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1,4-Butanediammonium tetrachloromercurate(II)

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Key indicators

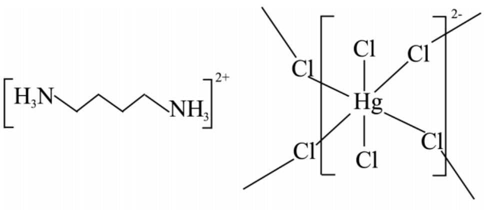
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.018 Å
R factor = 0.036
wR factor = 0.073
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_4H_{14}N_2)[HgCl_4]$, contains layers of tilted corner-sharing chloromercurate octahedra. Each Hg^{II} ion lies on a center of symmetry, and has four long bonds to the halide ions, forming puckered sheets parallel to the *bc* plane plus two short bonds to halide ions axial to the sheets, completing a tetragonally compressed octahedral coordination. Adjacent sheets have axial halide ions in an eclipsed conformation. The diammonium ions provide links between sheets, hydrogen bonding to the halides. The organic chains have the two ends of the diammonium ions equivalent by a center of symmetry, with C4 chains *trans* around the central bond and *gauche* for N *versus* C positioning around each terminal C—C bond. No phase transition before the decomposition temperature has been detected by differential scanning calorimetry.

Comment

Much attention has been devoted to the synthesis and characterization of organic–inorganic multilayered perovskites, owing to the tunability of their structural features (de Jongh *et al.*, 1974; Needham *et al.*, 1984; Ishihara *et al.*, 1990; Calabrese *et al.*, 1991). The physical and structural properties of these compounds can be tuned by substituting the organic layers or by modulating the thickness of the inorganic perovskite slabs. Applications of the layered perovskite materials involve the development of functional electronic, magnetic and optoelectronic materials (Papavassiliou, 1994; Papavassiliou *et al.*, 1994; Bednorz & Mueller, 1986; Millis *et al.*, 1996). Several examples of conducting layered perovskites generally exhibit a trend from semiconducting to metallic behavior, with increasing 'thickness' of the perovskite layer (Cava, 1992).



(I)

This investigation is the latest in a series of structure determinations of compounds formed by the reaction of substituted ammonium halides with metal halides. We report here the crystal structure, at room temperature, of the title compound, namely 4DA–$HgCl_4$ or (I).

The packing diagram of (I) (Fig. 1) shows that the structure consists of alternating perovskite sheets and layers of alkyl-

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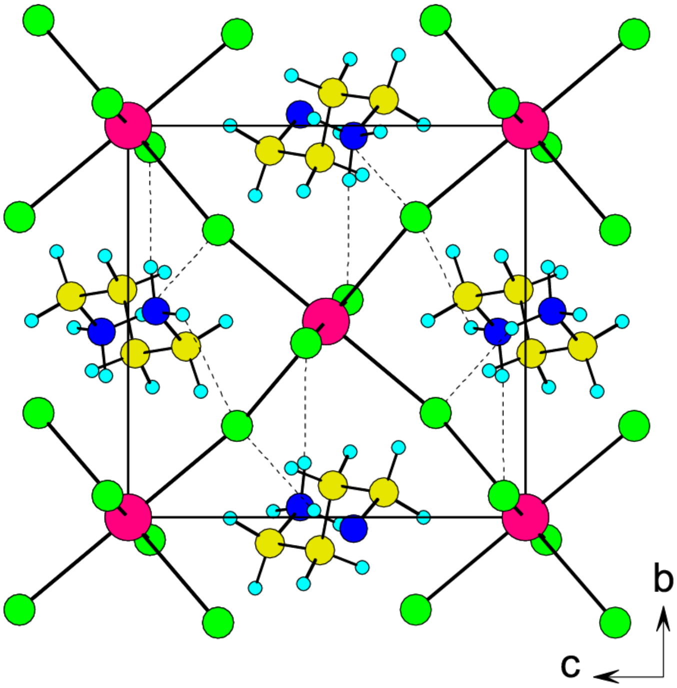

Figure 1
Projection in the *bc* plane of the unit cell of 4DA–$HgCl_4$, showing the perovskite-layered $HgCl_6$ octahedra.

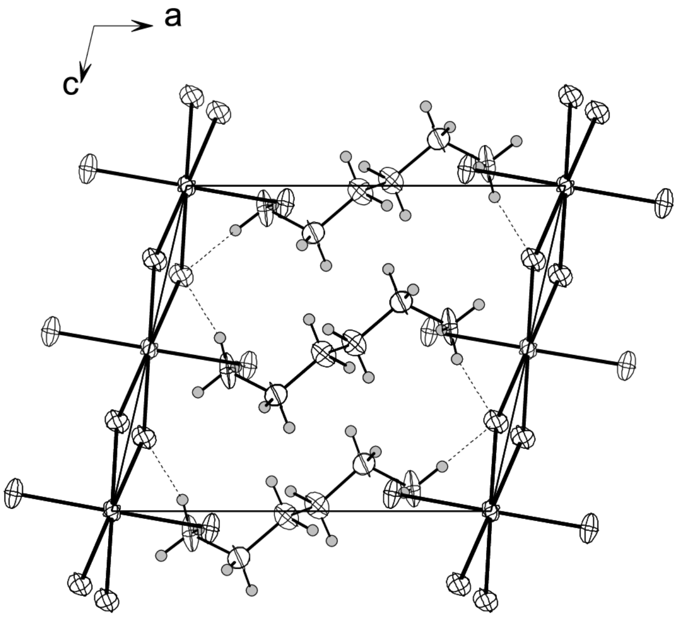

Figure 2
Projection on the *ac* plane of the unit cell of 4DA–$HgCl_4$, showing the 'orthorhombic hydrogen-bond scheme' according to Chapuis *et al.* (1976). Displacement ellipsoids are shown at the 50% probability level.

ammonium dications. The perovskite sheet consists of distorted $HgCl_6$ octahedra, each sharing corners with four adjacent octahedra through the bridging chlorine Cl2 and three symmetry equivalents. The symmetry of this first layer of the structure taken alone is pseudo-*A*2/*m*. The Hg—Cl bond lengths (Table 1) vary from 2.428 (3) to 2.819 (3) Å. The Hg—Cl1 distance of 2.428 (3) Å is a little longer than the value found in the literature for a terminal Cl, but in good agreement with the value found by Garland *et al.* (1990). This difference is correlated with the hydrogen bonding to the cation. The four other Hg—Cl distances are considerably longer and nearly equal [2.794 (3)–2.819 (3) Å], and involve bridging Cl atoms; a nearly equal value was found by Spengler *et al.* (1997) for the 1,3-propanediammonium (3DA) salt. The *cis* bond angles around Hg, which occupies a center of symmetry, vary between 88.40 (10) and 91.60 (10)°, while the *trans* angles are, of course, 180°. The bridging angle Hg—Cl2—Hg^{iv} is 163.86 (13)°, which is an indication of the rotation and tilt between adjacent octahedra. Simple cubic perovskites typically have unit cell axis $a_p \simeq 6.2$, 5.8 and 5.6 Å for I, Br and Cl, respectively. The perovskite layer in the present compound, which is the *bc* plane, has axes *b* and *c* close to $\sqrt{2}a_p$. This has been observed for many organic inorganic layered perovskite structures (Mousdis *et al.*, 2000, and references therein).

The 1,4-butanediammonium (4DA) chains lie close to the *a* axis direction and connect the tetrachloromercurate layers; they build the second layer of the structure and have only $P2_1/c$ symmetry (Fig. 2). The *gauche* N-atom ends of the 4DA chains have one hydrogen bond to an axial halide and two to halides in the puckered layer (Table 2). These three hydrogen bonds can be described by the orthorhombic configuration scheme (Chapuis *et al.*, 1976), where two equatorial and one axial position (related to the organic layers) for Cl atoms are involved. Such a hydrogen-bond configuration has been found in the room-temperature phase of 4DA–$CdCl_4$ (Khechoubi *et al.*, 1994), 4DA–$PdCl_4$ (Maris *et al.*, 1996), 4DA–$PdBr_4$ (Zouari *et al.*, 1998) and 4DA–$CuCl_4$ (Garland *et al.*, 1990). The 4DA in (I) are twisted identically at both ends, with the N atom *gauche* to the C_4 chain. This combines with the monoclinic slant to shorten the interlayer separation. The end C atoms of the C_4 chain are *trans* around the central C—C bond, so the 4DA chains are *gtg* (*gauche, trans, gauche*) (Halvorson & Willett, 1988), with terminal C—C—C—N torsion angles of 73.1 (13)°. This particular configuration contrasts with the all-*trans* conformation found in the manganese homologous 4DA–$MnCl_4$ (Tichý *et al.*, 1980). The structure is closely related to the analogous copper halide compounds (Willett, 1990; Garland *et al.*, 1990) and to a palladium halide compound previously reported by Zouari *et al.* (1998); (i) the layer of the corner-connected octahedra contains nearly equivalent distances in the plane and a shorter distance perpendicular to it, which is similar to the $CuBr_4$ compound; (ii) in contrast to the $CdCl_4$ compound, there are two contacts of the diammonium cation to bridging halide and only one to the terminal halide, which is a similar situation to the $CuCl_4$ compounds; (iii) the arrangement of cation chains is equivalent to the situation in 4DA–$PbBr_4$ (Zouari *et al.*, 1998) and could alternatively be described as a *gauche*–*gauche* orientation; (iv) the similarities in the lattice parameters of all related compounds (4DA–$PdBr_4$, 4DA–$CuBr_4$ and 4DA–$CuCl_4$) can be seen.

We performed the differential scanning calorimetry on a DSC–Perkin–Elmer system. No phase transition was detected before the thermal decomposition of the compound occurred at 450 K. This behavior, also observed for 4DA–PdBr$_4$ (Zouari *et al.*, 1998), differs from the polymorphism of 4DA–CdCl$_4$ and 4DA–CuCl$_4$. For these latter compounds, it has been shown that structural phase transitions lead to an organic chain in the all-*trans* conformation in the high temperature phase. Analysis of the series of 1,4-butanediammonium compounds shows that, given a diammonium chain length, substitution of the metal and halogen in the inorganic layers can give rise to various conformations for the chain with different associated thermal behavior.

Experimental

The title compound was obtained by mixing a solution of 1,4-butyldiammonium chloride and mercury chloride in an acetone–ethanol solution, in the stoichiometric ratio 1:1. After a few weeks, colorless non-hygroscopic crystals were obtained by slow evaporation. The chemical analysis was in good agreement with the formula.

Crystal data

$(C_4H_{14}N_2)[HgCl_4]$
$M_r = 432.56$
Monoclinic, $P2_1/c$
$a = 9.082\ (2)$ Å
$b = 7.720\ (5)$ Å
$c = 7.996\ (5)$ Å
$\beta = 102.907\ (12)^\circ$
$V = 546.5\ (5)$ Å^3
$Z = 2$
$D_x = 2.629$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–25°
$\mu = 15.01$ mm^{-1}
$T = 293\ (2)$ K
Polyhedral, colorless
0.40 × 0.32 × 0.25 mm

Data collection

Home-made (Huber, 2000) Image Plate diffractometer
ω scans
Absorption correction: by integration (local program; Hertlein, 1989)
$T_{min} = 0.026$, $T_{max} = 0.463$
803 measured reflections
741 independent reflections
571 reflections with $I > 2\sigma(I)$
$R_{int} = 0.076$
$\theta_{max} = 23.5^\circ$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.073$
$S = 1.15$
741 reflections
53 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.46$ e Å^{-3}
$\Delta\rho_{min} = -1.17$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.111 (6)

Table 1
Selected geometric parameters (Å, °).

Hg—Cl1	2.428 (3)	N1—C1	1.480 (17)
Hg—Cl2	2.794 (3)	C1—C2	1.521 (17)
Hg—Cl2^{i}	2.819 (3)	C2—C2^{ii}	1.49 (3)
Cl1—Hg—Cl2^{iii}	91.46 (10)	Hg—Cl2—Hg^{iv}	163.86 (13)
Cl1—Hg—Cl2	88.54 (10)	N1—C1—C2	111.7 (10)
Cl1—Hg—Cl2^{i}	91.60 (10)	C2^{ii}—C2—C1	113.7 (14)
Cl2—Hg—Cl2^{i}	91.10 (5)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl2^{i}	0.89	2.76	3.432 (11)	133
N1—H1B···Cl2^{ii}	0.89	2.42	3.245 (11)	154
N1—H1C···Cl1^{iii}	0.89	2.38	3.259 (9)	172

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

All H-atom positional parameters were idealized using the standard procedure of *SHELXL*97 (Sheldrick, 1997). H-atom isotropic displacement parameters were set at 1.5 U_{eq} of the attached C or N atom. The residual density showed maxima and minima close to the Hg and Cl atoms.

Data collection: local software (Huber, 2000); cell refinement: *MACH*3 in *CAD*-4 *UNIX Software* (Enraf–Nonius, 1998); data reduction: local software (Huber, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990).

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