associated with the oxygens that are double bonded to the carbon atoms. The oxygen atoms (O6, O7) are from structural waters, so the distances of In–O(6) and In–O(7) are short (2.158 Å). The distances of C–O bonds are normal in the range 1.254–1.263 Å. The O–In–O and O–C–O bond angles are in the range 71.42–174.83° and 125.8–127.5°, respectively (Table 6).

TGA curve for product I (Fig. 7) shows four weight-loss steps. The first weight loss of 11.5 wt% at the range of 60–150°C corresponds to the loss of three free water molecules (calculated 11.7 wt%). There is a 'plateau' around 150°C after the loss of water. X-ray powder diffraction reveals that the dehydrated product retains structural integrity after calcination at 150°C for 6 h in air. The following continuous three-step weight loss of 58.3 wt% at the range of 210–300°C, 310–420°C, 425–700°C can be assigned to the loss of organic amine and carbon dioxide (calculated 58.3 wt%). The final decomposed product (weight 30.2%) corresponds to the $In_2O_3$ (calculated 30.0 wt%). Different from product I, the weight loss for product II occurs in two steps. The weight loss of 18.0 wt% at the range 100–200°C can be assigned to the loss of three water molecules (calculated 17.9 wt%). The second weight loss step of 35.3 wt% occurs in the range 250–350°C corresponding to the loss of carbon dioxide (calculated 35.9 wt%). The final decomposed product (weight 46.7%) corresponds to the $In_2O_3$ (calculated 46.2 wt%).

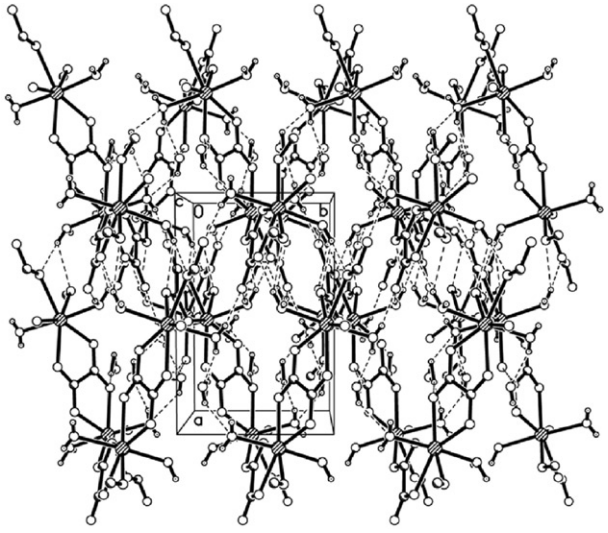

Fig. 6. Structure of indium oxalate open framework II, along *c*-axis, showing two layers. Dotted lines: hydrogen bond.

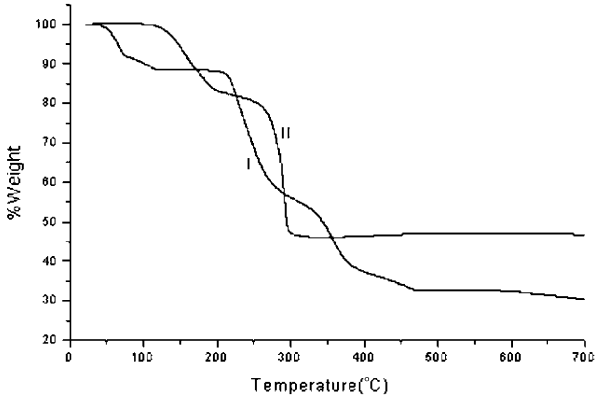


Fig. 7. TG analyses of indium oxalate I and II.

## 4. Discussion

Two indium oxalate open frameworks with two-dimensional structures, I, $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$ and II, $In(C_2O_4)_{1.5}(H_2O)_2$ have been hydrothermally synthesized at a low pH in the presence of phosphoric acid. The phosphoric anion was added to adjust the pH of the synthesis mixture, which does not construct the framework. We believe it may act as a mineralizer, similar to $F^-$ ions in some of the phosphate-based framework solids. The phenomenon has also been observed in the synthesis of tin(II) oxalates reported earlier by Rao and co-workers [9]. Product I is synthesized in the presence of 1,3-diaminopropane, while product II is an open-framework metal oxalate synthesized without the organic amine or other structure directing agents.

I and II are new members of indium oxalates family. Both of them involve the bonds between indium and oxalates and exhibit two-dimensional layered open-framework structure. I shows a 12-membered aperture only along *c*-axis, but II has a puckered layer with 12-membered aperture (along *a*-axis) and eight-membered aperture (along *b*-axis). These structures then owe differences to the distinct coordination of indium. In structure I, the indium atom is eight-coordinated with oxalate units. The eight-coordinated oxygen atoms form a distorted square antiprism. While in structure II, the indium atom is unusually seven-coordinated, of which two-coordinated atoms come from water not from oxalate oxygens. The oxygens of water molecules are nearly perpendicular to the plane formed by the five oxygens of the oxalate units. Such a real pentagonal bipyramidal unit for open-framework material is scarcely observed. The tin oxalate has similar building unit with II only when the long pair of electrons is considered [8,9]. Structure I consists of negative sheets and the organic amine used in the synthesis acts as a couterion and stabilizes the framework by interactions of hydrogen bonds. By contrast, framework II is neutral and shows a zigzag layered structure. A similar zigzag chain has been observed in zinc oxalates, the difference

between them is that the later reveals only one-dimensional structure [12,28].

The indium oxalates, I and II, are distinctly different from the open-framework Sn(II) and Zn oxalates reported recently. Both of the Sn [8–10] and Zn [11] atoms are six coordinated with oxygen, tending to form a layered structure. However, high coordination metal ions such as Cd [16], Y [23] favor to coordinate with four oxalate units and link the framework into a three-dimensional structure. Indium atoms of framework I and II are highly coordinated with oxalates similar to that for Cd and Y atoms and result in the formation of the high coordination arrangement. But not all of the oxalate units are bonded to the indium, which may result in a two-dimensional layered structure, implying a possibility to synthesize three-dimensional indium oxalates under appropriate conditions.

## 5. Conclusions

The two new layered indium oxalate open frameworks have been successfully prepared by hydrothermal methods at low temperature even, room temperature, in the presence or absence of organic amines. Indium oxalate I, $In(C_2O_4)_{2.5}(C_3N_2H_{12})(H_2O)_3$, can be formed at a wide synthesis condition by using 1,3-diaminopropane as structure directing agent and has a two-dimensional layered structure with a large 12-membered aperture ($7.8 \times 10.8$ Å) along *c*-axis. Another indium oxalate open framework, $In(C_2O_4)_{1.5}(H_2O)_2$, II, synthesized without any organic amine has a puckered layer with two channels of 12-membered aperture ($6.5 \times 9.6$ Å) along *a*-axis and an eight-membered aperture ($5.3 \times 8.5$ Å) along *b*-axis. The diversity of indium atom's coordinated number suggests a possibility to synthesize more complicated three-dimensional indium oxalates with large pore structures.

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