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)discandium(III) dihydrate (Hansson, 1972).

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# Structure of Ammonium and Sodium Bis(oxalato)indate(III) Dihydrate, $NH_4[In(C_2O_4)_2].2H_2O$ and $Na[In(C_2O_4)_2].2H_2O$

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**Abstract.** $NH_4[In(C_2O_4)_2].2H_2O$, $M_r = 344·92$, hexagonal, $P6_222$, $a = 9·025$ (1), $c = 11·343$ (1) Å, $V = 800·0$ Å$^3$, $Z = 3$, $D_c = 2·148$ Mg m$^{-3}$, $\lambda(Cu\,K\bar{\alpha}) = 1·5418$ Å, $\mu(Cu\,K\alpha) = 18·594$ mm$^{-1}$, $T = 293$ (1) K. $Na[In(C_2O_4)_2].2H_2O$, $M_r = 349·9$, isomorphous to $NH_4[In(C_2O_4)_2].2H_2O$, $a = 8·739$ (1), $c = 11·598$ (3) Å, $V = 767·0$ Å$^3$, $D_c = 2·273$ Mg m$^{-3}$. The structure of $NH_4[In(C_2O_4)_2].2H_2O$ 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).

**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 $2\theta$ values of 90 reflections, range $25° < 2\theta < 70°$, 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 × 0·21 × 0·13 mm from same diffractometer, Ni filter, $\lambda = 1·54051$ Å, $\omega–2\theta$ scan, $2\theta \le 150°$, $2\theta$ scan width (°) $= 0·6 + 0·2 \times \tan\theta$, 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, $R_{int} = 4·5\%$, 374 unique, 372 observed with $I > 3\sigma(I)$, standard reflections 203, $2\bar{2}3$, 023, intensity increase 3% from beginning to end of data collection; an exact absorption correction made (17 crystal faces, 10 × 10 × 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

molecule at 6($h$), anisotropic full-matrix least-squares, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.025$, H (from $\Delta F$ synthesis) included in last cycle with isotropic thermal parameters but were not refined, empirical weighting function $w = W_F \times W_S$, where $W_F(|F_o| < 10.0) = |F_o|/10.0$, $W_F(|F_o| > 30.0) = 30.0/|F_o|$, $W_F(10.0 < |F_o| < 30.0) = 1.0$ and $W_S(\sin \theta < 0.8) = (\sin \theta/0.8)^{2.0}$, $W_S(\sin \theta > 0.98) = 0.98/\sin \theta$, $W_S(0.8 < \sin \theta < 0.98) = 1.0$ applied in order to keep $\sum w|\Delta F|^2$ uniform over ranges of $(\sin \theta/\lambda)$ and $|F_o|$, ratio of maximum least-squares shift to error in final refinement cycle 0.1, average ratio 0.006, $m/n = 9.0$, $S\{= |\sum w(|F_o| - |F_c|)^2/(m - n)|^{1/2}\} = 0.69$, maximum and minimum heights in final difference Fourier map were 0.55 and $-0.62$ e Å$^{-3}$, isotropic extinction correction (Larson, 1967) = 2.27; $F(000) = 504$; atomic scattering and dispersion factors for neutral atoms In, C, N and O taken from Cromer & Mann (1968), 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 $U_{eq}$ (Hamilton, 1959) for non-H atoms are listed in Table 1.* A view of the unit cell is given in Fig. 1.

* 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 38122 (6 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* ($\times 10^4$) *and equivalent isotropic temperature factors* $U_{eq}(\times 10^4)$

|      | $x$      | $y$      | $z$      | $U_{eq}$(Å$^2$) |
|------|----------|----------|----------|-----------------|
| In   | 5000     | 5000     | 3333     | 173 (3)         |
| O(1) | 2681 (5) | 3468 (5) | 4386 (3) | 288 (16)        |
| O(2) | 4469 (5) | 6883 (5) | 4446 (4) | 329 (18)        |
| C(1) | 2109 (4) | 4219 (4) | 5000     | 204 (21)        |
| C(2) | 3098 (4) | 6195 (4) | 5000     | 215 (22)        |
| N    | 0        | 0        | 0        | 582 (38)        |
| O(3) | 2480 (9) | 0        | 5000     | 587 (35)        |

Table 2. *Molecular dimensions*

($a$) Interatomic distances In–O (Å)

| In–O(1) | 2.197 (4) | In–O(2) | 2.351 (5) |
|---------|-----------|---------|-----------|

($b$) Interatomic distances (Å) and angles (°) in the oxalate ligand

| C(1)–C(2) | 1.545 (1) | C(2)–O(2) | 1.243 (5) |
|-----------|-----------|-----------|-----------|
| C(1)–O(1) | 1.249 (6) |           |           |

| C(2)–C(1)–O(1) | 118.0 (3) | C(1)–C(2)–O(2) | 115.6 (3) |
|----------------|-----------|----------------|-----------|
| O(1)–C(1)–O(1) | 123.9 (2) | O(2)–C(2)–O(2) | 128.7 (2) |

($c$) Hydrogen-bond lengths and angles

| $D$–H$\cdots A$ | $D\cdots A$ (Å) | $D$–H (Å) | H$\cdots A$ (Å) | $D$–H$\cdots A$ (°) |
|-----------------|-----------------|-----------|-----------------|---------------------|
| N–H(1)$\cdots$O(3) | 2.930 (6) | 1.03 | 1.94 | 160 |
| N–H(1)$\cdots$O(1) | 3.082 (6) | 1.03 | 2.56 | 111 |
| O(3)–H(2)$\cdots$O(2) | 2.854 (5) | 0.96 | 1.91 | 166 |
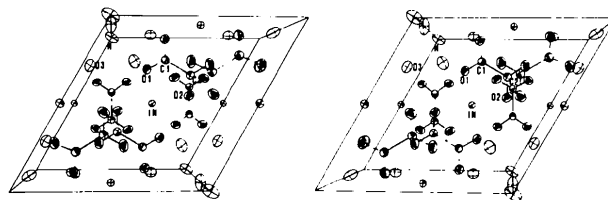


Fig. 1. Stereoview of the unit cell of NH$_4$[In(C$_2$O$_4$)$_2$].2H$_2$O.

The crystal structure consists of linked coordination units [In(C$_2$O$_4$)$_4$]. Each In atom is coordinated by eight O atoms from four oxalate groups, with a distorted Archimedean antiprismatic coordination. There are four In–O(1) bonds, 2.197 (4) Å, and four In–O(2) bonds, 2.351 (5) Å (Table 2$a$). The same high coordination for an In atom was also found by Lindel & Huber (1974) and Preut & Huber (1979).

The oxalate groups lie with the C–C bond along the twofold axis; each group coordinates to two In atoms. The bond distances and bond angles in the oxalate ligand are similar to the values in other oxalate complexes (Table 2$b$). The differences in the C–O bond distances are probably caused by hydrogen bonds to the O atoms.

The equation of the mean plane through the oxalate group is $5.703x - 2.852y + 8.791z = 4.395$ Å. The deviations of the O atoms from this plane are 0.05 Å. The angle between the planes of the carboxylic groups is 5.1°.

The ammonium ion lies on the special position in the cavities between anions. It is hydrogen-bonded to four water molecules, N–O(3) = 2.930 (6) Å, and to four oxalate atoms, N–O(1) = 3.082 (6) Å. Correspondingly, each water molecule O(3) is hydrogen-bonded to two ammonium ions, and to two O atoms from different oxalate groups, O(3)–O(2) = 2.854 (5) Å. All these hydrogen-bond lengths are within the normal range for N–H$\cdots$O and O–H$\cdots$O bonds respectively (Table 2$c$). It may be assumed that the hydrogen bonds from N are bifurcated with H–O bond distances H(1)–O(3) 1.94 Å and H(1)–O(1) 2.56 Å, with N–H$\cdots$O angles of 160 and 111° respectively.

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# Structure of Tris[2(1H)-pyridinethione-S]copper(I) Nitrate (TPTCN), [Cu(C5H5NS)3]NO3

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**Abstract.** $M_r = 459 \cdot 055$, triclinic, $P\bar{1}$, $a = 7 \cdot 187$ (1), $b = 10 \cdot 436$ (2), $c = 13 \cdot 835$ (3) Å, $\alpha = 109 \cdot 56$ (1), $\beta = 85 \cdot 15$ (1), $\gamma = 107 \cdot 91$ (1)°, $Z = 2$, $V = 930 \cdot 2$ (6) Å$^3$, $F(000) = 462$, $D_c = 1 \cdot 639$, $D_m = 1 \cdot 630$ Mg m$^{-3}$ (by flotation), m.p. $= 425–427$ K, $\mu$(Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å) $= 1 \cdot 56$ mm$^{-1}$; $R = 0 \cdot 059$ for 1162 independent non-zero reflexions. The structure consists of isolated $Cu(SC_5H_5N)_3^+$ ions connected to the $NO_3^-$ ions through $O \cdots H–N$ hydrogen bonds. The Cu atom in the complex ion is surrounded by three S atoms in a planar, distorted trigonal coordination.

**Introduction.** Copper–sulphur coordination compounds have been of considerable interest, mainly because of their stereochemistry and its relevance to certain oxidation–reduction reactions in biological systems. Of particular importance are Cu$^I$ compounds with the metal atom in the rather rare planar trigonal coordination. We report here the crystal and molecular structure of tris[2(1H)-pyridinethione]copper(I) nitrate (TPTCN hereafter), which was prepared for the first time by one of us (PK). Magnetic measurements showed the compound to be diamagnetic, indicating thus that copper is in the + 1 oxidation state.

**Experimental.** Pure bright-orange needle-like crystals, aqueous solution of copper(II) nitrate added to 2-mercaptopyridine in ethanol, $0 \cdot 42 \times 0 \cdot 10 \times$ 0·07 mm, computer-controlled Philips PW 1100 four-circle single-crystal diffractometer, cell constants and standard deviations by least-squares analysis of $\theta$ angles of 150 strong reflexions, intensity statistics indicated $P\bar{1}$, 3D data, graphite-monochromated Mo $K\alpha$, $\omega$-scan mode, 3235 unique reflexions, $\theta = 3–25°$, 1162 with $I > 2\sigma(I)$, no absorption correction, direct methods with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1977), phases of 220 strong reflexions determined, 16 non-hydrogen atoms, *i.e.* $MS_3$ core and two of the pyridine rings, located on $E$ map, remaining atoms with Fourier syntheses, full-matrix least squares, XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1976), atomic scattering factors and anomalous dispersion corrections for Cu and S from *International Tables for X-ray Crystallography* (1974), H atoms, at calculated positions, with isotropic temperature coefficients, not refined, $w = 1/\sigma^2(F)$, $R = 0 \cdot 059$ ($R_w = 0 \cdot 048$), mean shift/error ratio 0·18.

**Discussion.** The final positional parameters and equivalent isotropic temperature coefficients for the non-hydrogen atoms are given in Table 1.† Interatomic distances and angles are given in Table 2.

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† Lists of structure factors, anisotropic thermal parameters of the non-hydrogen atoms, H-atom parameters, bond lengths involving H atoms and various least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38150 (14 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.