

868 reflections
115 parameters
H atoms not located
 $w = 1/\sigma^2(F_o)$

Atomic scattering factors
from SDP (B. A. Frenz &
Associates Inc., 1982)

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Hueso, F., Moreno, M. N., Romero, M. A., Salas, J. M., Sanchez, M. P., Alvarez de Cienfuegos, G. & Faure, R. (1993). *J. Inorg. Biochem.* **51**, 613–632.
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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			B_{eq}
	x	y	z	
Zn	-0.8440 (5)	-1	-1/6	2.91 (8)
Br1	-0.9179 (5)	-0.8162 (5)	-0.1145 (2)	6.72 (9)
Br2	-0.7942 (4)	-1.1908 (3)	-0.1126 (1)	4.76 (7)
N1	-0.611 (2)	-0.453 (2)	-0.0605 (8)	3.7 (5)
C2	-0.606 (3)	-0.373 (3)	-0.0124 (8)	3.5 (5)
N3	-0.484 (2)	-0.229 (2)	0.0041 (7)	3.2 (5)
C4	-0.350 (3)	-0.141 (3)	-0.0280 (9)	3.1 (5)
C5	-0.338 (3)	-0.198 (3)	-0.0789 (9)	3.7 (6)
C6	-0.472 (3)	-0.360 (3)	-0.095 (1)	4.0 (6)
S2	-0.8019 (9)	-0.5088 (9)	0.0242 (3)	4.8 (2)
C21	-0.752 (4)	-0.359 (4)	0.0812 (9)	5.3 (8)
N4	-0.215 (3)	0.004 (2)	-0.0079 (8)	4.2 (6)
N6	-0.476 (3)	-0.434 (3)	-0.1462 (8)	4.7 (6)

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

Zn—Br1	2.400 (6)	N3—C4	1.31 (4)
Zn—Br2	2.354 (4)	C4—C5	1.38 (3)
N1—C2	1.37 (3)	C4—N4	1.33 (2)
N1—C6	1.37 (3)	C5—C6	1.38 (3)
C2—N3	1.25 (2)	C6—N6	1.42 (3)
C2—S2	1.78 (2)	S2—C21	1.83 (3)
Br1—Zn—Br1 ⁱ	105.2 (2)	N3—C4—C5	124 (2)
Br1—Zn—Br2 ⁱ	106.1 (2)	N3—C4—N4	116 (2)
Br1—Zn—Br2	112.4 (2)	C5—C4—N4	120 (2)
Br2—Zn—Br2 ⁱ	114.3 (2)	C4—C5—C6	117 (2)
C2—N1—C6	117 (2)	N1—C6—C5	119 (2)
N1—C2—N3	126 (2)	N1—C6—N6	118 (2)
N1—C2—S2	109 (2)	C5—C6—N6	123 (2)
N3—C2—S2	124 (2)	C2—S2—C21	96 (1)
C2—N3—C4	117 (2)		

Symmetry code: (i) $x - y - 1, -2 - y, -\frac{1}{3} - z$.

The high final R value of 0.075 is probably due to absorption problems [$\mu(\text{Mo } K\alpha) = 9 \text{ mm}^{-1}$]. All calculations were performed using the Enraf-Nonius SDP system (B. A. Frenz & Associates Inc., 1982) implemented on a DEC MicroVAX 3100-80 computer at the Centre de Diffractométrie Automatique, Université Lyon I. Molecular graphics were prepared using *SHELXTL-Plus* (Sheldrick, 1987).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: PA1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(4-nitroanilinium) Tetrachlorocadmate

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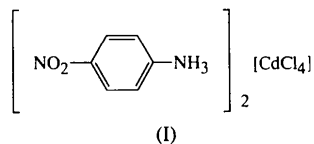
Abstract

An aromatic cation-based perovskite-type layered crystal of bis(4-nitroanilinium) tetrachlorocadmate, (C₆H₇N₂O₂)₂[CdCl₄], was obtained. X-ray diffraction analysis of a single crystal revealed it to have a layered structure consisting of alternating organic bilayers and inorganic sheets. Cd ions and Cl anions form six-coordinate octahedra whose equatorial corner anions are shared with the neighbouring octahedra. The organic bilayer has a 'tail-to-tail' structure, showing that the molecular arrangement is mainly determined by the inorganic layer structure, not by the intermolecular dipolar interaction of the 'push-pull' type molecule.

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Comment

Perovskite-type layered halide compounds [general formula $(RNH_3)_2MX_4$] have been attracting considerable interest because of their unique properties, such as third-order harmonic generation (Xu *et al.*, 1991), photoluminescence (Hong, Ishihara & Nurmikko, 1992; Papavassiliou, Patsis, Lagouvardos & Koutselas, 1993), electroluminescence (Era, Morimoto, Tsutsui & Saito, 1994) and electrical conductivity (Mitzi, Feild, Harrison & Guloy, 1994). They consist of segregated layers of organic and inorganic components; the former being a bilayer of alkylammonium cations and the latter comprising corner-sharing halogen octahedra each centered by a divalent metal atom. Using this inorganic–organic hetero structure, it has become possible to modify the function associated with the inorganic layer (Mitzi, Feild, Harrison & Guloy, 1994). Furthermore, based on this characteristic structure, a new strategy has been developed to arrange organic molecules in such a manner as is not easily realised by other techniques, although the organic molecules employed so far have been limited to simple molecules such as alkylammonium (Chapuis, 1978; Kind *et al.*, 1979), alkyldiammonium (Willett, Place & Middleton, 1988; Snively, Haines, Emerson & Drumheller, 1982; Arend, Tichy, Baberschke & Rys, 1976) and phenethylammonium (Era, Morimoto, Tsutsui & Saito, 1994). We report here the crystal structure of the title compound, (I), which represents an extension of the perovskite-type layered structure, with the aim of utilizing the inorganic layer as a host for arranging the cation of a ‘push-pull’ type molecule.



X-ray diffraction analysis of a single crystal of the title compound revealed that the crystal has a layered structure consisting of alternating organic bilayers and inorganic sheets (Fig. 2). Cd ions and Cl anions form six-coordinate octahedra whose equatorial corner anions are shared with the neighbouring octahedra. The organic bilayer has a ‘tail-to-tail’ structure in which the nitro groups of the molecules are positioned in the central portion of the organic layer. Fig. 3 shows the projection along the *a* axis, *i.e.* along the direction parallel to the layer normal.

The equatorial edges of adjacent octahedra do not meet at right angles; the Cd—Cl—Cd angle is $156.56(3)^\circ$. The NH_3 group of the 4-nitroanilinium cation is juxtaposed between the axial vertices of the Cl octahedra. The N atom of the ammonium group is bonded to the Cl octahedron through hydrogen bonds. Two of the three protons of the ammonium group are directed towards the two axial Cl atoms and the third

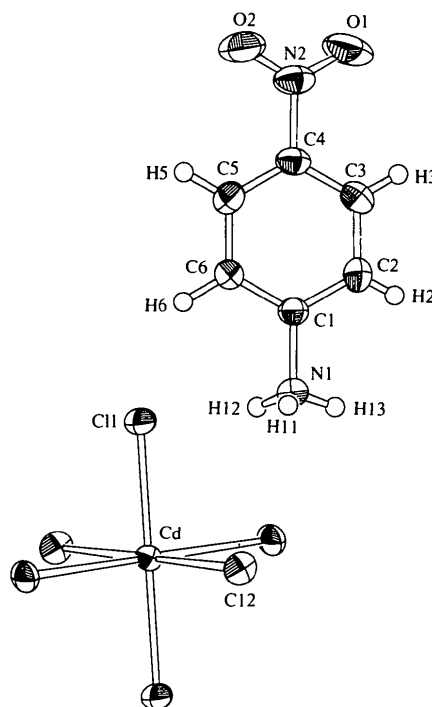


Fig. 1. Perspective view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

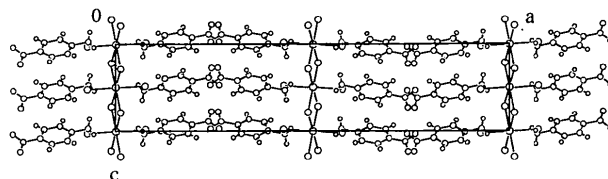


Fig. 2. Molecular packing viewed from the [010] axis.

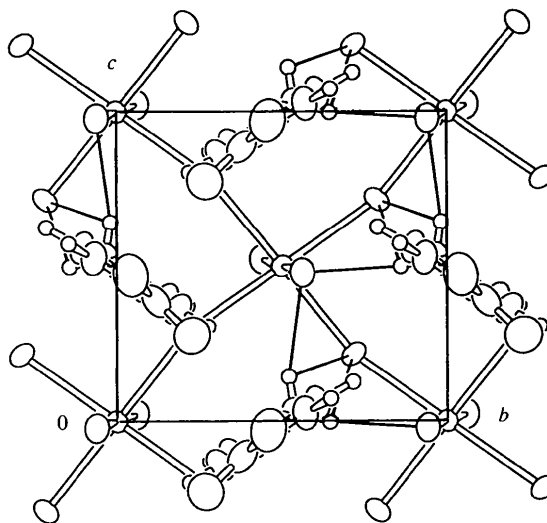


Fig. 3. Projection along the [100] axis. Solid lines indicate the hydrogen bonds.

towards an equatorial Cl atom. The molecular axis of the 4-nitroanilinium cation is thus tilted by *ca* 20° with respect to the layer normal. These features are similar to those of the *n*-alkylammonium derivatives [(C_nH_{2n+1}NH₃)₂MX₄] reported so far (Chapuis, 1978; Kind *et al.*, 1979).

The above results demonstrate the versatility of the perovskite-type layered structure in arranging organic functional molecules. The molecular arrangement of 4-nitroaniline in the present crystal is unique and is very different from those of the 4-nitroaniline.HCl salt (Trueblood, Goldish & Donohue, 1961) and 4-nitroaniline itself (Ploug-Sørensen & Andersen, 1982), where the occurrence of the 'head-to-tail' molecular alignment indicates the dominant role of the intermolecular dipolar interaction of the 'push-pull' type molecule in determining the molecular arrangement in the crystal. The 'tail-to-tail' structure in the present crystal shows that the molecular arrangement is mainly determined by the inorganic layer structure which acts as a host for the organic molecule.

Experimental

Crystals of the title compound were obtained by slow evaporation of a 2:1 mixture of 4-nitroaniline and cadmium chloride (CdCl₂) in a mixed solvent of aqueous HCl and ethanol.

Crystal data

(C₆H₇N₂O₂)₂[CdCl₄]
M_r = 532.49
 Orthorhombic
Pbca
a = 33.131 (3) Å
b = 7.792 (1) Å
c = 7.256 (1) Å
V = 1873.2 (3) Å³
Z = 4
D_x = 1.888 Mg m⁻³

Mo Kα radiation
 λ = 0.7107 Å
 Cell parameters from 23 reflections (Cu Kα radiation)
 θ = 10.7–17.7°
 μ = 1.762 mm⁻¹
T = 293 K
 Sphere
 0.1 mm (radius)
 Pale yellow

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: spherical
T_{min} = 0.766, *T_{max}* = 0.771
 2741 measured reflections
 2741 independent reflections

2120 observed reflections [*I* > 3σ(*I*)]
 θ_{\max} = 30.0°
h = 0 → 46
k = 0 → 10
l = 0 → 10
 3 standard reflections monitored every 50 reflections
 intensity decay: 1.47%

Refinement

Refinement on *F*²
R = 0.028
wR = 0.034
S = 2.17

$w = 1/[\sigma^2(F) + 0.000196F^2]$
 $(\Delta/\sigma)_{\max} = 0.015$
 $\Delta\rho_{\max} = 0.283 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.536 \text{ e \AA}^{-3}$

212 reflections
 143 parameters
 All H-atom parameters refined

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cd	0	0	0	0.0247 (1)
Cl1	0.07402 (2)	-0.0603 (1)	-0.0221 (1)	0.0347 (1)
Cl2	-0.01224 (2)	-0.28504 (9)	0.2145 (1)	0.0333 (1)
O1	0.24166 (8)	-0.7297 (4)	-0.2271 (4)	0.0692 (10)
O2	0.26068 (8)	0.5419 (4)	-0.0312 (5)	0.0692 (10)
N1	0.07142 (9)	-0.4643 (4)	0.0300 (5)	0.0353 (7)
N2	0.23457 (9)	-0.6190 (4)	-0.1150 (4)	0.0465 (9)
C1	0.11360 (9)	-0.5044 (4)	-0.0075 (4)	0.0307 (6)
C2	0.1232 (1)	-0.6488 (5)	-0.1054 (5)	0.0436 (10)
C3	0.1634 (1)	-0.6855 (5)	-0.1405 (5)	0.0462 (10)
C4	0.19204 (9)	-0.5769 (4)	-0.0773 (5)	0.0351 (9)
C5	0.1830 (1)	-0.4317 (5)	0.0242 (5)	0.0445 (10)
C6	0.14319 (10)	-0.3950 (4)	0.0598 (5)	0.0407 (9)

Table 2. Selected geometric parameters (Å, °)

Cd—Cl1	2.5021 (7)	Cd—Cl2'	2.6947 (7)
Cd—Cl2	2.7423 (7)		
H11...Cl1 ⁱⁱ	2.47 (4)	H13...Cl2 ⁱⁱⁱ	2.42 (4)
H12...Cl1	2.33 (4)		
Cl1—Cd—Cl2	91.68 (2)	Cl2—Cd—Cl2'	95.127 (9)
Cl1—Cd—Cl2'	91.07 (2)	Cd—Cl2—Cd ^{iv}	156.56 (3)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *MULTAN78* (Main *et al.*, 1978). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

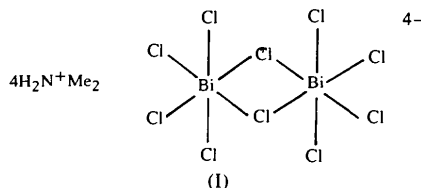
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1993). The coordination sphere of the metal is dominated by a tendency towards hexacoordination. Here we report the structure of the title compound, (I).



Examples of other reported species include BiCl_6^{3-} discrete octahedra (Lazarini, 1987), $\text{Bi}_2\text{Cl}_9^{3-}$ bi-octahedra sharing a face (Aurivillius & Stalhandske, 1978) and BiCl_4^- forming infinite chains of edge-sharing octahedra (Blázič & Lazarini, 1985).

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Dimethylammonium Pentachlorobismuthate(III)

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Abstract

The structure of $[\text{NH}_2(\text{CH}_3)_2]_2[\text{BiCl}_5]$ is characterized by hexacoordinate Bi, forming a $[\text{BiCl}_5]_2^{4-}$ dimer [*i.e.* di- μ -chloro-bis(tetrachlorobismuth)] with the geometry of two slightly distorted octahedra sharing one edge. The two bridging Cl atoms are connected to the Bi atom by long bonds [2.906 (3) and 2.922 (3) Å]. The other Bi—Cl distances are shorter [2.566 (3)–2.741 (3) Å] and are characteristic of 'free' Cl atoms. The dimethylammonium groups are connected *via* hydrogen bonds to the Cl atoms. The $\text{NH} \cdots \text{Cl}$ bonds vary in length from 3.22 (1) to 3.280 (9) Å.

Comment

The present work is part of a study of the interaction between organic cations and heavy-metal halogenides (Jarraya, Ben Salah, Daoud, Rothammel & Burszlauff,

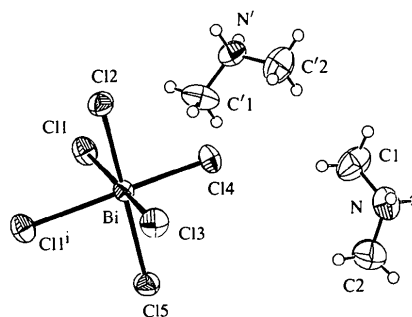


Fig. 1. View of the molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

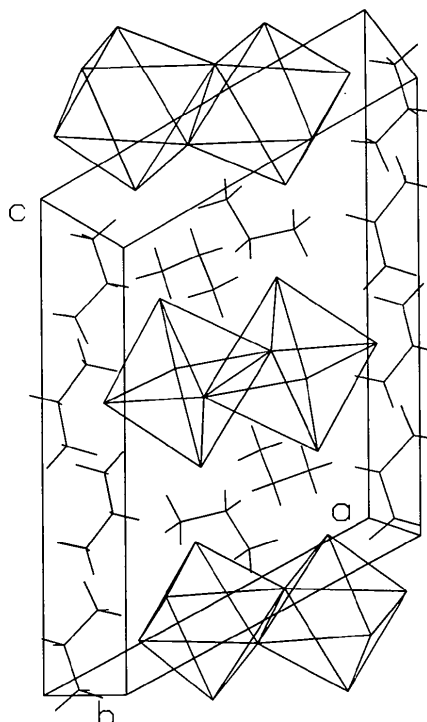


Fig. 2. The packing arrangement.