

Structure of Polymeric μ -(Oxalato- O^1 , O^2 : $O^{1'}$, $O^{2'}$)-bis[diaqua(oxalato- O^1 , O^2)indium] Dihydrate, $[\text{In}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$

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Abstract. $M_r = 601.78$, monoclinic, $P2_1/c$, $a = 10.189$ (1), $b = 6.651$ (1), $c = 11.162$ (1) Å, $\beta = 95.64$ (1)°, $V = 752.7$ Å³, $D_m = 2.559$ (by flotation), $D_x = 2.656$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 3.117$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $Z = 2$, $T = 293$ (1) K. The structure was solved by Patterson and Fourier methods from 2197 diffractometer data and refined to a final R value of 0.028 for 2083 contributing reflexions [$I > 2\sigma(I)$]. The In atom is coordinated by O atoms in the form of a pentagonal bipyramid. These polyhedra are linked through the oxalate groups as bridging ligands, thus forming infinite chains along the [001] direction. The average In–O bond distance is 2.234 (16) Å for oxalate O atoms, and 2.157 (2) Å for water molecules. There are three independent water molecules in the structure.

Introduction. The structure determination of the title compound was undertaken as part of studies of M^{III} oxalate and thiooxalate complexes. The structure provides another example of the coordination of In Bulc, Golič & Šiftar, 1978; Dietzsch, Bulc, Golič & Šiftar, 1981).

Experimental. Indium(III) oxalate hexahydrate is almost insoluble in water (Dejčman, 1959; Haritonov & Dejčman, 1965) and in organic solvents. Hence the crystals were prepared by slow diffusion of In^{3+} and $\text{C}_2\text{O}_4^{2-}$ ions from aqueous solutions of $\text{In}(\text{NO}_3)_3$ and $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at room temperature. White, needle crystals were grown in a diffusion U-tube filled with water. Cell dimensions determined by least-squares refinement using the θ values of 55 reflexions in the range $8^\circ < \theta < 15^\circ$, graphite-monochromatized $\text{Mo } K\alpha_1$ radiation, Enraf–Nonius CAD-4 diffractometer. Three-dimensional diffractometer data collected with $\text{Mo } K\alpha$ radiation, ω - 2θ scan, 2θ scan width $(0.7 + 0.3 \tan\theta)^\circ$, maximum scan time 40 s, $2\theta_{\text{max}} 60^\circ$, crystal $0.15 \times 0.13 \times 0.29$ mm, 8443 reflexions measured, 2197 averaged reflexions, mean discrepancy on I 3.9%, 2068 observed reflexions [$I > 2\sigma(I)$], $\sigma(I)$ based on counting statistics, transmission factor 0.58–0.69, average shift/error 0.05, maximum shift/error 0.66, data-to-variables (m/n) ratio 15.0,

$[\sum w(\Delta F)^2/(m-n)]^{1/2} 1.16$, maximum $\Delta\rho$ on final difference map $0.27 \text{ e } \text{Å}^{-3}$.

Position of the In atom determined from Patterson map, other non-hydrogen atoms found from a Fourier synthesis, full-matrix least-squares refinement with isotropic thermal parameters for all non-hydrogen atoms reduced R to 0.067, introduction of anisotropic thermal parameters yielded a final $R = 0.028$ and $R_w = 0.036$; a difference Fourier synthesis revealed the positions of the H atoms, except for H(92) and these were refined isotropically; the empirical weighting function $w = W_F \times W_S$ [where $W_F(|F_o| < 15.0) = |F_o|/15.0$, $W_F(|F_o| > 32.0) = 32.0/|F_o|$, $W_F(15.0 < |F_o| < 32.0) = 1.0$, and $W_S(\sin \theta < 0.32) = \sin \theta/0.32$, $W_S(\sin \theta > 0.42) = 0.42/\sin \theta$, $W_S(0.32 < \sin \theta < 0.42) = 1.0$] was applied to keep $\sum w(\Delta F)^2$ uniform over the ranges of $(\sin \theta/\lambda)$ and $|F_o|$; an isotropic-extinction correction (Larson, 1967) was taken into account (0.48); $F(000) = 580$; atomic scattering and dispersion factors for the neutral atoms In, C and O from Cromer & Mann (1968), and Cromer & Liberman (1970), and for H from Stewart, Davidson & Simpson (1965); CDC Cyber 172 computer at RRC Ljubljana; XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. The final fractional coordinates with U_{eq} values (Hamilton, 1959) for non-hydrogen atoms and isotropic U values for H atoms are listed in Table 1.* A view of the unit cell along [010] and the coordination polyhedron of the In atom are given in Figs. 1 and 2.

There are two crystallographically different oxalate groups; one is in a general position whilst the other is at a centre of symmetry.

The In atom is coordinated by seven O atoms in the form of a distorted pentagonal bipyramid. The five equatorial O atoms are those of the oxalate groups, and

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38107 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates ($\times 10^5$ for In, $\times 10^4$ for C and O, and $\times 10^3$ for H atoms) and equivalent isotropic temperature factors U_{eq} ($\times 10^4$), and for H atoms U ($\times 10^3$)

	x	y	z	U_{eq} or $U(\text{\AA}^2)$
In	76218 (2)	65298 (4)	47471 (2)	1390 (12)
C(1)	9872 (3)	8364 (5)	3478 (3)	159 (13)
C(2)	8679 (3)	8245 (5)	2502 (3)	154 (13)
C(3)	4730 (3)	5572 (6)	4436 (3)	168 (14)
O(1)	9630 (2)	7811 (4)	4517 (2)	198 (11)
O(2)	10946 (3)	8947 (5)	3192 (2)	170 (12)
O(3)	7630 (2)	7577 (5)	2839 (2)	209 (12)
O(4)	8885 (2)	8805 (4)	1465 (2)	186 (11)
O(5)	5550 (2)	6536 (5)	3891 (2)	215 (12)
O(6)	3519 (2)	5476 (5)	4136 (2)	213 (11)
O(7)	7046 (3)	9473 (5)	5319 (3)	223 (12)
O(8)	8294 (3)	3721 (4)	4062 (3)	213 (12)
O(9)	5127 (5)	1488 (7)	3617 (3)	431 (20)
H(71)	732 (6)	1014 (9)	572 (5)	21 (13)
H(72)	630 (9)	926 (15)	578 (8)	75 (25)
H(81)	841 (10)	375 (16)	342 (10)	83 (30)
H(82)	895 (9)	329 (13)	453 (8)	59 (22)
H(91)	534 (13)	153 (19)	303 (12)	117 (43)
H(92)	572	87	414	50

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

(a) Coordination polyhedron

In—O(1)	2.255 (2)	O(3)—In—O(5)	71.6 (1)
In—O(3)	2.242 (2)	O(3)—In—O(7)	91.5 (1)
In—O(4)	2.213 (2)	O(3)—In—O(8)	84.3 (1)
In—O(5)	2.230 (2)	O(4)—In—O(6)	75.3 (1)
In—O(6)	2.230 (3)	O(4)—In—O(7)	89.2 (1)
In—O(7)	2.158 (3)	O(4)—In—O(8)	92.4 (1)
In—O(8)	2.155 (3)	O(5)—In—O(6)	73.6 (1)
		O(5)—In—O(7)	81.5 (1)
O(1)—In—O(3)	71.7 (1)	O(5)—In—O(8)	99.8 (1)
O(1)—In—O(4)	71.3 (1)	O(6)—In—O(7)	101.9 (1)
O(1)—In—O(7)	88.1 (1)	O(6)—In—O(8)	83.2 (1)
O(1)—In—O(8)	87.9 (1)	O(7)—In—O(8)	175.0 (1)

(b) Oxalate ligands

Ligand I			
C(1)—C(2)	1.553 (4)	O(1)—C(1)—C(2)	114.8 (3)
C(1)—O(1)	1.263 (4)	O(2)—C(1)—C(2)	119.2 (3)
C(1)—O(2)	1.233 (4)	O(1)—C(1)—O(2)	126.0 (3)
C(2)—O(3)	1.249 (4)	C(1)—C(2)—O(3)	116.1 (3)
C(2)—O(4)	1.253 (4)	C(1)—C(2)—O(4)	116.3 (3)
		O(3)—C(2)—O(4)	127.6 (3)
Ligand II			
C(3)—C(3)	1.526 (5)	C(3)—C(31)—O(5)	116.8 (3)
C(3)—O(5)	1.257 (4)	C(3)—C(31)—O(6)	117.6 (3)
C(3)—O(6)	1.248 (4)	O(5)—C(3)—O(6)	125.7 (3)

(c) Hydrogen-bond lengths

O(7)—O(2 ⁱⁱ)	2.717 (4)	O(8)—O(1 ⁱⁱⁱ)	2.715 (4)
O(7)—O(9 ^{iv})	2.690 (5)	O(8)—O(2 ^v)	2.708 (4)
O(7)—O(9 ⁱ)	2.915 (5)	O(9)—O(5 ^{vi})	2.817 (5)

Symmetry code

(i) $x, 1+y, z$	(iv) $1-x, 1-y, 1-z$
(ii) $2-x, 2-y, 1-z$	(v) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$
(iii) $2-x, 1-y, 1-z$	(vi) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$

the two in the axial positions belong to the water molecules. The coordination polyhedra are connected alternately by the two different kinds of bridging oxalate groups forming a chain of double polyhedra along [001] (Fig. 1). The water molecules are involved

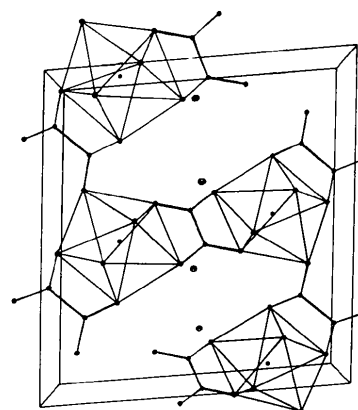


Fig. 1. Unit cell of $[\text{In}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$.

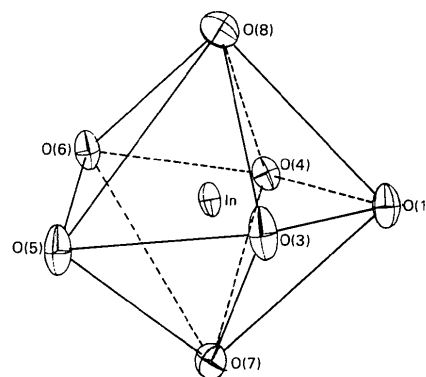


Fig. 2. Coordination polyhedron of the In atom.

in hydrogen bonds interconnecting the chains in the [100] direction.

The In—O bond distances (Table 2a) to the bridging oxalate group at the centre of symmetry are 2.230 (2) \AA . The In—O distances to the bridging oxalate group in the general position are slightly longer: 2.242 (3) and 2.255 (3) \AA . The shortest In—O distance is 2.213 (2) \AA with the oxalate group which has only one contact with the coordination polyhedron. The O atoms from water molecules are nearly at the same distance [2.155 (3) and 2.158 (3) \AA] from the In atom.

Distortion of the pentagonal bipyramid can be seen from the values of the bond angles between atoms in the equatorial plane which vary from 71.3 (1) to 75.3 (1) $^\circ$, and the bond angles between the axial and equatorial positions range from 81.5 (1) to 101.9 (1) $^\circ$.

The bridging oxalate group at the centre of symmetry is coordinated to two In atoms as a bidentate ligand, whereas the other at a general position acts as a monodentate ligand to one In atom, and has only one contact to the second.

The bond distances and bond angles in the oxalate ligands are similar to the values in other complexes (Table 2b). The oxalate ligands are essentially planar.

The three water molecules [O(7), O(8), O(9)] are involved in a full complement of six hydrogen bonds. These hydrogen bonds are similar to those in other crystal hydrates and range from 2.690 (5) to 2.915 (5) Å (Table 2c).

The crystal structure differs from the crystal structures of other oxalates of trivalent cations and from tetraaquatris(oxalato)indium(III) dihydrate (Hansson, 1972).

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Structure of Ammonium and Sodium Bis(oxalato)indate(III) Dihydrate, $\text{NH}_4[\text{In}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ and $\text{Na}[\text{In}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$

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Abstract. $\text{NH}_4[\text{In}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$, $M_r = 344.92$, hexagonal, $P6_22$, $a = 9.025$ (1), $c = 11.343$ (1) Å, $V = 800.0$ Å³, $Z = 3$, $D_c = 2.148$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 18.594$ mm⁻¹, $T = 293$ (1) K. $\text{Na}[\text{In}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$, $M_r = 349.9$, isomorphous to $\text{NH}_4[\text{In}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$, $a = 8.739$ (1), $c = 11.598$ (3) Å, $V = 767.0$ Å³, $D_c = 2.273$ Mg m⁻³. The structure of $\text{NH}_4[\text{In}(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ was refined to a final R value of 0.024 for 372 contributing reflexions. The In atom is coordinated by eight O atoms from four oxalate groups as bridging ligands, forming a distorted Archimedean antiprism; four In–O bond distances are 2.197 (4) Å and four are 2.351 (5) Å. Ammonium ions and water molecules occupy the cavities between the anions and are linked to the anions and to each other by hydrogen bonds.

Introduction. The determination of the unit-cell dimensions and crystal structure of the title compounds is a part of a research programme concerning the study of oxalate complexes (Bulc, Golič & Šiftar, 1979; Dejčman, 1958; Dejčman & Rodičeva, 1964; Haritonov & Dejčman, 1965).

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Experimental. Prepared from aqueous solution of indium chloride and ammonium oxalate (1:2), and of indium chloride and sodium oxalate (1:2) respectively; cell dimensions by least-squares from 2θ values of 90 reflections, range $25^\circ < 2\theta < 70^\circ$, Ni-filtered Cu $K\alpha$, $\lambda = 1.5418$ Å, Enraf–Nonius CAD-4 diffractometer; three-dimensional diffractometer data for ammonium bis(oxalato)indate(III) dihydrate, $0.22 \times 0.21 \times 0.13$ mm from same diffractometer, Ni filter, $\lambda = 1.54051$ Å, ω – 2θ scan, $2\theta \leq 150^\circ$, 2θ scan width ($^\circ$) = $0.6 + 0.2 \times \tan \theta$, aperture (mm) = $2.4 + 0.9 \tan \theta$, maximum scan time = 50 s, background $\frac{1}{4}$ of scan time at each of scan limits; 5053 reflections measured, equivalent reflections averaged, $R_{\text{int}} = 4.5\%$, 374 unique, 372 observed with $I > 3\sigma(I)$, standard reflections 203, 223, 023, intensity increase 3% from beginning to end of data collection; an exact absorption correction made (17 crystal faces, $10 \times 10 \times 10$ grid points), with minimum and maximum values of transmission 0.70 and 0.27 respectively; heavy-atom method; a Patterson function suggested placing In at 3(c) position (intersection of three twofold axes), positions of the other non-H from Fourier synthesis: oxalate-group C atoms are at 6(j), N atoms from ammonium ion at 3(a), and water