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# Polymeric aqua-1$\kappa O$-bis[$\mu$-($R$,$R$)-tartrato-1$\kappa^2O^1,O^2$:2$\kappa^2O^3,O^4$]dicadmium(II) trihydrate

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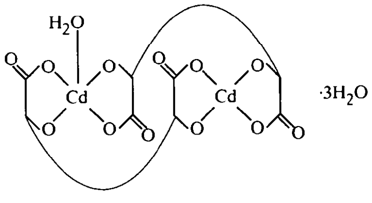
## Abstract

The structure of the title compound, {[$Cd_2(C_4H_4O_6)_2(H_2O)$]·$3H_2O$}$_n$, consists of corrugated polymeric sheets of dimeric [$Cd_2(C_4H_4O_6)_2(H_2O)$] units and three water molecules of crystallization. Both cadmium ions are coordinated by two ($R$,$R$)-tartrate ligands in a *cis* arrangement, and the octahedral geometry for each cation is completed by two carboxyl O atoms of different neighbouring dimers or by one carboxyl O atom and a water molecule. Additional water molecules are held in the crystal lattice, forming a hydrogen-bonding network to keep the dimers together in the non-planar sheets.

## Comment

This work is part of a research project concerning the investigation of the dielectric properties of tartrate salts with divalent cations as related to their crystalline structure. The electrical properties of cadmium tartrate, as well as the X-ray diffraction powder patterns, reveal the occurrence of two successive phase changes of structural origin (Torres *et al.*, 1998). In order to investigate the transition mechanisms, the structure of a single crystal of the title compound, (I), at room temperature, has been solved.



(I)

The smallest structural subunit appears to be the dimeric entity [$Cd_2(C_4H_4O_6)_2(H_2O)$] (Fig. 1). The bond geometry for each tartrate is usual and does not deviate significantly from that of the reported pseudo-isomorphous tartrate complexes of Ni, Cu, Zn and Mn (Bostelaar *et al.*, 1984; Prout *et al.*, 1971; Templeton *et al.*, 1985; Ruiz-Pérez *et al.*, 1996). Bond lengths averaged for the two tartrates are C—C 1.529 (5), C—O(hydroxyl) 1.419 (4) and C—O(carboxyl) 1.254 (5) Å, and the averaged bond angles are C—C—C 110.8 (3), C—C—O(hydroxyl) 110.6 (3), C—C—O(carboxyl) 117.5 (3) and O—C=O 124.8°. Each $Cd^{2+}$ ion is coordinated by two halves of two different tartrate dianions *via* chelation through the hydroxyl and the carboxyl groups. Such chelate rings (–Cd—OCCO–) are nearly planar; the mean deviation from the least-squares plane varies between 0.0203 and 0.0665 Å. The octahedral coordination geometry around the Cd1 atom is completed by a water molecule (O$W$1) and a non-chelating carboxylate O atom (O8$a$) of another dimer. The sixfold coordination of the Cd2 atom is com-

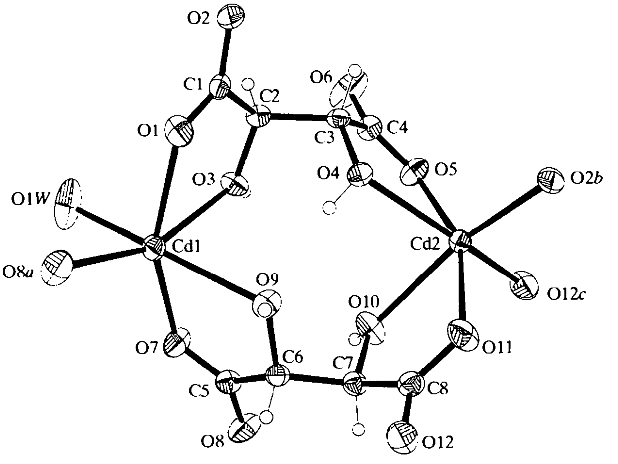


Fig. 1. Perspective drawing of the dimeric unit of the title compound showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Water molecules O2$W$, O3$W$ and O4$W$ have been omitted for clarity. Symmetry codes: ($a$) $\frac{1}{2}+x, -\frac{3}{2}-y, -1-z$; ($b$) $-x, \frac{1}{2}+y, -\frac{1}{2}-z$; ($c$) $x-\frac{1}{2}, -\frac{1}{2}-y, -1-z$.

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pleted by two non-chelating carboxyl O atoms (O2*b* and O12*c*; see Fig. 1 for symmetry codes) from two different dimers. The Cd—O distances vary between 2.188 (3) and 2.425 (3) Å, forming a distorted octahedron (Table 1). Such distortion is in accordance with the valence bond sum (Brown, 1992) around the Cd1 and Cd2 atoms [2.216 and 2.178 valence units, respectively; obtained using *VALMAP*2.0 (González-Platas *et al.*, 1999)], where Cd1 is overbonded.

The crystals can be regarded as a stacked pile of corrugated polymeric sheets of the dimeric units described above and the water molecules are linked to the tartrate ligands by intermolecular hydrogen-bonding distances. Within each sheet, the dimers are linked together through the carboxylate O atoms. Fig. 2 shows that in the crystal packing, the dimers in the polymeric sheets are positioned on top of one another in the *c* direction. Between the sheets, the interactions are of the hydrogen-bond type, in addition to van der Waals contacts (see Table 2 and Fig. 3).

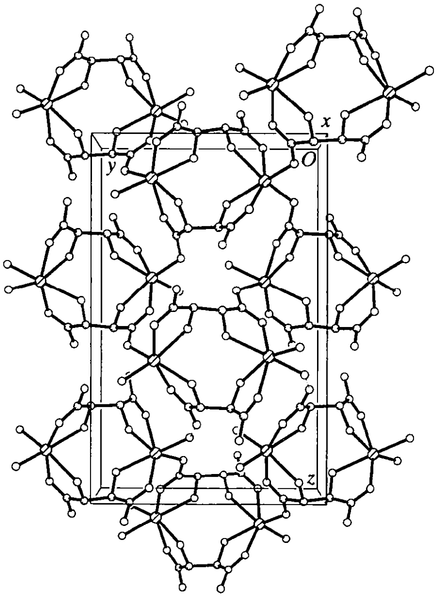

Fig. 2. A projection of the crystal structure of the title compound along the *a* axis. Calculated H atoms have been omitted for clarity.

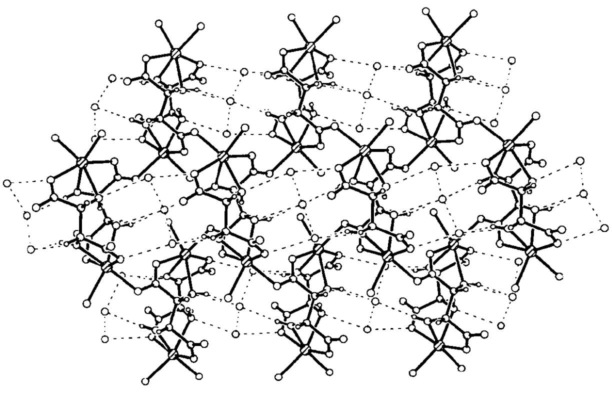

Fig. 3. View of the crystal structure along the *c* axis showing the hydrogen-bonding scheme between the sheets.

A comparison with the reported tartrate complexes reveals that these structures contain the same structural subunit, but with different numbers of coordinating water molecules and water molecules of crystallization, building slightly different binding schemes within the polymeric layers. These nearly isostructural compounds, with space groups $P2_12_12$, $P2_1$ and $P2_12_12_1$ (in which the *b* axis is doubled), point to the possibility of new phases when the temperature is increased and some water molecules are lost. Future works will deal with a detailed study of the phase-transition mechanism of the title compound, based on the present X-ray structure, and new studies at higher temperatures.

## Experimental

Single crystals of cadmium tartrate were grown in a silica-gel medium using the techniques described by Henisch (1970). A solution of sodium metasilicate nonahydrate (approximately 1 *M*) was added to a volume of L-tartaric acid (1 *M*, pH 4–5). The mixture was introduced into test tubes, covered, and allowed to set for 48 h at room temperature. A solution of cadmium chloride (1 *M*) was introduced above the gel, care being taken to avoid damaging the surface of the gel. The tubes were stored at 313 K. Crystals appeared in the gel and at the interface within about one week, and well formed crystals had grown after two weeks. They were then carefully removed from the gel, washed free of any adhering gel particles and dried at room temperature.

*Crystal data*

$[Cd_2(C_4H_4O_6)_2(H_2O)]\cdot 3H_2O$
$M_r = 593.00$
Orthorhombic
$P2_12_12_1$
$a = 7.654\,(2)$ Å
$b = 11.578\,(2)$ Å
$c = 17.771\,(3)$ Å
$V = 1574.8\,(6)$ Å$^3$
$Z = 4$
$D_x = 2.501$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$25°$
$\mu = 2.789$ mm$^{-1}$
$T = 293\,(2)$ K
Prism
0.31 × 0.22 × 0.20 mm
Pale yellow

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: empirical azimuthal ($\psi$) scans (North *et al.*, 1968)
$T_{min} = 0.505$, $T_{max} = 0.572$
9802 measured reflections
4572 independent reflections

4543 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 29.98°$
$h = -10 \rightarrow 2$
$k = -16 \rightarrow 16$
$l = -24 \rightarrow 24$
3 standard reflections frequency: 120 min intensity decay: 1%

*Refinement*

Refinement on $F^2$
$R(F) = 0.028$
$wR(F^2) = 0.072$
$S = 1.204$
4572 reflections
238 parameters
Only H-atom $U$'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 2.1830P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.799$ e Å$^{-3}$
$\Delta\rho_{min} = -0.643$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0022 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.02 (3)

Table 1. *Selected bond lengths (Å)*

| | | | |
|---|---|---|---|
| Cd1—O8$^{i}$ | 2.188 (3) | Cd2—O5 | 2.207 (3) |
| Cd1—O7 | 2.217 (3) | Cd2—O12$^{ii}$ | 2.226 (3) |
| Cd1—O1$W$ | 2.257 (3) | Cd2—O2$^{iii}$ | 2.244 (3) |
| Cd1—O1 | 2.296 (3) | Cd2—O11 | 2.247 (3) |
| Cd1—O3 | 2.314 (2) | Cd2—O10 | 2.406 (3) |
| Cd1—O9 | 2.400 (3) | Cd2—O4 | 2.425 (3) |

Symmetry codes: (i) $\frac{1}{2}+x, -\frac{3}{2}-y, -1-z$; (ii) $x-\frac{1}{2}, -\frac{1}{2}-y, -1-z$; (iii) $-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

Table 2. *Contact distances and hydrogen-bonding geometry (Å, °)*

| | | | |
|---|---|---|---|
| O1$W\cdots$O6$^{i}$ | 2.613 (6) | O2$W\cdots$O4$W^{i}$ | 2.795 (9) |
| O1$W\cdots$O2$^{ii}$ | 2.843 (4) | O2$W\cdots$O4$^{iv}$ | 2.841 (5) |
| O1$W\cdots$O8$^{iii}$ | 2.925 (5) | O3$W\cdots$O4$W^{v}$ | 2.817 (9) |
| O2$W\cdots$O5 | 2.753 (6) | O3$W\cdots$O1$^{vi}$ | 2.891 (6) |

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O3—H3O$\cdots$O3$W^{ii}$ | 0.820 | 1.805 | 2.584 (5) | 158.26 |
| O4—H4O$\cdots$O9 | 0.820 | 2.121 | 2.896 (4) | 157.52 |
| O4—H4O$\cdots$O3 | 0.820 | 2.316 | 2.769 (3) | 115.44 |
| O9—H9O$\cdots$O4$W^{ii}$ | 0.820 | 2.009 | 2.785 (7) | 157.66 |
| O10—H10O$\cdots$O4$W^{i}$ | 0.820 | 2.313 | 3.085 (7) | 156.86 |

Symmetry codes: (i) $-1-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (ii) $-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (iii) $\frac{1}{2}+x, -\frac{3}{2}-y, -1-z$; (iv) $x-1, y, z$; (v) $1+x, y, z$; (vi) $1-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

H atoms from the tartrate molecules were located from difference syntheses, in positions reliable enough to determine the intermolecular hydrogen bonding. In the final refinement, such positions were fixed, maintaining the geometry, and refined with fixed individual isotropic displacement parameters [$U_{iso} = 1.2U_{eq}$(C) and $1.5U_{eq}$(O hydroxyl)] using a riding model with C—H distances of 0.98 Å and O—H distances of 0.82 Å. Water H atoms could not be located.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms, 1996). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST*95 (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1241). Services for accessing these data are described at the back of the journal.

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# Bis[iodo($N$,$N$,$N'$,$N''$,$N''$-pentamethyldiethylenetriamine-$\kappa^3N$)platinum(II)] di-$\mu$-iodo-bis[diiodoplatinate(II)]

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## Abstract

The title compound, $2[PtI(C_9H_{23}N_3)][Pt_2I_6]$ or $2[Pt(Me_5dien)I][Pt_2I_6]$, where $Me_5$dien is pentamethyldiethylenetriamine, has been synthesized and its X-ray structure solved. In the asymmetric unit, there are two platinum(II) complex moieties, *i.e.* $[Pt(Me_5dien)I]^+$ cations, in which the metal has distorted square-planar coordination geometry, and half an iodo-bridged $[Pt_2I_6]^{2-}$ anion, in which the Pt center has a regular square-planar arrangement.