

was carried out using *SHELXTL* (Sheldrick, 1985). The Au-atom position was determined by direct methods and the remaining non-H atoms were located using difference Fourier techniques. All non-H atoms were refined anisotropically and H atoms were placed in idealized positions with fixed isotropic displacement parameters [$U(H) = 0.08 \text{ \AA}^2$].

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: ST1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Adams, H.-N., Hiller, W. & Strahle, J. (1982). *Z. Anorg. Allg. Chem.* **485**, 81–91.
 Braunstein, P., Muller, A. & Bogge, H. (1986). *Inorg. Chem.* **25**, 2104–2106.
 Hendrickson, A. R. & Martin, R. L. (1973). *J. Org. Chem.* **38**, 2548–2549.
 Sheldrick, G. M. (1985). *SHELXTL User's Manual*. Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
 Uson, R., Laguna, A. & Laguna, M. (1989). *Inorg. Synth.* **26**, 85–91.

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Bis(tetraethylammonium) Tetrabromocadmate

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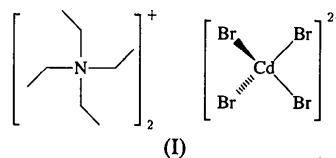
Abstract

The crystal structure of the title compound, $[(C_2H_5)_4N]_2[CdBr_4]$, has been determined by single-crystal X-ray diffraction methods. The crystal structure consists of isolated $CdBr_4$ tetrahedra, two cations in a swastika conformation (one ordered, one disordered) and one cation in a *trans* conformation. All cations show strong thermal motion. Automatic structure solution packages failed to yield a chemically relevant result. The structure solution by manual interpretation of the Patterson map is reported here.

Comment

Bis(tetraethylammonium) tetrahalometallates(II), $[(C_2H_5)_4N]_2[MX_4]$, with $M = Fe, Co, Ni, Cu, Zn, Cd$, and $X = Cl, Br, I$, have been the subject of numerous investigations. So far only the crystal structures of the room-temperature phase of $[(C_2H_5)_4N]_2[NiCl_4]$ and the isotopic Co compound have been reported (Stucky, Folkers & Kistenmacher, 1967), in which the metal was found to be tetrahedrally coordinated by Cl atoms and the cation to have a disordered swastika conformation.

Ross, Siddiqi & Tyrrell (1972) confirmed the tetrahedral coordination of Cd in the corresponding tetrabromo- and tetraiodocadmates. Investigations of the optical birefringence showed that the title compound, (I), belongs to the tetragonal crystal system and undergoes two phase transitions at 39 and 311 K (Vlokh, Polovinko, Mokryi & Sveleba, 1991; Sveleba *et al.*, 1993). In this work we present the crystal structure of the compound in its room-temperature phase.



Buerger-precession and de Jong Bouman photographs show a $\sqrt{2}/2a \times \sqrt{2}/2b \times c$ substructure. This substructure may be the reason why neither automatic heavy-atom nor direct methods using *Xtal3.2* (Hall, Flack & Stewart, 1992) and *SHELXS86* (Sheldrick, 1985) yielded anything chemically discernible. Therefore, the structure solution by manual interpretation of the Patterson map was attempted.

Inspection of the $(uv0)$ -Harker plane confirmed $P\bar{4}2_1m$ as the correct space group. Furthermore, this Harker plane exhibits three prominent vectors (marked with 'X' in Fig. 1) which delimit an equilateral triangle, the sides of which correspond to interatomic distances of about 3.5 Å identifying it as a face of a $CdBr_4$ tetrahedron.

Thus, the basic feature of this structure is $CdBr_4$ tetrahedra each with their threefold axis parallel to the crystallographic c axis. This is confirmed by a strong vector at $(00w)$ corresponding to an interatomic distance of 2.6 Å, which in turn is consistent with a Cd—Br bond distance.

In projection along the crystallographic c axis the anions should appear as equilateral triangles with a Cd and a Br atom at the centre of mass. Assuming an ordered arrangement of the tetrahedra and avoiding close contacts (*i.e.* less than 3.5 Å) between Br atoms, it is possible to confine the triangles to positions where one of their bisectors lies on the mirror line of the plane group $p4gm$. Thus two Br atoms and the Cd atom should lie on the positions $2b$ or $4m$ of $p4gm$. The substructure mentioned above leads to a very strong vector in $(\frac{1}{2} \frac{1}{2} 0)$.

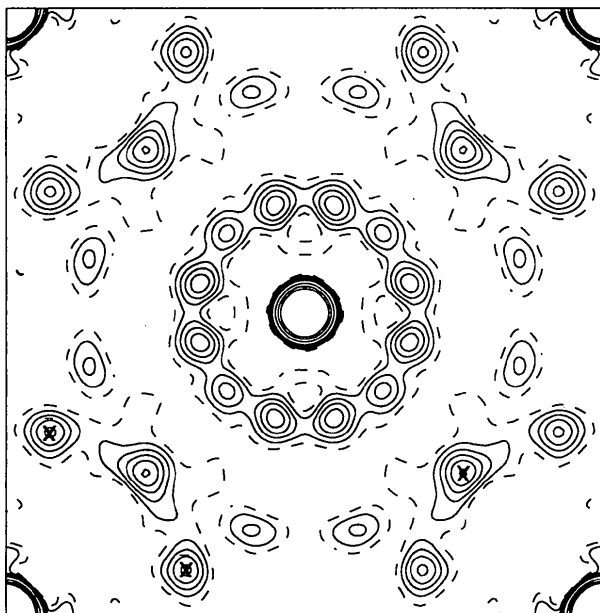


Fig. 1. Contour plot of $(uv0)$ -Harker plane of a sharpened (ExF) Patterson map.

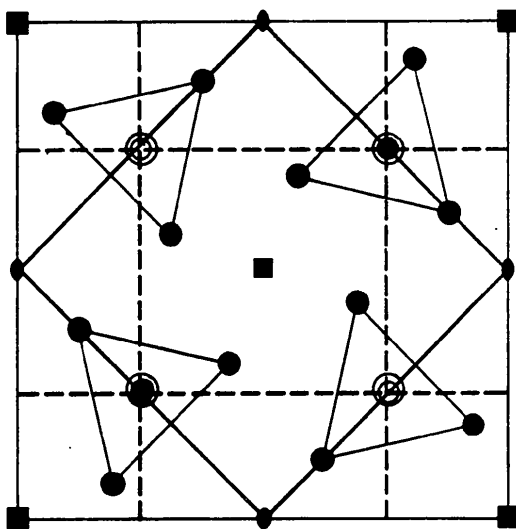


Fig. 2. Projection along $[001]$ showing the arrangement of $CdBr_4$ tetrahedra deduced from the Patterson map.

This can be accounted for by putting heavy atoms in $(0\frac{1}{2})$ or $(\frac{1}{4}\frac{1}{4})$. Considering the stoichiometry the only arrangement possible is the one shown in Fig. 2. By inspection of the $(\frac{1}{2}vw)$ -Harker plane this arrangement is confirmed and the z coordinates of the heavy atoms are easily deduced.

Using the heavy-atom positions the cations could be located from subsequent difference Fourier syntheses. Refinement of the absolute-structure parameter showed

that the initial parameters had to be inverted. As a result of rather strong thermal motion the cations are not well defined, which made it necessary to impose restraints on the N—C and C—C bond lengths. Except for the H atoms the structure was refined by weighted full-matrix least-squares on F . Since no intensity worth measuring could be found beyond 46° in 2θ , not enough data were available to refine the C atoms anisotropically. H atoms were positioned geometrically and maintained at the calculated positions. The H-atom isotropic displacement parameters were fixed at 0.2 \AA^2 .

As can be seen from Fig. 3, the structure consists of almost ideal isolated $CdBr_4$ tetrahedra, each with one of their threefold axes tilted slightly away from the crystallographic c axis; all face one another. Thus, three kinds of interstitial site are formed: one layer-like and two roughly spherical. To optimize packing the layer-like interstitial is occupied by a cation in a *trans* conformation, whereas the other cations adopt the swastika conformation. Furthermore, one of the cations in the swastika conformation is disordered, which can be understood by considering the shortest $C \cdots Br$ contact distances; these are to the methylene C atoms in the ordered cation and the methyl C atoms in the disordered cation. The ordered cation is prevented from reorientation because the methylene C atoms are 'bracketed' by Br atoms. In the disordered cation only the methyl C atoms are bracketed by Br atoms, which enables reorientation of the molecule by cooperative rotation of the methyl groups around the C—C bonds. This type of disorder is similar to that observed in the analogous Ni compound mentioned above.

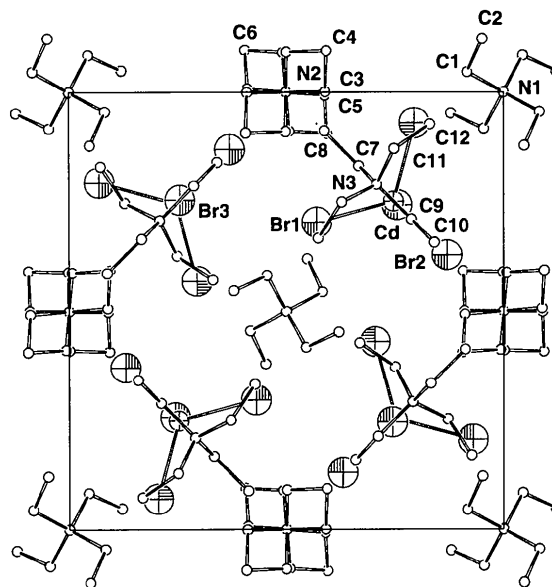


Fig. 3. ORTEP (Johnson, 1965) view along $[001]$. H atoms are omitted and N and C atoms are drawn as spheres of arbitrary radii for clarity.

Pohl & Saak (1984) state that they have determined the crystal structure of bis(tetraethylammonium) tetraiodoferrate. From the lattice parameters and space group, these authors found that the compound should be isotypic with the title compound. However, to date, the crystal structure determination of the ferrate has not been reported.

The lattice parameters of the Ni compound correspond with the substructure observed in the present work. Since the title compound undergoes a phase transition at 311 K, one can suppose that the high-temperature structure is isotypic with the room-temperature structure of the Ni compound.

Experimental

The title compound was prepared by adding a stoichiometric amount of a concentrated methanolic solution of tetraethylammonium bromide to a hot concentrated solution of cadmium bromide tetrahydrate in methanol. After cooling to room temperature the colourless precipitate was filtered off and recrystallized from hot 90% ethanol/water to yield colourless square platelets which were dried *in vacuo*.

Crystal data

(C ₈ H ₂₀ N) ₂ [CdBr ₄]	Mo K α radiation
$M_r = 692.53$	$\lambda = 0.71069 \text{ \AA}$
Tetragonal	Cell parameters from 25 reflections
$P4_2/m$	$\theta = 2.56\text{--}10.82^\circ$
$a = 13.4530 (9) \text{ \AA}$	$\mu = 6.92 \text{ mm}^{-1}$
$c = 14.3945 (8) \text{ \AA}$	$T = 298 \text{ K}$
$V = 2605.2 (4) \text{ \AA}^3$	Platelet
$Z = 4$	$0.25 \times 0.225 \times 0.075 \text{ mm}$
$D_x = 1.766 \text{ Mg m}^{-3}$	Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer	$R_{\text{int}} = 0.048$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 22.96^\circ$
Absorption correction: empirical	$h = -11 \rightarrow 14$
$T_{\text{min}} = 0.49$, $T_{\text{max}} = 0.99$	$k = -14 \rightarrow 14$
4842 measured reflections	$l = -11 \rightarrow 15$
1106 independent reflections	3 standard reflections
1401 observed reflections	frequency: 120 min
$[F > 2.00\sigma(F)]$	intensity variation: none

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.104$
$R = 0.058$	$\Delta\rho_{\text{max}} = 1.37 \text{ e \AA}^{-3}$
$wR = 0.079$	$\Delta\rho_{\text{min}} = -1.21 \text{ e \AA}^{-3}$
$S = 1.847$	Extinction correction: none
740 reflections	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2B and 2.3.1)
82 parameters	
H-atom parameters not refined	
$w = 1/[\sigma^2(F_o) + 0.0015 F_o ^2]$	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Cd	0.7474 (1)	0.7526 (1)	0.7273 (1)	0.062 (1)
Br1	0.5700 (2)	0.7048 (2)	0.7793 (2)	0.101 (2)
Br2	0.8700 (2)	0.6300 (2)	0.8032 (3)	0.094 (2)
Br3	0.7554 (2)	0.7445 (2)	0.5479 (2)	0.086 (2)
N1	1/2	1/2	1/2	0.05 (1)
C1	0.545 (2)	0.417 (1)	0.558 (2)	0.094 (8)
C2	0.621 (2)	0.452 (2)	0.628 (2)	0.100 (8)
N2	1	1/2	0.486 (3)	0.09 (2)
C3	0.910 (3)	0.501 (4)	0.421 (4)	0.17 (3)
C4	0.907 (3)	0.593 (3)	0.360 (4)	0.15 (2)
C5	0.911 (3)	0.493 (3)	0.551 (2)	0.09 (1)
C6	0.906 (2)	0.406 (2)	0.618 (2)	0.11 (1)
N3	0.791 (1)	0.291 (1)	0.921 (1)	0.06 (1)
C7	0.833 (1)	0.333 (1)	1.011 (2)	0.11 (1)
C8	0.912 (2)	0.412 (2)	0.997 (3)	0.15 (2)
C9	0.712 (2)	0.212 (2)	0.945 (3)	0.13 (2)
C10	0.659 (3)	0.159 (3)	0.867 (3)	0.16 (2)
C11	0.751 (2)	0.372 (2)	0.858 (1)	0.105 (8)
C12	0.669 (2)	0.427 (2)	0.911 (2)	0.13 (1)

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

N1—C1	1.53 (2)	C5—C6	1.52 (5)
C1—C2	1.51 (3)	N3—C7	1.53 (3)
Cd—Br1	2.582 (3)	N3—C9	1.53 (3)
Cd—Br2	2.576 (3)	N3—C11	1.52 (3)
Cd—Br3	2.587 (4)	C7—C8	1.51 (4)
N2—C3	1.53 (5)	C9—C10	1.52 (5)
N2—C5	1.53 (4)	C11—C12	1.52 (4)
C3—C4	1.52 (6)		
C1—N1—C1 ⁱ	113 (1)	C3—N2—C5 ^{vi}	110 (2)
C1—N1—C1 ⁱⁱ	108 (1)	C5—N2—C5 ^v	105 (3)
C1—N1—C1 ⁱⁱⁱ	108 (1)	C5—N2—C3 ^{iv}	114 (2)
C1 ⁱ —N1—C1 ⁱⁱ	108 (1)	C5—N2—C3 ^{vi}	110 (2)
C1 ⁱ —N1—C1 ⁱⁱⁱ	108 (1)	N2—C3—C4	112 (3)
C1 ⁱⁱ —N1—C1 ⁱⁱⁱ	113 (1)	N2—C5—C6	118 (3)
N1—C1—C2	114 (2)	C7—N3—C9	109 (2)
Br1—Cd—Br2	108.0 (1)	C7—N3—C11	111 (1)
Br1—Cd—Br3	108.5 (1)	C7—N3—C11 ^{vi}	111 (1)
Br1—Cd—Br1 ^{iv}	112.1 (1)	C9—N3—C11	113 (2)
Br2—Cd—Br3	111.7 (1)	C9—N3—C11 ^{vi}	113 (2)
Br2—Cd—Br1 ^{iv}	108.0 (1)	C11—N3—C11 ^{vi}	99 (1)
Br3—Cd—Br1 ^{iv}	108.5 (1)	N3—C7—C8	115 (2)
C3—N2—C3 ^v	105 (4)	N3—C9—C10	119 (3)
C3—N2—C5 ^{iv}	114 (2)	N3—C11—C12	108 (2)

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

Data collection and cell refinement: Enraf–Nonius CAD-4 software. All calculations were performed using the *Xtal3.2* crystallographic program package (Hall, Flack & Stewart, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal3.2 Reference Manual*. Univs. of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

- Pohl, S. & Saak, W. (1984). *Z. Naturforsch. Teil B*, **39**, 1236–1240.
 Ross, S. D., Siddiqi, I. W. & Tyrrell, H. J. V. (1972). *J. Chem. Soc. Dalton Trans.* **15**, 1611–1614.
 Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
 Stucky, G. D., Folkers, J. B. & Kistenmacher, T. J. (1967). *Acta Cryst.* **23**, 1064–1070.
 Sveleba, S., Mokryi, V., Polovinko, I., Kapustyanik, V., Trybula, Z., Petrenko, P., Kiosse, G. & Kravtsov, V. (1993). *Acta Phys. Pol.* **A83**, 777–784.
 Vlokh, O. G., Polovinko, I. I., Mokryi, V. I. & Sveleba, S. A. (1991). *Kristallografiya*, **36**, 227–228.

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Complexes of HgCl₂ and HgBr₂ with Nitrilotriacetamide

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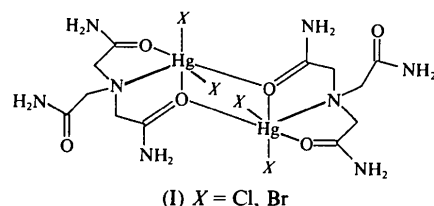
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Abstract

The two complexes bis(μ -nitrilo- κN -triacetamide)- $1\kappa O,1:2\kappa^2 O'$; $2\kappa O,1:2\kappa^2 O'$ -bis(dichloromercury), [HgCl₂(C₆H₁₂N₄O₃)₂]₂, and bis(μ -nitrilo- κN -triacetamide)- $1\kappa O,1:2\kappa^2 O'$; $2\kappa O,1:2\kappa^2 O'$ -bis(dibromomercury), [HgBr₂(C₆H₁₂N₄O₃)₂]₂, are isostructural, and represent the third case of metal complexes with nitrilotriacetamide [NTAM = N(CH₂CONH₂)₃]. [Pb and Co complexes have been reported by Sucheck, Finnen, Pinkerton, Skrzypczak-Jankun, Vijayakumar & Smith (1991). *Am. Crystallogr. Assoc. Meet.*, Toledo, Abstract PJ17.] The (NTAM:HgX₂)₂ complexes are centrosymmetric oxygen-bridged dimers. Each metal ion binds to six donors (2X, 1N, 3O; X = Br, Cl) at distances of 2.3–2.9 Å, although retaining the hexagonal bipyramidal configuration observed in complexes where Hg^{II} is eight-coordinate. Two 'empty sites' are occupied by donors from other molecules (X and N atoms) at distances of 3.7–4.1 Å. Two out of three amine groups of NTAM participate in hydrogen bonds, while the third is utilized as a ligand in the 'empty site' of the coordination sphere of the neighboring Hg^{II}.

Comment

In our continuing study of novel amide chelating ligands, we have prepared and characterized the symmetrical unalkylated nitrilotriacetamide and a variety of mono-, di- and trialkylated derivatives (Skrzypczak-Jankun & Smith, 1994; Smith, Cramer, Sucheck & Skrzypczak-Jankun, 1992). These compounds are obtained by divergent synthesis from nitrilotriacetic acid *via* transamidation and cyclization to the dioxopiperazineacetamide, followed by nucleophilic ring opening with primary amines. We have studied the coordination chemistry of these ligands with a variety of metals and have reported the first isolable crystalline complex of nitrilotriacetamide with lead, which is also the first example of both a completely acyclic ligand and a 2:1 ligand–metal ratio in a ten-coordinate lead complex (Smith, Sucheck & Pinkerton, 1992). In this paper we report the structure of the complexes (I) of nitrilotriacetamide with HgCl₂ and HgBr₂.



Two NTAM:HgX₂ moieties related by a center of symmetry form a dimer sharing O₃ atoms. However, this is not a typical bi-mercury complex. The Hg···Hg distance in typical bi-mercury complexes is about 2.5 Å (Taylor, 1977), while in the title complexes the shortest Hg···Hg distances are 4.4377 (3) and 4.4858 (5) Å within the chloride and bromide dimers, respectively, and 5.0284 (3) and 5.0989 (6) Å between dimers. In the Hg coordination sphere, a distorted hexagonal bipyramid, the halogen atoms, at distances of 2.3–2.5 Å, occupy axial sites with an average X—Hg—O,N,X angle of 88°; the average angle between bonds to atoms in the pyramid base is 61°. The distortion of the geometry of the coordination sphere seems to be normal for many organometallic complexes with transition metals (Brown & Kunz, 1992). Eight-coordinate Hg^{II} and the hexagonal bipyramidal coordination sphere have also been observed in bis(1-methylthymine)mercury(II) (Kosturko, Folzer & Stewart, 1974) and polyethers coordinated to mercury(II) halides (Bond & Rogers, 1993; Paige & Richardson, 1984; Kawasaki & Matsuura, 1984). Although the primary coordination number for Hg^{II} in (NTAM:HgX₂)₂ complexes is six, the molecule retains an arrangement of atoms around Hg^{II} based on a hexagonal bipyramid with two 'empty sites'. The deviation of the halogen atoms from the vertical axis of the pyramid and the lengthening of the Hg—X₂ bond in relation to Hg—X₁ are directly related to the nature of the intra-