

## Poly[[pentaquasulfato- $\mu_4$ -(*R,R*)-tartrato-dicadmium(II)] trihydrate]

Aleksandra Drzewiecka, Krystyna Stepniak, Anna Barcicka‡ and Anna E. Koziol\*

Faculty of Chemistry, Maria Curie-Skłodowska University, 20031 Lublin, Poland  
Correspondence e-mail: akoziol@hermes.umcs.lublin.pl

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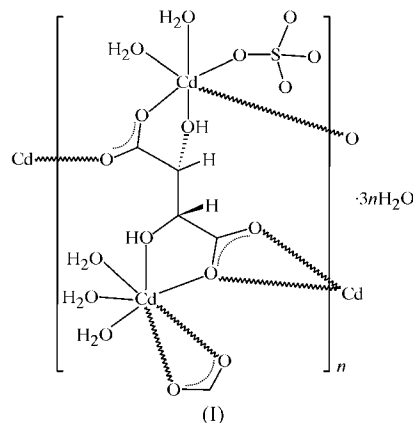
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The asymmetric unit in the title compound,  $\{[\text{Cd}_2(\text{C}_4\text{H}_4\text{O}_6)(\text{SO}_4)(\text{H}_2\text{O})_5] \cdot 3\text{H}_2\text{O}\}_n$ , is composed of two cadmium cations, one (*R,R*)-tartrate and one sulfate anion, five aqua ligands and three solvent water molecules. One of the cadmium ions is coordinated in an octahedral environment, whereas the second is surrounded by seven O atoms in a pentagonal-bipyramidal geometry. Both types of coordination polyhedra form two sets of perpendicular non-intersecting polymeric chains.  $\text{CdO}_6$  octahedra share two corners, while  $\text{CdO}_7$  units are joined by a bridging carboxylate group. An extensive hydrogen-bond pattern involving all of the OH groups contributes to the stabilization of the structure.

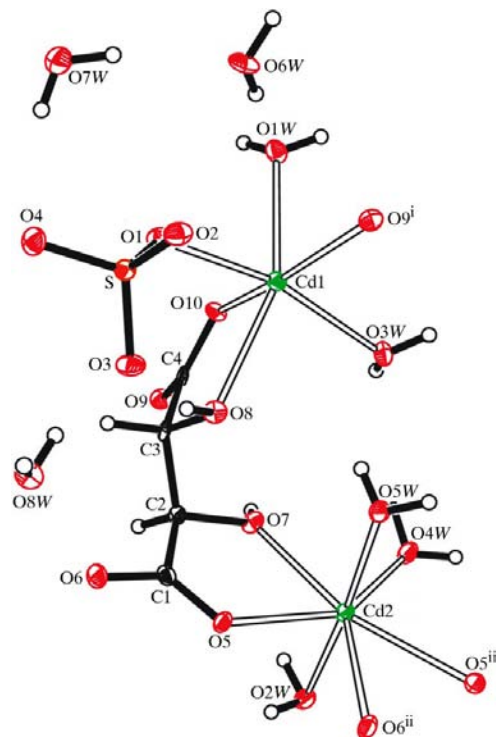
### Comment

Tartaric acid and its anions are flexible multidentate O-donor ligands, and many salts and complexes with metal cations have been reported. A search of the Cambridge Structural Database (CSD; Version 5.28; Allen, 2002) for solid phases containing a transition metal cation and a tartrate anion showed over 60 crystal structures. In those structures, besides the requested contents, accompanying inorganic and/or organic units were present in the form of cations, anions or neutral components. The search, however, showed no examples of structures containing a single type of cation and inorganic anion. To date, only three structures of cadmium tartrates have been published. Two of these complexes contain additional organic ligands, *viz.* a hydrated complex of cadmium (*R,R*)-tartrate with hexamethylenetetramine (Ng, 2004), and a cadmium complex with racemic tartrate and thiourea (Zhou *et al.*, 2001). Moreover, two crystal structures of simple cadmium tartrate have been reported, for one of which, of proposed formula  $\text{Cd}(\text{C}_4\text{H}_4\text{O}_6) \cdot 5\text{H}_2\text{O}$  (Hopwood & Nicol, 1972), the structure has not been determined. The second structure,  $\{[\text{Cd}_2(\text{C}_4\text{H}_4\text{O}_6)_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$ , was published by González-Silgo *et al.* (1999). In this crystal structure, two symmetry-independent cadmium cations are present, both

of them six-coordinated ( $\text{CdO}_6$ ). In one of the cations, the coordination environment includes six tartrate O atoms, while in the other, one aqua ligand is present. Since three out of four carboxylate groups are bridging bidentate, a three-dimensional polymeric structure is formed.



We have now synthesized the new title cadmium complex  $[\text{Cd}_2(\text{C}_4\text{H}_4\text{O}_6)(\text{SO}_4)(\text{H}_2\text{O})_5] \cdot 3\text{H}_2\text{O}$ , (I), with mixed organic–inorganic anions (Cd/tartrate/sulfate/water in a 2:1:1:8 ratio). The present structure also contains two independent cadmium cations, but the two have different coordination numbers and coordinated ligands (Fig. 1). The distorted octahedral geometry for atom Cd1 is completed by three O atoms from tartrate anions, one sulfate O atom and two water molecules. The Cd2 cation exhibits sevenfold coordination; the pentagonal bipyramid is formed by four O atoms from tartrate



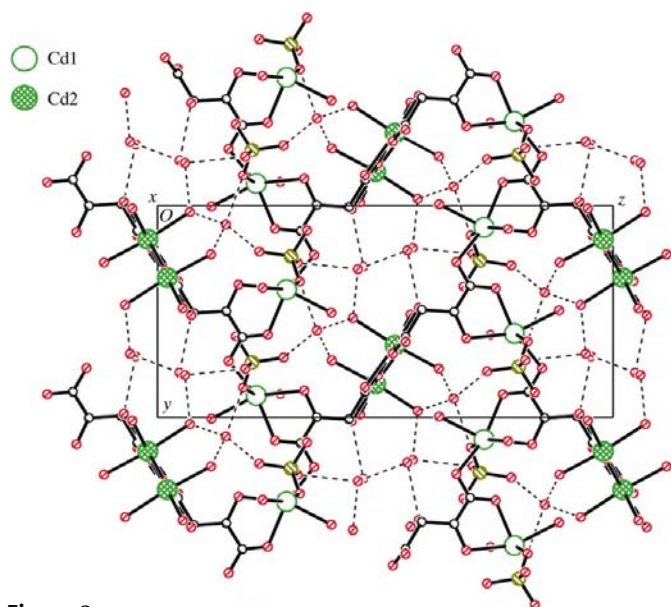
**Figure 1**  
The atom-numbering of (I) and the coordination polyhedra of the cadmium cations (symmetry codes are as in Table 1).

‡ Deceased.

ligands and by three water molecules. Thus, the sulfate anion behaves as a monodentate ligand, while the (*R,R*)-tartrate dianion is heptadentate. The Cd—O distances range from 2.233 (3) to 2.397 (2) Å for atom Cd1, and from 2.278 (3) to 2.488 (2) Å for Cd2 (Table 1). The shortest distances are observed for Cd—O<sub>water</sub> bonds, while a longer than normal value is found for the O5—Cd2 bond as a result of the tridentate and chelating–bridging character of the carboxylate group containing the O atom.

The geometry of the tartrate ion is typical and does not differ significantly from those reported in the literature (*e.g.* tartrates of the divalent cations Cd<sup>2+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>; González-Silgo *et al.*, 1999; Ruiz-Pérez *et al.*, 1996; Hawthorne *et al.*, 1982; Bostelaar *et al.*, 1984; Templeton *et al.*, 1985). The conformation around the C2—C3 bond is *trans* with a planar zigzag carbon chain. The C1—C2—C3—C4 torsion angle is 175.1 (3)°, which is typical for the *T* conformer (Gawronski *et al.*, 1997).

The Cd1 and Cd2 coordination environments form separate linear polymers of different topology. The Cd1 cations are linked through the O9—C4—O10 bridging carboxylate group, forming chains along [010] (shown in projection in Fig. 2, running top to bottom), whereas within the second type of chain (running along [100], coming out of the plane in Fig. 2), neighbouring Cd2 cations share carboxylate atom O5. Fig. 2 also shows the way in which these two columns are interconnected by the whole tartrate backbone, through its carboxylate arms and the hydroxyl group, leading to a three-dimensional architecture that leaves columnar voids along *a* which are filled by the solvent water molecules. The very complex hydrogen-bonding scheme arising from the superabundance of donors and acceptors is shown in Fig. 2 and full details are given in Table 2.



**Figure 2**

A view of the packing arrangement along the *a* axis, showing the two different types of chains as well as their interconnection. O...O interactions arising from the complex hydrogen-bonding scheme (H atoms omitted) are represented by broken lines.

A comparison with the reported cadmium tartrate tetrahydrate (González-Silgo *et al.*, 1999) reveals that the inclusion of an SO<sub>4</sub><sup>2-</sup> anion in (I) forces an increased number of (coordinated) water molecules in the structure, with the corresponding environment change around the Cd cations.

## Experimental

Single crystals of hydrated cadmium sulfate tartrate were grown in a silica-gel medium using the technique described by Henisch (1970). A gel was prepared by adding (*R,R*)-tartaric acid to sodium metasilicate, with continuous stirring in order to avoid excessive local ion concentration. The final pH of the gel was 5.4 and the mixture was found to set in 3 d at room temperature. A solution of cadmium sulfate was poured over the set gel. The crystallization was carried out in glass tubes of diameter 1.7 cm. The tubes were kept at 308 K and after seven weeks colourless crystals of suitable size were carefully removed from the gel.

### Crystal data

[Cd <sub>2</sub> (C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> )(SO <sub>4</sub> )(H <sub>2</sub> O) <sub>5</sub> ].3H <sub>2</sub> O	<i>V</i> = 1716.2 (8) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 613.06	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Mo <i>K</i> α radiation
<i>a</i> = 8.365 (2) Å	<i>μ</i> = 2.69 mm <sup>-1</sup>
<i>b</i> = 9.795 (3) Å	<i>T</i> = 100 (2) K
<i>c</i> = 20.946 (5) Å	0.15 × 0.15 × 0.13 mm

### Data collection

Kuma KM-4 CCD area-detector diffractometer	20890 measured reflections
Absorption correction: analytical ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2003)	6950 independent reflections
<i>T</i> <sub>min</sub> = 0.689, <i>T</i> <sub>max</sub> = 0.721	4968 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.061

### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.037	Δρ <sub>max</sub> = 1.30 e Å <sup>-3</sup>
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.059	Δρ <sub>min</sub> = -1.05 e Å <sup>-3</sup>
<i>S</i> = 0.90	Absolute structure: Flack (1983),
6950 reflections	2201 Friedel pairs
228 parameters	Flack parameter: -0.05 (2)
H-atom parameters constrained	

**Table 1**

Selected bond lengths (Å).

Cd1—O9 <sup>i</sup>	2.233 (3)	Cd2—O5W	2.283 (2)
Cd1—O10	2.275 (3)	Cd2—O2W	2.311 (2)
Cd1—O3W	2.290 (3)	Cd2—O5	2.317 (3)
Cd1—O1	2.310 (3)	Cd2—O6 <sup>ii</sup>	2.378 (2)
Cd1—O1W	2.323 (2)	Cd2—O7	2.381 (3)
Cd1—O8	2.397 (2)	Cd2—O5 <sup>ii</sup>	2.488 (2)
Cd2—O4W	2.278 (3)		

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

H atoms bonded to C and O atoms of the tartrate anion were positioned geometrically. The C—H bond lengths were set at 1.00 Å and the O—H bond lengths at 0.84 Å. The positions of the water H atoms were found in difference maps and then the O—H distances were fixed at 0.84 Å. All H atoms were included in the refinement in the riding-model approximation, with *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub>(C) and 1.5*U*<sub>eq</sub>(O).

Data collection: *KM-4 CCD Software* (Kuma, 1999); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997);

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...O5W <sup>iii</sup>	0.84	1.93	2.737 (4)	162
O1W—H2W1...O2W <sup>iv</sup>	0.84	1.94	2.776 (4)	174
O2W—H1W2...O7W <sup>v</sup>	0.84	2.09	2.673 (4)	126
O2W—H2W2...O8W <sup>vi</sup>	0.84	2.05	2.692 (4)	133
O3W—H1W3...O2 <sup>iii</sup>	0.84	1.82	2.661 (4)	177
O3W—H2W3...O4 <sup>vi</sup>	0.84	1.92	2.753 (4)	169
O4W—H1W4...O2 <sup>iii</sup>	0.84	1.98	2.816 (4)	176
O4W—H2W4...O6 <sup>vi</sup>	0.84	1.89	2.709 (4)	165
O5W—H1W5...O8W <sup>vi</sup>	0.84	1.78	2.621 (4)	173
O5W—H2W5...O3W	0.84	2.13	2.861 (4)	145
O6W—H1W6...O7W <sup>iii</sup>	0.84	1.92	2.731 (4)	162
O6W—H2W6...O1W	0.84	2.12	2.956 (4)	173
O7W—H1W7...O6W	0.84	2.18	2.952 (4)	153
O7W—H2W7...O4	0.84	2.03	2.796 (4)	151
O8W—H1W8...O3	0.84	1.82	2.647 (4)	166
O8W—H2W8...O1 <sup>viii</sup>	0.84	1.98	2.788 (4)	161
O7—H7...O6W <sup>iii</sup>	0.84	2.07	2.876 (4)	160
O8—H8...O3	0.84	1.85	2.661 (4)	163

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

program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3040). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bostelaar, L. J., de Graaff, R. A. G., Hulsbergen, F. B., Reedijk, J. & Sachtler, W. M. H. (1984). *Inorg. Chem.* **23**, 2294–2297.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gawronski, J., Gawronska, K., Skowronek, P., Rychlewska, U., Warzajtis, B., Rychlewski, J., Hoffmann, M. & Szarecka, A. (1997). *Tetrahedron*, **53**, 6113–6144.
- González-Silgo, C., González-Platas, J., Ruiz-Pérez, C., López, T. & Torres, M. E. (1999). *Acta Cryst.* **C55**, 710–712.
- Hawthorne, F. C., Borys, I. & Ferguson, R. B. (1982). *Acta Cryst.* **B38**, 2461–2463.
- Hensch, H. K. (1970). *Crystal Growth in Gels*. University Park, USA: The Pennsylvania State University Press.
- Hopwood, J. S. & Nicol, A. W. (1972). *J. Appl. Cryst.* **5**, 437–438.
- Kuma (1999). *KM-4 CCD Software*. Version 1.161. Kuma Diffraction, Wrocław, Poland.
- Ng, S. W. (2004). Private communication (refcode IXEQIL). CCDC, Union Road, Cambridge, England.
- Oxford Diffraction (2003). *CrysAlis CCD and CrysAlis RED*. Versions 1.171. Oxford Diffraction Poland, Wrocław, Poland.
- Ruiz-Pérez, C., Hernández-Molina, M., González-Silgo, C., López, T., Yanes, C. & Solans, X. (1996). *Acta Cryst.* **C52**, 2473–2475.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Templeton, L. K., Templeton, D. H., Zhang, D. & Zalkin, A. (1985). *Acta Cryst.* **C41**, 363–365.
- Zhou, M., Yu, W. T., Xu, D., Lu, M. K., Yuan, D. R., Wang, X. Q., Gou, S. Y. & Meng, F. Q. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 201–204.