

Tetramethylammonium Tetraiodocadmate(II)

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Abstract. $[\text{N}(\text{CH}_3)_4]_2[\text{CdI}_4] \cdot 2\text{C}_4\text{H}_{12}\text{N}^+ \cdot \text{CdI}_4^{2-}$, orthorhombic, *Pnma*, $a = 13.403$ (3), $b = 9.724$ (2), $c = 16.893$ (9) Å, $V = 2202$ (2) Å³, $Z = 4$, $M_r = 768.29$, $D_c = 2.32$, $D_m = 2.30$ (5) Mg m⁻³, $\mu = 6.60$ mm⁻¹. 1020 non-equivalent reflections were measured up to $\sin \theta/\lambda = 0.48$ Å⁻¹; $R(F) = 0.067$, $R_w(F) = 0.050$. The structure consists of isolated CdI_4 and $\text{N}(\text{CH}_3)_4$ tetrahedra and is isomorphous with its Fe, Co, Ni, Cu, Zn and Hg halogenide analogues. The average Cd–I length is 2.790 (3) Å; the I–Cd–I angles range from 108.05 (6) to 113.13 (8)°. The $\text{N}(\text{CH}_3)_4$ groups are affected by large oscillations.

Introduction. Colourless crystals of the title compound were obtained from an aqueous solution of $\text{N}(\text{CH}_3)_4\text{I}$ and CdI_2 . A crystal $0.12 \times 0.16 \times 0.22$ mm was selected for the experiments. Precession photographs showed orthorhombic symmetry with the space group either *Pn2₁a* or *Pnma*.

Data were collected on a Syntex *P2₁* diffractometer with Nb-filtered Mo $K\alpha$ radiation. Three equivalent reflections were measured up to $\sin \theta/\lambda = 0.48$ Å⁻¹, yielding 3251 reflections. Background corrections were made by profile analysis (Blessing, Coppens & Becker, 1974). A test reflection observed after every 50 reflections showed long-range fluctuations up to 13%, attributed to variations in the incident-beam intensity and counter response. The data were rescaled with respect to the standard. An absorption correction resulted in transmission factors ranging from 0.36 to 0.48. The equivalent reflections were averaged ($R = \sum |I - \langle I \rangle| / \sum I = 0.036$), resulting in 1111 non-equivalent reflections. 1020 of them had $I > 0$ and were used for the structure determination and refinement.

The positions of the Cd and I atoms were determined with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The positions of C and N

Table 1. *Positional parameters and equivalent Debye–Waller factors*

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Cd	0.7538 (1)	0.75	0.9061 (1)	5.8
I(1)	0.8226 (1)	0.75	1.0596 (1)	9.8
I(2)	0.5474 (1)	0.75	0.8959 (1)	7.9
I(3)	0.8249 (1)	0.9842 (1)	0.8321 (1)	10.3
N(1)	0.348 (2)	0.25	0.400 (1)	7.6
N(2)	0.029 (1)	0.25	0.662 (1)	6.1
C(1)	0.392 (3)	0.25	0.460 (3)	24
C(2)	0.246 (3)	0.25	0.402 (2)	23
C(3)	0.376 (3)	0.348 (4)	0.351 (2)	25
C(4)	0.058 (2)	0.25	0.745 (2)	13
C(5)	0.105 (2)	0.25	0.605 (2)	19
C(6)	−0.024 (2)	0.360 (3)	0.643 (1)	22

Table 2. *Bond lengths (Å) and angles (°)*

	Uncorrected	Corrected for libration	
Cd–I(1)	2.753 (3)	2.781 (3)	
Cd–I(2)	2.771 (2)	2.790 (2)	
Cd–I(3)	2.767 (2)	2.798 (2)	
N(1)–C(1)	1.18 (5)	1.39 (5)	
N(1)–C(2)	1.36 (4)	1.58 (4)	
N(1)–C(3)	1.31 (4)	1.55 (4)	
N(2)–C(4)	1.45 (4)	1.51 (4)	
N(2)–C(5)	1.40 (3)	1.59 (4)	
N(2)–C(6)	1.33 (3)	1.56 (4)	
I(1)–Cd–I(2)	113.13 (8)	C(2)–N(1)–C(3)	108 (2)
I(1)–Cd–I(3)	108.05 (6)	C(3)–N(1)–C(3)	93 (3)
I(2)–Cd–I(3)	108.43 (5)	C(4)–N(2)–C(5)	119 (2)
I(3)–Cd–I(3)	110.76 (7)	C(4)–N(2)–C(6)	112 (2)
C(1)–N(1)–C(2)	118 (3)	C(5)–N(2)–C(6)	103 (2)
C(1)–N(1)–C(3)	114 (2)	C(6)–N(2)–C(6)	107 (2)

resulted from an additional difference synthesis. The structure was refined in the centrosymmetric space group *Pnma* to $R(F) = 0.067$, $R_w(F) = 0.050$ and $S = [\sum w(F_o - F_c)^2 / (n_o - n_v)]^{1/2} = 2.25$. Scattering factors were from *International Tables for X-ray Crystallography* (1974). Anomalous-dispersion factors were

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applied to Cd and I (Cromer & Liberman, 1970). An isotropic extinction correction was made (Larson, 1969). A final difference synthesis showed no peaks higher than $0.6 \text{ e } \text{\AA}^{-3}$. No H atoms could be located because of the high thermal vibrations of the methylammonium groups. The calculations were carried out with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on the Univac 1108 computer of the University of Frankfurt. The atomic coordinates are reported in Table 1, bond lengths and angles in Table 2.*

Discussion. This study is part of the determination of the crystal structures with general formula $[\text{NH}_4-xR_x]_2[\text{MX}_4]$, where R = alkyl, X = Cl, Br or I, and M is a divalent metal atom. Some of these structures contain isolated MX_4 groups, while others contain linear chains of corner-sharing MX_6 octahedra with short $M \cdots M$ interactions. The latter are of interest because of possible low-dimensional magnetic interactions.

A stereoscopic view of the title compound is shown in Fig. 1. The structure consists of isolated $\text{N}(\text{CH}_3)_4$ and CdI_4 tetrahedra. The average Cd—I distance (corrected for libration) is $2.790(3)$, the average C—N distance $1.53(4)$ \AA.

The structure is isomorphous with the corresponding $[\text{ZnCl}_4]^{2-}$, $[\text{CoCl}_4]^{2-}$, $[\text{NiCl}_4]^{2-}$ (Wiesner, Srivastava, Kennard, Divaira & Lingafelter, 1967),

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35737 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

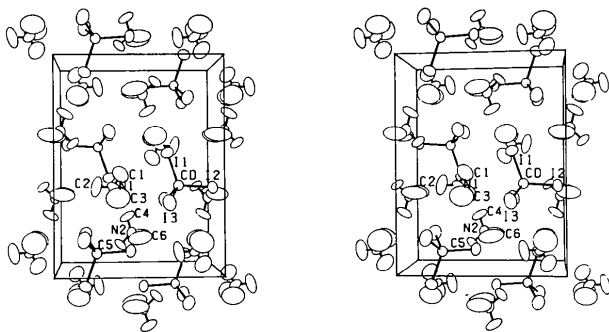


Fig. 1. Stereoscopic view of the structure. The thermal ellipsoids are the 50% probability surfaces.

$[\text{FeCl}_4]^{2-}$ (Lauher & Ibers, 1975), $[\text{CuCl}_4]^{2-}$ (Clay, Murray-Rust & Murray-Rust, 1975), $[\text{HgBr}_4]^{2-}$, $[\text{HgCl}_4]^{2-}$ and $[\text{HgI}_4]^{2-}$ (Kamenar & Nagl, 1976) complexes. The I—Cd—I angles range from $108.05(6)$ to $113.13(8)^\circ$. A similar distortion has been found in the analogous complexes and may result from packing effects. Only for $[\text{N}(\text{CH}_3)_4]_2[\text{CuCl}_4]$, where a Jahn-Teller distortion is significant, has a much more distorted tetrahedron been reported.

All the C atoms of the tetramethylammonium groups show large thermal parameters ($\langle U^2 \rangle^{1/2} \approx 0.51$ \AA). This indicates either disorder or rotation of these groups. A rigid-body analysis (Schomaker & Trueblood, 1968) of these groups gave no significant differences between the observed and calculated thermal parameters. This indicates that large oscillations are the most likely explanation for the thermal parameters of the C atoms.

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