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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.010 \text{ \AA}$

Disorder in main residue

R factor = 0.062

wR factor = 0.203

Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Hemi[4-(carboxymethoxy)phenylsulfanylaceto- $\kappa^2\text{O},\text{O}'$]hemi[4-(carboxymethylsulfanyl)phenyloxyacetato]bis(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$)cadmium(II) 4-(carboxymethoxy)phenylsulfanylacetate dihydrate

The reaction of cadmium nitrate with 4-(carboxymethoxy)-phenylsulfanylacetic acid in the presence of phenanthroline at a pH of 6 affords the salt, $[\text{Cd}(\text{C}_{10}\text{H}_9\text{O}_5\text{S})(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{C}_{10}\text{H}_9\text{O}_5\text{S})\cdot 2\text{H}_2\text{O}$. The Cd atom in the cation is chelated by two phenanthroline units and one carboxylate from the mono-anionic ligand in a distorted octahedral geometry. The coordinated monoanion shows disorder which results in a 50:50 mixture of 4-(carboxymethoxy)phenylsulfanylacetate and 4-(carboxymethylsulfanyl)phenyloxyacetate coordinated to the cadmium. The cation and uncoordinated anion interact to form a linear chain.

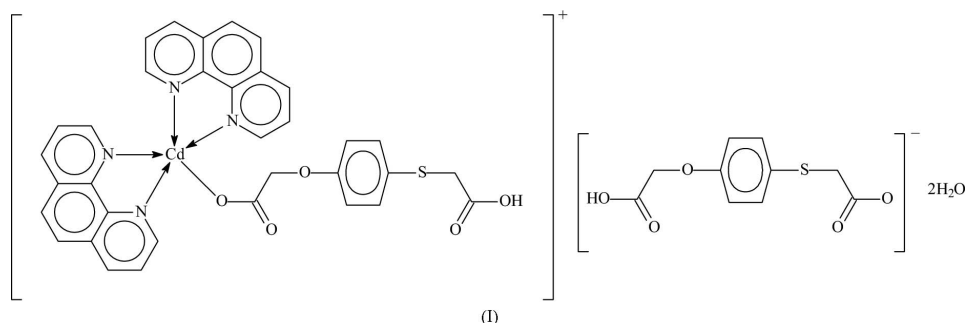
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Comment

The cadmium complex with 4-(carboxymethoxy)phenylsulfanylacetic acid exists as a diaqua compound in which both $-\text{X}-\text{CH}_2\text{CO}_2$ (where $\text{X} = \text{O}$ or S) carboxylate groups of the dianion chelate to the metal atom to result in a chain structure (Gao *et al.*, 2005). The structure shows disorder of the O and S atoms. A review (Ye *et al.*, 2005) of the 2,2'-bipyridine and 1,10-phenanthroline complexes of transition metal carboxylates has suggested that the dimensionality of polymeric carboxylate-bridged compounds can be lowered by such heterocycles. In the present study, the replacement of the two coordinated water molecules by one chelating phenanthroline heterocycle resulted in the isolation of an ion-pair complex whose $[\text{Cd}(\text{C}_{10}\text{H}_9\text{O}_5\text{S})(\text{C}_{12}\text{H}_8\text{N}_2)_2]^+$ cation shows distorted octahedral geometry at the metal. The charge is balanced by a 4-(carboxymethoxy)phenylsulfanylacetate counter-ion; the salt crystallizes as a dihydrate, (I) (Fig. 1).



In this structure, the coordinated anion also shows disorder, such that it forms a 50:50 mixture of the 4-(carboxymethoxy)phenylsulfanylacetic acid anion and the 4-(carboxymethylsulfanyl)phenyloxyacetic acid anion (Fig. 2), leading to $[\text{Cd}(\text{HO}_2\text{CCH}_2\text{OC}_6\text{H}_4\text{SCH}_2\text{CO}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2]^+$ and $[\text{Cd}(\text{HO}_2\text{CCH}_2\text{SC}_6\text{H}_4\text{OCH}_2\text{CO}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2]^+$, respectively. The uncoordinated monoanion is ordered and exists as the 4-

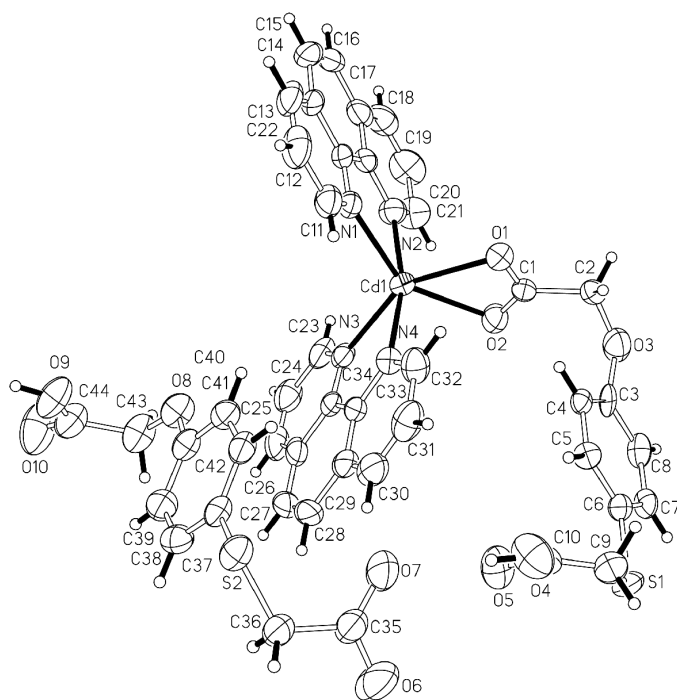


Figure 1
ORTEP plot (Johnson, 1976) of (I); the alternative disorder component is not shown. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii. The two water molecules are not shown.

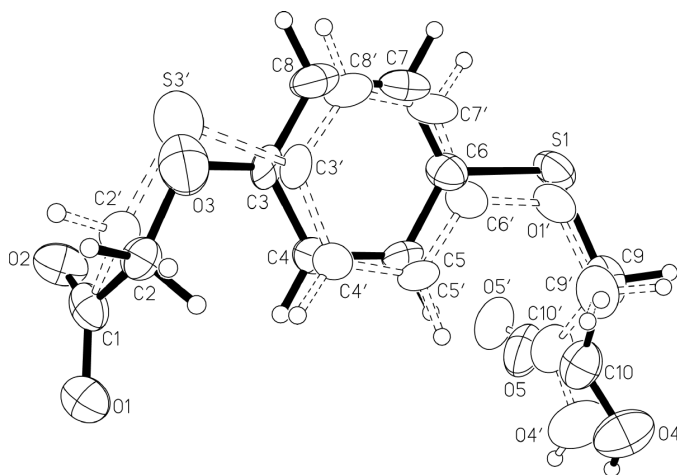


Figure 2
ORTEP plot (Johnson, 1976), illustrating the disorder in the coordinated $C_{10}H_9O_5S^-$ anion; the two components share a common $-CO_2$ set of atoms.

(carboxymethoxy)phenylsulfanylacetic acid anion. The cation and anion interact through hydrogen bonds to form a chain; the water molecules interact with the chain (Table 2) to form a ribbon motif of two chains and a tetramer of water molecules.

Experimental

The dicarboxylic acid was synthesized by the method for synthesizing benzene-1,4-dioxyacetic acid (Liu *et al.*, 2004). Cadmium dinitrate tetrahydrate (0.62 g, 2 mmol), 1,10-phenanthroline (0.40 g, 2 mmol)

and 4-(carboxymethoxy)phenylsulfanylacetic acid (0.48 g, 2 mmol) were heated in water; the pH was raised to 6 with 0.2 M sodium hydroxide. Colorless prismatic crystals separated from the filtered solution after several days.

Crystal data

$[Cd(C_{10}H_9O_5S)(C_{12}H_8N_2)_2] \cdot (C_{10}H_9O_5S) \cdot 2H_2O$
 $M_r = 991.30$
 Triclinic, $P\bar{1}$
 $a = 11.496(2) \text{ \AA}$
 $b = 13.755(3) \text{ \AA}$
 $c = 15.052(3) \text{ \AA}$
 $\alpha = 110.74(1)^\circ$
 $\beta = 93.45(1)^\circ$
 $\gamma = 100.09(1)^\circ$
 $V = 2172.2(8) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.516 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 20057 reflections
 $\theta = 3.2\text{--}27.5^\circ$
 $\mu = 0.67 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Prism, colorless
 $0.36 \times 0.25 \times 0.14 \text{ mm}$

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.723$, $T_{\max} = 0.912$
 21315 measured reflections

9744 independent reflections
 6669 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\max} = 27.5^\circ$
 $h = -14 \rightarrow 14$
 $k = -17 \rightarrow 17$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.062$
 $wR(F^2) = 0.203$
 $S = 1.07$
 9744 reflections
 583 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1247P)^2 + 0.1528P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.96 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cd1—O1	2.399 (4)	Cd1—N2	2.334 (5)
Cd1—O2	2.346 (4)	Cd1—N3	2.305 (4)
Cd1—N1	2.290 (4)	Cd1—N4	2.314 (4)
O1—Cd1—O2	55.3 (1)	O2—Cd1—N4	95.6 (2)
O1—Cd1—N1	94.9 (1)	N1—Cd1—N3	114.2 (1)
O1—Cd1—N2	100.7 (2)	N1—Cd1—N2	72.6 (2)
O1—Cd1—N3	148.5 (1)	N1—Cd1—N4	100.9 (2)
O1—Cd1—N4	90.6 (1)	N2—Cd1—N3	99.5 (2)
O2—Cd1—N1	146.1 (1)	N2—Cd1—N4	167.3 (2)
O2—Cd1—N2	95.6 (2)	N3—Cd1—N4	72.8 (2)
O2—Cd1—N3	98.8 (1)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4 \cdots O7	0.85	2.25	2.97 (2)	144
O4'—H4' \cdots O7	0.85	1.75	2.55 (2)	156
O9—H9 \cdots O6 ⁱ	0.85	1.70	2.55 (1)	177
O1 w —H1 w \cdots O2	0.87	1.97	2.84 (1)	171

Symmetry code: (i) $1 + x, y, z$.

The structure shows disorder of the $C_{10}H_9O_5S^-$ monoanion coordinated to the Cd atom. The coordinated carboxylate unit itself is ordered. The whole of the rest of this ligand is disordered over two half-occupied sites, with the O and S atoms interchanged for the two orientations. The following distances were restrained to be the same

within 0.01 Å: C1—C2 and C1—C2'; O3—C2, O3—C3, O1'—C6' and O1'—C9'; S3'—C2', S3'—C3', S1—C6, S1—C9 and the C—O distances of the disordered carboxyl group, as well as the O4···O5 and O4'···O5' interactions. The atomic displacement parameters (adps) for atom S1 were set equal to those of atom O1', and those of the pair S3'/O3 were similarly constrained. For all other disordered atoms, the adps of the primed atoms were set equal to those of the unprimed atoms and restrained to be approximately isotropic. The phenylene entities were constrained to be regular hexagons, with C—C distances of 1.39 Å.

The two water molecules show large displacements; these were restrained to be nearly isotropic. Their H atoms were found by using the *HYDROGEN* (Nardelli, 1999) option in the *WinGX* (Farrugia, 1999) suite but were not refined. The carbon-bound H atoms were placed at calculated positions [aromatic C—H = 0.93 Å and aliphatic C—H = 0.97 Å] and were included in the refinement in the riding-model approximation. The acid H atoms were also placed geometrically (O—H = 0.85 Å). The U_{iso} values for all H atoms was set at $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK and Rigaku, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *ORTEP II* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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