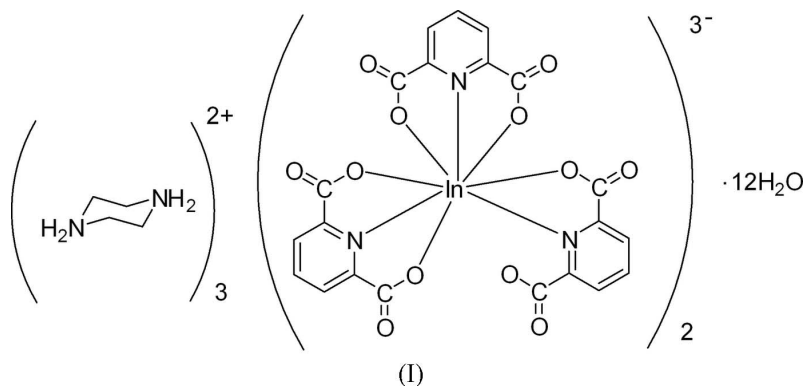


**Tris(piperazinediium) bis[tris(pyridine-2,6-dicarboxylato)- $\kappa^6O,N,O'$ ;  $\kappa^2O,N$ -indate(III)] dodecahydrate****Hossein Aghabozorg,<sup>a\*</sup>  
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aghabozorg@saba.tmu.ac.ir**Key indicators**Single-crystal X-ray study  
 $T = 294$  K  
Mean  $\sigma(C-C) = 0.003$  Å  
 $R$  factor = 0.031  
 $wR$  factor = 0.081  
Data-to-parameter ratio = 17.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The asymmetric unit of the title compound,  $(C_4H_{12}N_2)_3\text{[In}(C_7H_3NO_4)_3\text{]}\cdot 12H_2O$ , contains one and a half cations, one anion and six water molecules. The  $\text{In}^{\text{III}}$  atom is eight-coordinated by two tridentate and one bidentate pyridine-2,6-dicarboxylate ligand. Intra- and intermolecular  $N-H\cdots O$  and  $O-H\cdots O$  hydrogen bonds seem to be effective in the stabilization of the crystal structure, resulting in the formation of a supramolecular structure.

**Comment**

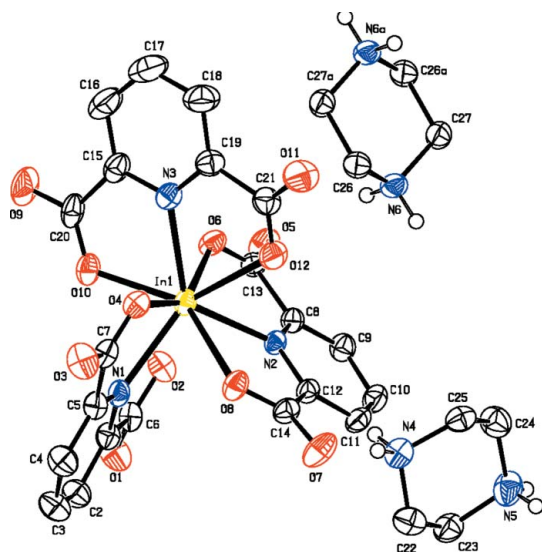
Recently, several metal complexes containing anionic forms of pyridine-2,6-dicarboxylic acid,  $\text{pydcH}_2$ , have been synthesized, (Lü *et al.*, 2005; Ghosh & Bharadwaj, 2004; Brouca-Cabarrecq *et al.*, 2002; Moghimi *et al.*, 2002, 2004; Aghabozorg, Ghadermazi *et al.*, 2006; Aghabozorg, Nakhjavan *et al.*, 2006). In recent years, we have synthesized a few complexes of the proton-transfer compound piperazinediium pyridine-2,6-dicarboxylate,  $(\text{pipzH}_2)(\text{pydc})$ , such as  $(\text{pipzH}_2)[\text{Ti}_2(\text{pydc})_2\text{Cl}_4(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  and  $(\text{pipzH}_2)[\text{Pd}(\text{pydc})_2]\cdot 2\text{H}_2\text{O}$  (Aghabozorg, Ramezanipour *et al.*, 2006). We report here the synthesis and crystal structure of the title complex, (I).



The asymmetric unit of (I) (Fig. 1) contains one and a half cations, one anion and six water molecules. The bond lengths and angles (Table 1) are within normal ranges (Allen *et al.*, 1987). The piperazine rings *A* (N4/N5/C22–C25) and *B* (N6/N6a/C26/C26a/C27/C27a) are not planar, having total puckering amplitudes,  $Q_T$ , of 0.906 (5) and 1.431 (4) Å and chair conformations [ $\varphi = 24.69$  (5)°,  $\theta = 54.57$  (4)° and  $\varphi = -165.86$  (5)°,  $\theta = 0.00$  (3)°] (Cremer & Pople, 1975). The  $\text{In}^{\text{III}}$  atom is eight-coordinated by two tridentate and one bidentate pyridine-2,6-dicarboxylate ligands. The central  $\text{In}^{\text{III}}$  atom is linked to the ligands by  $\text{In}-\text{O}$  and  $\text{In}-\text{N}$  bonds. These distances are almost in the same range in the  $\text{In}^{\text{III}}$  complexes (Ramezanipour *et al.*, 2005). The  $\text{In}-\text{O}$  and  $\text{In}-\text{N}$  bonds are

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**Figure 1**  
The asymmetric unit of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Water molecules and H atoms attached to carbon are omitted for clarity.

in the ranges 2.2434 (14)–2.4532 (15) and 2.2777 (16)–2.3586 (15) Å, respectively (Table 1).

Intra- and intermolecular N–H···O and O–H···O hydrogen bonds (Table 2) seem to be effective in the stabilization of the crystal structure, resulting in the formation of a supramolecular structure (Fig. 2).

### Experimental

A solution of  $\text{In}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  (518 mg, 1 mmol) in water (20 ml) was added to an aqueous solution of (pipzH<sub>2</sub>)(pydc) (506 mg, 2 mmol, 20 ml water) in a 1:2 molar ratio. Colorless crystals of (I) were obtained after allowing the mixture to stand for three weeks at room temperature.

#### Crystal data

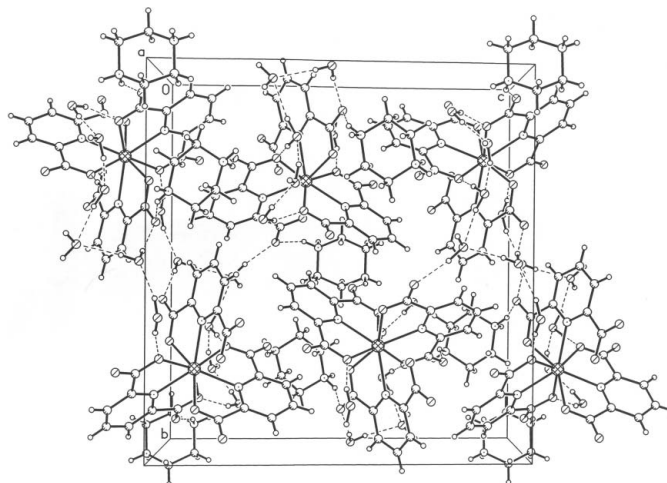
$(\text{C}_4\text{H}_{12}\text{N}_2)_3[\text{In}(\text{C}_7\text{H}_3\text{NO}_4)_3]_2 \cdot 12\text{H}_2\text{O}$   
 $M_r = 1700.92$   
 Monoclinic,  $P2_1/c$   
 $a = 10.5327$  (6) Å  
 $b = 18.1833$  (10) Å  
 $c = 17.5903$  (10) Å  
 $\beta = 94.687$  (5)°  
 $V = 3357.6$  (3) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.682$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.79$  mm<sup>-1</sup>  
 $T = 294$  (2) K  
 Prism, colorless  
 $0.30 \times 0.30 \times 0.20$  mm

#### Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)  
 $T_{\min} = 0.797$ ,  $T_{\max} = 0.858$   
 33553 measured reflections  
 8030 independent reflections  
 6914 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$   
 $\theta_{\text{max}} = 28.0^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.081$   
 $S = 1.02$   
 8030 reflections  
 469 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 3.2P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 1.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.52$  e Å<sup>-3</sup>



**Figure 2**  
A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

**Table 1**

Selected geometric parameters (Å, °).

In1–O4	2.2434 (14)	O3–C7	1.243 (3)
In1–N2	2.2777 (16)	O4–C7	1.265 (3)
In1–O10	2.2857 (15)	O5–C13	1.253 (3)
In1–N3	2.3132 (18)	O6–C13	1.249 (3)
In1–O6	2.3270 (15)	O7–C14	1.244 (3)
In1–N1	2.3586 (18)	O8–C14	1.255 (3)
In1–O12	2.4419 (16)	O9–C20	1.234 (3)
In1–O8	2.4532 (15)	O10–C20	1.275 (3)
O1–C6	1.262 (3)	O11–C21	1.245 (3)
O2–C6	1.242 (3)	O12–C21	1.247 (3)
O10–In1–N3	69.90 (6)	N3–In1–O12	66.60 (6)
N2–In1–O6	69.72 (5)	O6–In1–O12	90.98 (6)
O10–In1–O6	77.14 (6)	N2–In1–O8	67.67 (5)
O4–In1–N1	70.41 (6)	O6–In1–O8	136.66 (5)
O4–In1–O12	83.78 (6)	O12–In1–O8	71.04 (6)
O10–In1–O12	136.50 (6)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4–H4B···O7	0.90	2.01	2.791 (3)	145
N4–H4C···O1 <sup>i</sup>	0.90	1.84	2.702 (3)	159
N5–H5A···O14 <sup>ii</sup>	0.90	1.95	2.792 (3)	155
N5–H5B···O3 <sup>iii</sup>	0.90	1.99	2.800 (3)	149
N6–H6A···O11	0.90	1.94	2.780 (3)	155
N6–H6B···O5 <sup>i</sup>	0.90	2.00	2.836 (3)	154
O13–H13A···O8	0.96	1.82	2.761 (3)	166
O13–H13B···O17	0.96	2.08	3.026 (4)	170
O14–H14A···O18 <sup>iv</sup>	0.96	1.93	2.861 (3)	165
O14–H14B···O10	0.96	1.85	2.798 (3)	168
O15–H15A···O13	0.96	1.85	2.761 (3)	159
O15–H15B···O2 <sup>i</sup>	0.96	2.00	2.870 (3)	150
O16–H16A···O12	0.96	1.96	2.868 (3)	157
O16–H16B···O15	0.96	1.91	2.862 (3)	171
O17–H17A···O1 <sup>i</sup>	0.97	1.91	2.817 (3)	156
O17–H17B···O5 <sup>v</sup>	0.96	1.96	2.901 (3)	167
O18–H18A···O3	0.96	1.91	2.826 (3)	159
O18–H18B···O17	0.96	2.09	3.023 (4)	164

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

H atoms of water molecules were located in difference syntheses, and refined as riding atoms with distance constraints of O–H = 0.96–0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . The remaining H atoms were positioned geometrically, with N–H = 0.90 Å (for NH<sub>2</sub>) and C–H = 0.93 and 0.97 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ . The highest peak is located 0.99 Å from atom H13A.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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