

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cadmium(II) *N*-(*p*-Tolylsulfonyl)-glutamate

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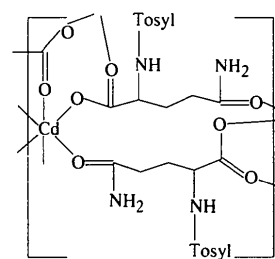
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Abstract

Crystals of $[\text{Cd}(\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_5\text{S})_2]$ contain a two-dimensional polymeric network in which Cd^{2+} ions are octahedrally coordinated by O atoms.

Comment

In the title compound, (I), the Cd^{2+} ion lies on a crystallographic twofold axis and exhibits octahedral coordination, being attached to six different amino acid residues, thereby giving rise to a layer structure in the *ab* plane. Each amino acid residue is linked to three different Cd atoms through its carboxylic and amide O atoms; the carboxylate group bridges two Cd atoms in a *syn-syn* configuration. The same type of amino acid coordination has been found previously in $[\text{Mn}(\text{tsgln})_2]$ [tsgln = *N*-(*p*-tolylsulfonyl)glutamate] (Brückner, Menabue, Saladini & Tolazzi, 1993), while in $[\text{Cu}(\text{bpy})(\text{tsasn})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ [tsasn = *N*-(*p*-tolylsulfonyl)asparaginate, bpy = 2,2'-bipyridine] (Battistuzzi Gavoli *et al.*, 1990) it was found that the amino acid coordinates through one carboxylic O atom only and the amide O atom is not involved in metal ligation.



(I)

Carboxylates normally act as bidentate chelating or bridging ligands towards Cd^{II} , leading to the formation of polymeric structures (Allman, Goel, Jha & Beauchamp, 1984). However, in the title complex, (I), the carboxylate coordination is very unsymmetrical: the Cd—O1 bond [2.384 (6) Å] is significantly longer than Cd—O2 [2.196 (7) Å]. Crystal packing is mainly due to ring–ring intra- and interlayer contacts in the range 3.52 (1)–3.90 (1) Å, and there is only one hydrogen bond: $\text{N1} \cdots \text{O1}^i = 2.91$ (1), $\text{H6} \cdots \text{O1}^i = 2.12$ Å, $\text{N1}—\text{H6} \cdots \text{O1}^i = 134^\circ$ [symmetry code: (i) $x - 1/2, y + 1/2, z$]; the relatively acute angle at H(6) is attributed to the constraint imposed by the coordination of the amide group by the metal.

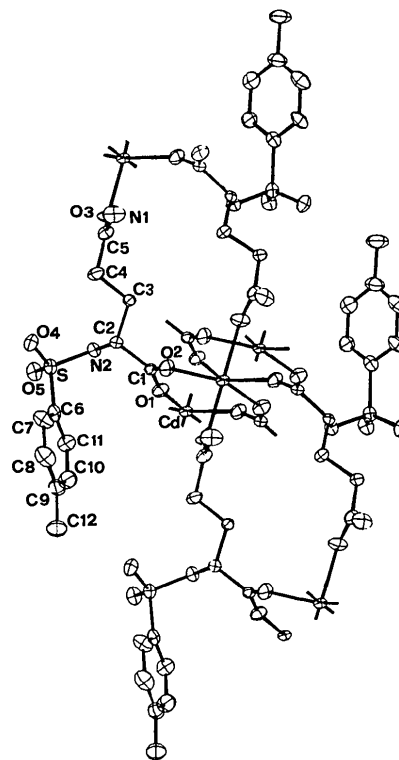


Fig. 1. ORTEP (Johnson, 1965) view, with 40% probability displacement ellipsoids, of $\text{Cd}(\text{tsgln})_2$. The H atoms have been omitted for clarity.

Experimental

An aqueous solution (0.05 dm³) of cadmium(II) acetate (0.02 mol dm⁻¹) was added to an aqueous solution (0.02 dm³) of the L-amino acid (0.1 mol dm⁻¹). After a few days a white crystalline compound separated (yield 80%). Elemental analysis: found C 40.21, H 4.34, N 7.87%; C₂₄H₃₀N₄O₁₀S₂ requires C 40.52, H 4.25, N 7.88%. The density D_m was measured by flotation in CHCl₃/CHCl₂CCl₃.

Crystal data

[Cd(C₁₂H₁₅N₂O₅S)₂] $M_r = 710.8$

Monoclinic

C2

 $a = 17.755 (2) \text{ \AA}$ $b = 5.290 (5) \text{ \AA}$ $c = 17.383 (3) \text{ \AA}$ $\beta = 121.48 (1)^\circ$ $V = 1392 (1) \text{ \AA}^3$ $Z = 2$ $D_x = 1.69 \text{ Mg m}^{-3}$ $D_m = 1.65 \text{ Mg m}^{-3}$ Mo K α radiation $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 5.5\text{--}12^\circ$ $\mu = 0.98 \text{ mm}^{-1}$ $T = 298 (2) \text{ K}$

Irregular prism

 $0.40 \times 0.15 \times 0.15 \text{ mm}$

White

N2	-0.0615 (3)	0.232 (1)	0.1933 (3)	0.025 (2)
S	0.0002 (1)	0.180 (1)	0.3016 (1)	0.0243 (7)
O4	-0.0265 (3)	0.3531 (9)	0.3462 (3)	0.034 (2)
O5	-0.0040 (4)	-0.081 (1)	0.3129 (4)	0.031 (2)
C6	0.1110 (4)	0.248 (1)	0.3365 (4)	0.031 (3)
C7	0.1523 (5)	0.457 (1)	0.3895 (5)	0.042 (3)
C8	0.2403 (5)	0.496 (3)	0.4190 (5)	0.053 (3)
C9	0.2873 (4)	0.333 (2)	0.3979 (5)	0.049 (4)
C10	0.2428 (5)	0.126 (2)	0.3437 (5)	0.049 (4)
C11	0.1560 (5)	0.083 (2)	0.3129 (5)	0.040 (3)
C12	0.3846 (5)	0.374 (3)	0.4340 (6)	0.072 (5)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cd—O1	2.384 (6)	C2—C3	1.527 (8)
Cd—O2 ⁱ	2.196 (7)	C7—C8	1.38 (1)
Cd—O3 ⁱⁱ	2.264 (3)	C2—N2	1.47 (1)
S—O4	1.432 (6)	C8—C9	1.38 (2)
N2—S	1.633 (4)	C3—C4	1.52 (1)
S—O5	1.402 (6)	C9—C10	1.39 (1)
O1—C1	1.21 (1)	C4—C5	1.49 (1)
S—C6	1.767 (7)	C9—C12	1.51 (1)
O2—C1	1.28 (1)	C5—N1	1.33 (1)
C6—C7	1.38 (1)	C10—C11	1.36 (1)
C1—C2	1.53 (1)	C5—O3	1.225 (9)
C6—C11	1.38 (1)		
O3 ⁱⁱⁱ —Cd—O3 ⁱⁱⁱⁱ	178.5 (3)	S—C6—C11	118.8 (6)
O2 ^v —Cd—O3 ⁱⁱⁱⁱ	93.8 (2)	S—C6—C7	120.0 (6)
O2 ⁱⁱ —Cd—O3 ⁱⁱⁱⁱ	87.0 (2)	O1—C1—O2	124.8 (6)
O2 ⁱⁱ —Cd—O2 ^{iv}	112.4 (2)	C7—C6—C11	121.1 (8)
O1 ^v —Cd—O3 ⁱⁱ	91.4 (2)	O2—C1—C2	113.1 (6)
O1 ^v —Cd—O2 ⁱ	160.2 (2)	C6—C7—C8	118.1 (8)
O1—Cd—O3 ⁱⁱ	87.4 (2)	O1—C1—C2	122.1 (7)
O1—Cd—O2 ^{iv}	160.2 (2)	C7—C8—C9	122.2 (9)
O1—Cd—O2 ⁱ	86.9 (2)	C1—C2—N2	111.4 (5)
O1—Cd—O1 ^v	74.3 (2)	C8—C9—C12	121.4 (9)
C4—C5—N1	118.5 (8)	C1—C2—C3	110.7 (4)
N1—C5—O3	121.4 (8)	C8—C9—C10	117.6 (8)
C2—N2—S	116.6 (4)	C3—C2—N2	110.5 (5)
N2—S—C6	108.5 (3)	C10—C9—C12	120.9 (9)
N2—S—O5	106.0 (3)	C2—C3—C4	110.4 (5)
N2—S—O4	107.6 (3)	C9—C10—C11	121.7 (9)
O5—S—C6	106.5 (4)	C3—C4—C5	113.4 (6)
O4—S—C6	107.9 (3)	C6—C11—C10	119.2 (8)
O4—S—O5	119.9 (4)	C4—C5—O3	120.1 (8)

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

Data collection

Enraf-Nonius CAD-4 diffractometer

 $\omega/2\theta$ scansAbsorption correction: refined from ΔF_o (Ugozzoli, 1987) $T_{\min} = 0.88, T_{\max} = 1.00$

2844 measured reflections

2740 independent reflections

1380 observed reflections [$I > 2\sigma(I)$] $R_{\text{int}} = 0.021$ $\theta_{\text{max}} = 25^\circ$ $h = -21 \rightarrow 21$ $k = 0 \rightarrow 6$ $l = 0 \rightarrow 20$

3 standard reflections

frequency: 180 min
intensity decay: 10%

Refinement

Refinement on F $R = 0.041$ $wR = 0.038$ $S = 0.56$

1330 reflections

185 parameters

Unit weights applied

 $(\Delta/\sigma)_{\text{max}} = 0.004$ $\Delta\rho_{\text{max}} = 1.36 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -3.04 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^*$$

	x	y	z	U_{eq}
Cd	0	0	0	0.0201 (2)
O1	-0.0003 (3)	0.359 (1)	0.0827 (4)	0.034 (2)
O2	-0.0159 (3)	0.769 (1)	0.0956 (4)	0.036 (2)
C1	-0.0248 (3)	0.535 (4)	0.1089 (4)	0.023 (2)
C2	-0.0688 (3)	0.496 (2)	0.1637 (3)	0.019 (2)
C3	-0.1654 (4)	0.579 (1)	0.1097 (4)	0.026 (3)
C4	-0.2004 (4)	0.619 (2)	0.1718 (5)	0.036 (3)
C5	-0.2967 (5)	0.677 (1)	0.1228 (5)	0.031 (3)
N1	-0.3218 (5)	0.916 (1)	0.1165 (5)	0.046 (3)
O3	-0.3508 (2)	0.506 (1)	0.0875 (3)	0.037 (2)

The structure was solved by conventional Patterson and Fourier techniques, and was refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically. H atoms were located in a difference synthesis map and were treated as fixed contributors. The final $\Delta\rho$ synthesis was 'noisy' in the vicinity of the Cd atom but was otherwise featureless. All calculations were carried out on an IBM personal computer.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1988). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976). Program(s) used to refine structure: *SHELX76*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1179). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Hexamethylenetetramine)diiodomercury(II), HgI₂.hmt

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Abstract

The reaction of 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane, trivial name hexamethylenetetramine (hmt), and HgI₂ (molar ratio 1:1) in ethanol or acetone diiodide (1:1), gives the title compound, *catena*-poly[diiodomercury- μ -1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane-*N*¹:*N*⁵], [HgI₂(C₆H₁₂N₄)] (HgI₂.hmt). The crystal and molecular structure of the title compound have been determined by X-ray structure analysis. HgI₂.hmt belongs to the class of donor–acceptor complexes between hmt and metal salts. Hg is fourfold coordinated by two I and two hmt ligands. hmt acts as a bifunctional bridging ligand forming bent (–Hg–hmt–)_n chains in the **b** direction of the *Pnma* space group.

Comment

A large number of hexamethylenetetramine (hmt) complexes were reviewed in 1931 (Alpeter, 1931). Only a few of the complexes have been structurally analysed. hmt has four N-atom lone electron pairs which allow various coordination types in complex chemistry. Five types of hmt coordination in complexes with metal salts can be distinguished:

(1) hmt as a non-metal-coordinated structure element. Compounds of this type are often found in complexes containing water of crystallization, for instance in *MX*₂.2hmt.10H₂O, with *MX*₂ = CaBr₂ (Mazzarella, Kovacs, de Santis & Liquori, 1967), CoCl₂ (Ganesh, Seshasayee, Aravamudan, Heijdenrijk & Schenk, 1990), MgCl₂ (Kovacs & Mazzarella, 1966) or Co(NO₃)₂ (Viostat, Khodadad & Rodier, 1981), in *M*Cr₂O₇.2hmt.yH₂O, with *M* = Ca, *y* = 7 (Dahan, 1975) or *M* = Mg, *y* = 6 (Dahan, 1974), or in hexacyanoferrate complexes *M*_a[Fe(CN)₆]_b.xhmt.yH₂O of various composition with *M* = Li, Mg, Sr, Ba, *x* = 1–4 and *y* = 4–11 (Meyer & Pickardt, 1988*a,b,c*, 1989; Pickardt, Kahler, Rautenberg & Riedel, 1984). In all these compounds hmt is not part of the metal-coordination sphere.

(2) hmt as a monofunctional ligand. This coordination type has only been found in a few complexes: Mo(CO)₅.hmt (Hui, Chan & Mak, 1984), (ZnCl₂)₃.hmt.12H₂O (Mak & Huang, 1987), Cd{P(S₂O-C₂H₅)₂}₂.2hmt (Shimoi, Ouchi, Aikawa, Sato & Saito, 1982). The structures of these compounds consist of isolated molecular units or networks formed by μ -halogeno bridges.

(3) hmt as a bifunctional bridging ligand. This is the most common type of hmt coordination. Depending on coordination number and the shape of the metal, different networks are formed, *e.g.* in (CdCl₂)₂.hmt.5H₂O (Lai & Mak, 1983), Cd(NO₃)₂.hmt.2H₂O (Viostat, Khodadad & Rodier, 1982), (CdI₂)₃.2hmt.4H₂O (Mak, 1982; Pickardt 1981*b*), [Hg(SCN)₂]_x.hmt, *x* = 1, 2 (Mak & Wu, 1985, 1986), (CuCN)₃.2hmt (Pickardt & Rautenberg, 1982) or [Cu(CH₃COO)₂]₂.hmt (Pickardt 1981*a*).

(4) hmt as a trifunctional bridging ligand. To our knowledge, there is only one structure of this type published. AgNO₃.hmt consists of Ag–hmt–Ag–hmt chains. These chains are linked by additional Ag–hmt bonds. Every hmt ligand thus connects three Ag atoms (Michelet, Viostat, Khodadad & Rodier, 1981).

(5) hmt as a tetrafunctional bridging ligand. This coordination type is known for (AgX)₄.hmt with X = Cl, Br (Mak, 1984, 1985). All four N-atom lone pairs of each cage molecule serve as ligands, giving rise to octahedral AgX₅N, tetrahedral AgX₃N and tetragonal pyramidal AgX₄N, forming a three-dimensional network.

Alpeter (1931) described the following mercury halide hmt complexes: HgX₂.hmt with X = Cl, Br, I; 2(HgX₂)₂.hmt with X = Cl, Br; (HgX₂)₃.2hmt with X = Cl, I. However, no crystal structure of these com-