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4,4'-Oxydianilinium Tetrachlorocadmiate(II), an Intercalation Compound

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Abstract

The title compound, $(C_{12}H_{14}N_2O)[CdCl_4]$, is a typical two-dimensional organic intercalated compound. The inorganic layers of the compound are formed by $CdCl_6$ octahedra sharing corner Cl atoms (*i.e.* *catena*-poly[dichlorocadmium-di- μ -chloro]). The organic diammonium cations are intercalated between every two metal–halogen layers and form the organic layers of the compound through hydrogen bonding.

Comment

Molecular assembling has recently become an exciting research field because it is a key technique in the development of new materials. The title compound, (I), belongs to the family of layer perovskites that have the general formula $(NH_3-R)_2MCl_4$ or $(NH_3-R'-NH_3)MCl_4$ ($M = Cd, Mn, Cr, Cu, Fe, Pt, Pd$). Around 20 years ago many layer perovskites in which group R is C_nH_{2n+1} and R' is C_nH_{2n} were investigated with respect to their thermal and magnetic properties (Arend & Huber, 1978; Needham & Willett, 1984). We found that the structure of this kind of compound is very similar

to that of a Langmuir–Blodgett film and seems to offer a new route to two-dimensional molecular assemblies. In this paper we report the crystal structure of the title salt, (I).

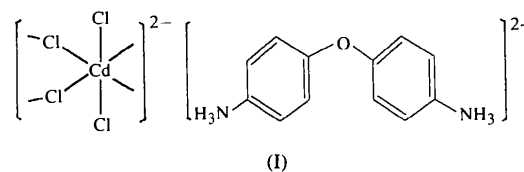


Fig. 1 shows the atom-numbering scheme and Fig. 2 shows the packing of the ions in the unit cell. It can be seen from Fig. 2 that the structure of the title compound consists of two types of layers: metal–halogen layers and organic diammonium layers. The metal–halogen layer is formed by $CdCl_6$ octahedra sharing corners in the xy plane of the crystal cell; the stoichiometry of the layer is $[CdCl_4]_n^{2n-}$. The $-NH_3^+$ groups of each 4,4'-oxydianilinium cation are positioned in the 'hole' enclosed by four $CdCl_6$ octahedra. The 4,4'-oxydianilinium ions are sandwiched between two metal–halogen layers and form organic layers. These layers stack on top of each other, forming a two-dimensional structure which is similar to that of the Langmuir–Blodgett film.

In the $CdCl_6$ octahedron, the distance of the Cd atom to the bridging Cl(2) atoms is significantly longer (*ca* 0.12 Å) than that of the Cd atom to the axial Cl(1) atoms. The $CdCl_6$ octahedron is therefore compressed. Each $-NH_3^+$ group of the 4,4'-oxydianilinium ion is surrounded by four Cl(1) and four Cl(2) atoms. The distances of an N atom to one Cl(2) and to two Cl(1) atoms are 3.257 (5), 3.158 (4) and 3.168 (4) Å, respectively; these are all quite reasonable N–H...Cl hydrogen-bonding distances. As a result of hydrogen bonding, the bonded Cl atoms are brought closer to the N atom and the $CdCl_6$ octahedron is tipped *ca* 9.3 (4)° out of the xy plane of the crystal cell. This results in puckering of the metal–halogen layers, as shown in Fig. 2. The Cd–Cl–Cd bond is not linear but forms an angle of 152.19 (4)° and the dihedral angle between the two benzene rings of the 4,4'-oxydianilinium ion is 73.22 (4)°.

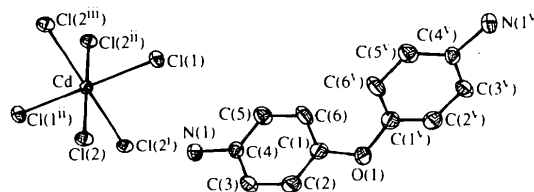
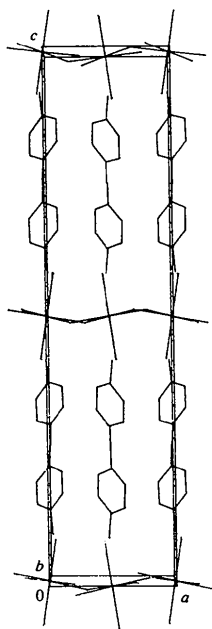


Fig. 1. The numbering of the atoms of the title compound. Displacement ellipsoids are plotted at the 30% probability level. H atoms are omitted for clarity.

Fig. 2. A view of the unit cell down the *b* axis.

1272 reflections
112 parameters
H atoms refined isotropically
 $w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\max} = 0.02$

Extinction coefficient:
 5.2556×10^{-6}
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)
$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Cd	1	1/2	1/2	1.46 (3)
Cl(1)	1.0522 (2)	0.4806 (1)	0.58196 (4)	2.33 (5)
Cl(2)	0.7005 (1)	0.3002 (1)	0.51248 (3)	2.04 (4)
O(1)	1	-0.2325 (6)	3/4	3.9 (3)
N(1)	1.0209 (6)	0.0541 (7)	0.5818 (1)	2.4 (2)
C(1)	0.9937 (5)	-0.1434 (6)	0.7105 (2)	2.4 (2)
C(2)	0.8874 (6)	-0.2182 (5)	0.6785 (1)	2.8 (2)
C(3)	0.8917 (6)	-0.1507 (5)	0.6363 (1)	2.3 (2)
C(4)	1.0020 (5)	-0.0059 (5)	0.6275 (2)	2.0 (2)
C(5)	1.1047 (6)	0.0749 (6)	0.6596 (1)	2.8 (2)
C(6)	1.1009 (8)	0.0071 (6)	0.7016 (2)	3.0 (2)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

Cd—Cl(1)	2.535 (1)	C(1)—C(6)	1.388 (7)
Cd—Cl(2)	2.664 (1)	C(2)—C(3)	1.384 (6)
Cd—Cl(2 ¹)	2.688 (1)	C(3)—C(4)	1.367 (6)
O(1)—C(1)	1.377 (5)	C(4)—C(5)	1.370 (7)
N(1)—C(4)	1.471 (7)	C(5)—C(6)	1.379 (6)
C(1)—C(2)	1.362 (6)		
Cl(1)—Cd—Cl(1 ⁱⁱ)	180.00	C(4)—C(3)—C(2)	118.7 (4)
Cl(1)—Cd—Cl(2)	87.15 (4)	C(3)—C(4)—C(5)	121.6 (5)
Cl(1)—Cd—Cl(2 ⁱⁱ)	92.85 (4)	C(3)—C(4)—N(1)	118.6 (4)
Cl(1)—Cd—Cl(2 ⁱ)	90.65 (4)	C(5)—C(4)—N(1)	119.7 (4)
Cl(1)—Cd—Cl(2 ⁱⁱⁱ)	89.35 (4)	C(4)—C(5)—C(6)	119.7 (4)
Cl(2)—Cd—Cl(2 ⁱ)	90.33 (4)	C(5)—C(6)—C(1)	119.0 (4)
Cl(2)—Cd—Cl(2 ⁱⁱⁱ)	89.67 (4)	Cl(1)—Cd—Cl(2)	92.85 (4)
Cl(2)—Cd—Cl(2 ⁱⁱ)	180.00	Cl(1)—Cd—Cl(2)	87.15 (4)
Cd—Cl(2 ⁱⁱⁱ)—Cd ^{iv}	152.19 (4)	Cl(1)—Cd—Cl(2)	89.35 (4)
C(1)—O(1)—C(1 ⁱ)	122.7 (5)	Cl(1)—Cd—Cl(2)	90.65 (4)
C(2)—C(1)—O(1)	116.8 (4)	Cl(2)—Cd—Cl(2)	180 (2)
C(2)—C(1)—C(6)	120.6 (4)	Cl(2)—Cd—Cl(2)	89.67 (2)
O(1)—C(1)—C(6)	122.4 (4)	Cl(2)—Cd—Cl(2)	90.33 (2)
C(1)—C(2)—C(3)	120.4 (4)		

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

Table 3. Contact distances (\AA)

Cl(1)···N(1 ⁱ)	3.158 (4)	Cl(2)···N(1 ⁱⁱ)	3.257 (5)
Cl(1)···N(1)	3.168 (5)	Cl(2)···N(1 ⁱⁱⁱ)	3.340 (5)

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

Data were collected using *CAD-4 Software* (Enraf-Nonius, 1989). The ω -scan width was $(0.75 + 0.35 \tan \theta)^\circ$ and the scan speed was $3\text{--}17^\circ \text{min}^{-1}$. The structure was solved by direct methods and refined with unit weights by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms. Calculations were performed on a VAX3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1987) program package. *PLUTO* (Motherwell & Clegg, 1978) was used to prepare molecular graphics.

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Experimental

The title compound was recrystallized from 2 mol l^{-1} aqueous HCl solution.

Crystal data

(C₁₂H₁₄N₂O)[CdCl₄]

M_r = 456.48

Orthorhombic

Pbcn

a = 7.286 (2) \AA

b = 7.408 (2) \AA

c = 30.52 (1) \AA

V = 1648 (1) \AA^3

Z = 4

D_x = 1.84 Mg m⁻³

Mo *K*α radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 13.97\text{--}14.95^\circ$

$\mu = 1.971 \text{ mm}^{-1}$

T = 296 K

Cubic

$0.6 \times 0.5 \times 0.5 \text{ mm}$

Faint brown

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scans (*TEXSAN*; Molecular Structure Corporation, 1987)

*T*_{min} = 0.869, *T*_{max} = 1.000

1747 measured reflections

1747 independent reflections

1272 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 25^\circ$

h = 0 → 8

k = 0 → 8

l = 0 → 36

3 standard reflections

frequency: 60 min

intensity decay: 1.4%

Refinement

Refinement on *F*

R = 0.041

wR = 0.054

S = 1.86

$\Delta\rho_{\max} = 0.978 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.987 \text{ e \AA}^{-3}$

Extinction correction:

secondary

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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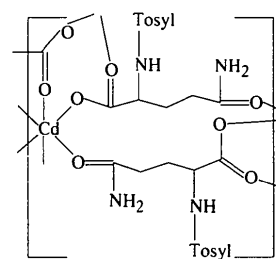
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Abstract

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.

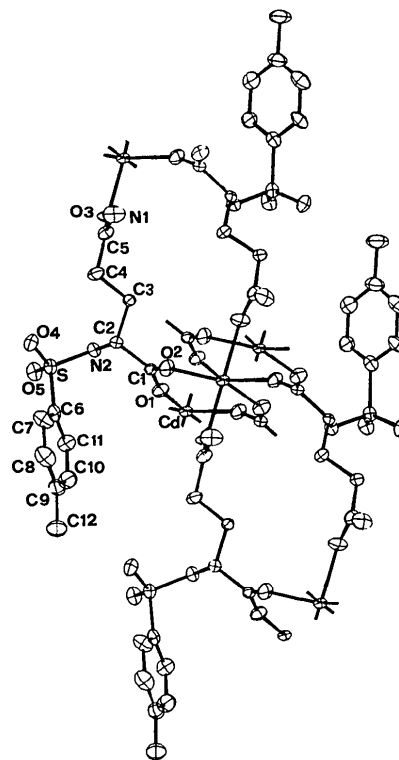


Fig. 1. ORTEP (Johnson, 1965) view, with 40% probability displacement ellipsoids, of $\text{Cd}(\text{tsgln})_2$. The H atoms have been omitted for clarity.