Crystal structure of {(oxalato)-*bis*-[(pyridine-2,6-di-carboxylato)-diaqua)-indium(III)]}dihydrate: $[In(C_2O_4)(C_7H_3N_1O_4)_2(H_2O)_4]\cdot 2H_2O$, $C_{16}H_{18}In_2N_2O_{18}$

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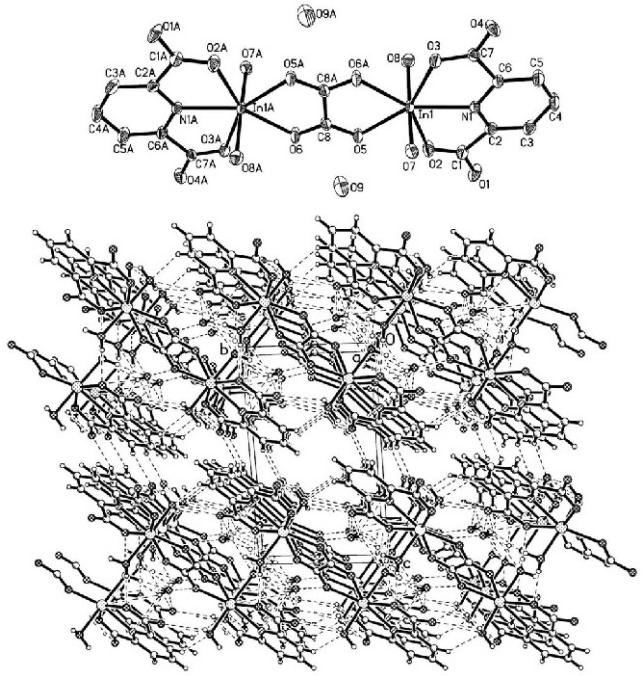

Table 1. Data collection and handling.

Crystal:	colourless prisms, size 0.15×0.18×0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	21.50 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II area-detector, φ and ω
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4616, 1958
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1894
$N(param)_{refined}$:	172
Programs:	SHELXS-97 [15]

Abstract

$C_{16}H_{18}In_2N_2O_{18}$, triclinic, $P\bar{1}$ (no. 2), a = 6.7024(3)Å, b = 7.2135(4)Å, c = 12.2077(6)Å, α = 90.281(1)°, β = 104.976(1)°, γ = 99.427(1)°, V = 561.78(5)Å^3, Z = 1, $R_{gt}(F)$ = 0.0268, $wR_{ref}(F^2)$ = 0.0836, T = 298(2) K.

Source of material

The title compound was synthesized by a hydrothermal method from a mixture of $In(NO_3)_3$ (0.11g, 0.36 mmol), pyridine-2,6-dicarboxylic acid (0.089g, 0.53 mmol), 2,2'-dipyridylamine (0.33 mmol, 0.056g) and distilled water (18.0 mL) in a 30 mL Teflon-lined stainless steel reactor. The solution was heated at 423 K for five days and then cooled slowly to room temperature. Good quality colourless crystals of the title compound were collected for *X*-ray analysis.

Experimental details

The all H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of Csp_2–H = 0.93Å with $U_{iso} = 1.2U_{eq}$ and O–H = 0.85Å with $U_{iso} = 1.5U_{eq}$.

Discussion

In the fields of coordination chemistry, carboxylic ligands like oxalic acid and pyridine-2,6-dicarboxylic acid have been extensively used, based on their diverse coordination modes and rich hydrogen bonding interactions [1-3]. Many complexes, constructed from oxalic acid or pyridine-2,6-dicarboxylic acid ligands with potential as functional materials in magnetism, catalysis and photo-luminescence, have been synthesized [4-7]. A few complexes containing mixed oxalate and pyridine-2,6-dicarboxylate ligands have also been reported [8]. In these complexes the oxalate ligands were introduced in form of oxalic acid. However, oxalic acid can also be obtained by chemical rearrangement of pyridine- carboxylic acid [9] or oxidative coupling of methanol [10] under solvothermal (including hydrothermal) synthetic conditions. Here we report a new dinuclear indium(III) complex with mixed oxalate and pyridine-2,6-dicarboxylate ligands, $[In_2(oxa)(pdc)_2(H_2O)_4]\cdot 2H_2O$, (oxa = oxalate, pdc = pyridine-2,6-dicarboxylate), synthesized from a chemical rearrangement of pyridine-2,6-dicarboxylate to oxalate in a self-assembly chemical process under hydrothermal condition. In the title complex, each In(III) ion is sevenfold-coordinated, with one N atom and two carboxyl O atoms from one pdc ligand, two carboxyl O atoms from one oxa ligand and two water O atoms, forming a distorted pentagonal-bipyramid enviroment (Fig. top). The pdc ligand coordinates to the In(III) centre in tridentate chelating mode. Each carboxylate group of the oxa ligand functions as μ_2-bridge to link two different In(III) ions, forming a dinuclear unit. The In1–N1 bond length is 2.236(4) Å, and the In1–O bond legnths are in the range of 2.139(4)Å to 2.306(3)Å, in accordance with typical bond distances of reported In(III) complexes [11-14]. The O8–In1–O7 angle of the pentagonal bipyramid is 171.85(13)° and the other angles are in the range from 70.01(13) to 146.92(13)°. In the crystal structure, there are four types of intermolecular hydrogen-bonding interactions. The coordinated water molecules (O7) form a hydrogen bond [O7–H7A···O1^{i}] with uncoordinated carboxylate oxygen atoms (O1) from an pdc ligand. The second coordinated water molecule (O8) forms three hydrogen bonds [O8–H8A···O3^{ii}, O8–H8A···O6^{iii}, O8–H8B···O9^{iii}] with coordinated carboxylate oxygen pdc atoms (O3), coordinated carboxylate oxygen oxa atoms (O6), and with

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free water molecules (O9), respectively. The free water molecule (O9) forms two hydrogen bonds [O9–H9A···O4^{iv}, O9–H9A···O8^{v}] with uncoordinated carboxylate oxygen atoms (O4) from an pdc ligand and coordinated water molecules (O8), respectively. All above intermolecular hydrogen-bonding interactions enhance the stability of the solid structure and form a three-dimensional network structure (Fig. bottom).

Symmetry codes:

i: x+1, y, z; **ii**: -x+1, -y, -z; **iii**: x, y-1, z; **iv**: x-1, y+1, z; **v**: -x, -y+1, -z

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7A)	2*i*	0.7466	0.3214	0.3498	0.035
H(7B)	2*i*	0.8170	0.4122	0.2634	0.035
H(8A)	2*i*	0.2789	0.0282	–0.0184	0.038
H(8B)	2*i*	0.2016	–0.0675	0.0644	0.038
H(9A)	2*i*	–0.0126	0.8020	0.1244	0.070
H(9B)	2*i*	0.0637	0.6406	0.1616	0.070
H(3)	2*i*	0.1281	–0.1064	0.4661	0.033
H(4)	2*i*	0.3008	–0.3660	0.4839	0.039
H(5)	2*i*	0.5572	–0.3751	0.3866	0.037

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In(1)	2*i*	0.45322(5)	0.22228(4)	0.16670(2)	0.0237(3)	0.0166(3)	0.0198(3)	0.0088(2)	0.0128(2)	0.0083(2)
O(1)	2*i*	0.0307(6)	0.2117(6)	0.3782(3)	0.034(2)	0.047(2)	0.030(2)	0.023(2)	0.024(2)	0.015(2)
O(2)	2*i*	0.2154(6)	0.2928(5)	0.2527(3)	0.042(2)	0.029(2)	0.036(2)	0.021(2)	0.026(2)	0.017(2)
O(3)	2*i*	0.6713(6)	0.0056(5)	0.1680(3)	0.032(2)	0.024(2)	0.025(2)	0.015(2)	0.017(2)	0.010(1)
O(4)	2*i*	0.7731(7)	–0.2569(5)	0.2380(4)	0.035(2)	0.020(2)	0.044(2)	0.016(2)	0.025(2)	0.011(2)
O(5)	2*i*	0.3520(6)	0.4872(5)	0.0975(3)	0.035(2)	0.021(2)	0.027(2)	0.013(2)	0.019(2)	0.012(2)
O(6)	2*i*	0.3809(6)	0.6958(6)	–0.0326(3)	0.039(2)	0.025(2)	0.032(2)	0.018(2)	0.024(2)	0.018(2)
O(7)	2*i*	0.7130(6)	0.3853(5)	0.2916(3)	0.025(2)	0.020(2)	0.027(2)	0.005(1)	0.009(2)	0.005(1)
O(8)	2*i*	0.2287(6)	0.0398(5)	0.0380(3)	0.026(2)	0.026(2)	0.025(2)	0.002(2)	0.010(2)	0.001(2)
O(9)	2*i*	0.0722(8)	0.7297(7)	0.1178(5)	0.050(3)	0.039(2)	0.069(3)	0.022(2)	0.040(2)	0.021(2)
N(1)	2*i*	0.4157(6)	0.0105(5)	0.2962(3)	0.021(2)	0.018(2)	0.018(2)	0.008(2)	0.009(2)	0.005(2)
C(1)	2*i*	0.1638(8)	0.1890(7)	0.3254(4)	0.022(2)	0.026(3)	0.022(2)	0.010(2)	0.009(2)	0.006(2)
C(2)	2*i*	0.2689(8)	0.0183(7)	0.3520(4)	0.021(2)	0.022(3)	0.018(2)	0.007(2)	0.008(2)	0.002(2)
C(3)	2*i*	0.226(1)	–0.1168(9)	0.4253(5)	0.034(3)	0.035(3)	0.022(3)	0.014(2)	0.016(2)	0.007(2)
C(4)	2*i*	0.331(1)	–0.2698(8)	0.4372(5)	0.047(3)	0.029(3)	0.033(3)	0.017(3)	0.024(3)	0.020(2)
C(5)	2*i*	0.482(1)	–0.2762(9)	0.3779(5)	0.041(3)	0.030(3)	0.032(3)	0.019(3)	0.022(3)	0.015(2)
C(6)	2*i*	0.5184(8)	–0.1365(7)	0.3072(4)	0.025(3)	0.021(2)	0.021(2)	0.011(2)	0.013(2)	0.007(2)
C(7)	2*i*	0.6678(7)	–0.1293(6)	0.2322(4)	0.018(2)	0.015(2)	0.021(2)	0.001(2)	0.009(2)	0.002(2)
C(8)	2*i*	0.4238(8)	0.5530(7)	0.0187(5)	0.021(2)	0.016(2)	0.022(2)	0.002(2)	0.008(2)	0.004(2)

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