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1,4-Butanediammonium Tetrabromopalladate(II)

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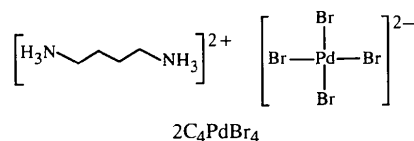
Abstract

The title structure, (C₄H₁₄N₂)[PdBr₄], presents a two-dimensional arrangement of alternating mineral layers composed of [PdBr₄]²⁻ units and organic layers containing 1,4-butanediammonium chains [NH₃-(CH₂)₄-NH₃]²⁺. The [PdBr₄]²⁻ units are square planar and are disposed nearly perpendicular to the crystallographic *bc* plane. The organic chains are centrosymmetric and are characterized by a left-handed conformation at both

ends. The link between the organic and mineral moieties is achieved by N—H···Br hydrogen bonds. No phase transition before the decomposition temperature has been detected by powder X-ray diffraction *versus* temperature and differential scanning calorimetry.

Comment

Extensive studies have been carried out on the crystal structures, phase transitions and physical properties of two-dimensional perovskite-like compounds of the families (RNH₃)₂MX₄ and [NH₃-R'-NH₃]MX₄, and related materials (*M* = Cd, Mn, Pb, Cu; *X* = Cl, Br; *R* and *R'* are organic radicals). The few palladium compounds of these families which have been structurally characterized are some chloride derivatives: (C₃H₇NH₃)₂[PdCl₄] (Willett & Willett, 1977), [NH₃-(CH₂)₂-NH₃][PdCl₄] (Berg & Søtofte, 1976) and [NH₃-(CH₂)₄-NH₃][PdCl₄] (Maris *et al.*, 1996). As part of our study of phase transitions in the 1,4-butanediammonium tetrahalogenometalate(II) series (Khechoubi *et al.*, 1994; Courseille *et al.*, 1994), we report here the crystal structure at room temperature of the palladium–bromine compound [NH₃-(CH₂)₄-NH₃][PdBr₄] (hereafter 2C₄PdBr₄).



The crystallographic organization can be described as a succession of organic and inorganic layers. The inorganic layer consists of discrete [PdBr₄]²⁻ anions which pack to form a puckered two-dimensional network. The Pd atom lies on an inversion center and displays a square-planar coordination of the four Br atoms. The Pd—Br distances [2.4422 (9) and 2.4529 (9) Å] are comparable with the distance observed in the tetragonal compound K₂PdBr₄ [2.444 (3) Å; Martin *et al.*, 1975].

A short Pd···Br contact of 3.2712 (10) Å was detected (Table 2). Similar contacts are found for [CuCl₄]²⁻, [CuBr₄]²⁻ (Garland *et al.*, 1990) and [PdCl₄]²⁻ salts (Maris *et al.*, 1996). For copper derivatives, these contacts result from an octahedral distortion explained by a Jahn–Teller effect in relation to the electronic configuration of the Cu²⁺ ions. The Pd²⁺ ions are generally known to adopt square-planar coordination geometry. Willett & Willett (1977) have also observed such a contact in (C₃H₇NH₃)₂[PdCl₄] and have interpreted this interaction as a weak repulsive one. However, in 2C₄PdBr₄, this weak interaction contributes to the formation of a two-dimensional network in the inorganic layer resulting in a packing close to a perovskite-like structure.

The cations also lie on inversion centers and adopt a left-handed conformation at both ends (*gtg'* confor-

mation), with terminal C—C—N torsion angles of $73.4(8)^\circ$. The displacement of the N atoms from the least-squares plane formed by the four C atoms is $1.299(6) \text{ \AA}$.

The same conformation of organic 1,4-butanedi-ammonium chains exists in the chloride compounds when the metal is palladium ($2C_4PdCl_4$; Maris *et al.*, 1996), cadmium ($2C_4CdCl_4$; Khechoubi *et al.*, 1994) or copper ($2C_4CuCl_4$; Garland *et al.*, 1990). This particular conformation contrasts with the all-*trans* conformation found in the manganese homologs $2C_4MnCl_4$ (Tichy *et al.*, 1980) and with the left-handed conformation of the lead derivative (Courseille *et al.*, 1994).

The link between the two moieties and the crystal packing is achieved by hydrogen bonds involving the H atoms of the ammonium group and the Br atoms. These three hydrogen bonds (Table 3) can be described by the 'orthorhombic configuration scheme' of Chapuis *et al.* (1976), where two equatorial and one axial position (related to the inorganic layers) for Br atoms are involved. The same hydrogen-bond configuration has been found in the room-temperature phase of $2C_4CdCl_4$ and also of $2C_4PdCl_4$.

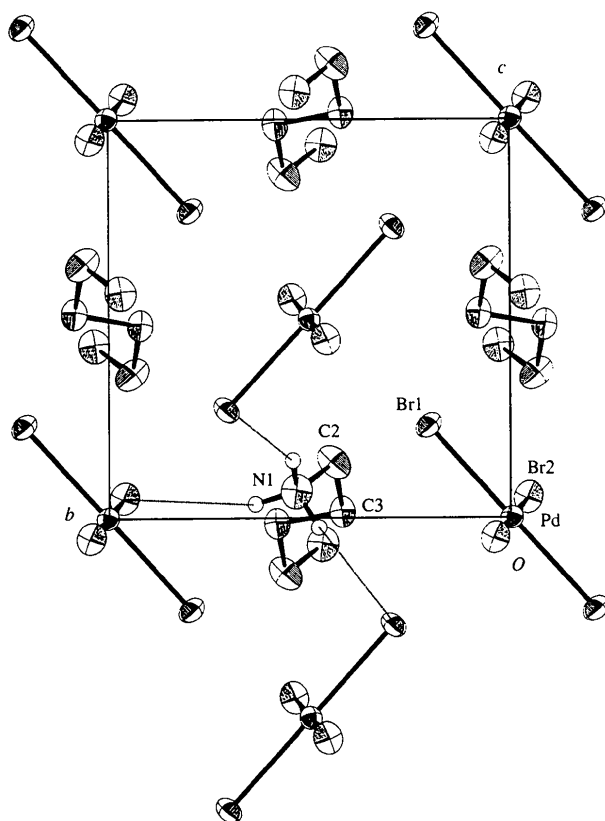


Fig. 1. Projection in the *bc* plane of the unit cell of $2C_4PdBr_4$ showing the 'orthorhombic hydrogen-bond scheme' according to Chapuis *et al.* (1976). Displacement ellipsoids are shown at 50% probability levels.

X-ray powder diffraction measurements *versus* temperature have been performed using a Guinier–Lenne camera in the 300–490 K temperature range, completed with differential scanning calorimetry on a DSC-7 Perkin–Elmer system. No phase transition was detected before the thermal decomposition of the compound occurred at 455 K.

This behavior, also observed for the chloride homologues, differs from the polymorphism of $2C_4CdCl_4$ and $2C_4CuCl_4$. 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. These first-order phase transitions are strongly reconstructive and result in a complete rearrangement of both the inorganic and the organic moieties with a modification of the hydrogen-bonding network. Hydrogen bonds in the high-temperature phase are organized following the 'monoclinic configuration scheme' of Chapuis *et al.* (1976). In this configuration, two axial sites and only one equatorial position for the halogen atoms are connected to the ammonium group.

Analysis of the series of 1,4-butanedi-ammonium compounds shows that, given a diammonium chain length, substitution of the metal and the halogen in the inorganic layers can give rise to various conformations for the chain with different associated thermal behavior.

Experimental

Crystals for X-ray structural analysis were grown by slow evaporation at room temperature of a saturated aqueous solution obtained by dissolving stoichiometric amounts of $PdBr_2$ and $NH_2(CH_2)_4NH_2$ (Fluka, purity > 97%), with HBr in excess.

Crystal data

$(C_4H_{14}N_2)[PdBr_4]$

$M_r = 516.18$

Monoclinic

$P2_1/c$

$a = 9.291(1) \text{ \AA}$

$b = 7.957(2) \text{ \AA}$

$c = 8.093(2) \text{ \AA}$

$\beta = 103.11(1)^\circ$

$V = 582.7(2) \text{ \AA}^3$

$Z = 2$

$D_x = 2.942 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10\text{--}25^\circ$

$\mu = 15.258 \text{ mm}^{-1}$

$T = 298(2) \text{ K}$

Prism

$0.17 \times 0.09 \times 0.03 \text{ mm}$

Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

by integration (PLATON;

Spek, 1990)

$T_{\min} = 0.330$, $T_{\max} = 0.890$

829 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

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

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 9$

$l = -9 \rightarrow 9$

1157 measured reflections
1001 independent reflections

2 standard reflections
frequency: 90 min
intensity decay: none

Software used to prepare material for publication: *PLATON* (Spek, 1990).

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.074$
 $S = 1.223$
1002 reflections
53 parameters
H-atom parameters
constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 1.5167P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.669 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.597 \text{ e } \text{\AA}^{-3}$
Extinction correction:
SHELXL93
Extinction coefficient:
0.01410 (10)
Scattering factors from
International Tables for Crystallography (Vol. C)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1029). Services for accessing these data are described at the back of the journal.

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

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Pd	0	0	0	0.0204 (2)
Br1	0.03489 (8)	0.20516 (8)	0.23012 (8)	0.0269 (2)
Br2	0.26806 (7)	−0.04122 (9)	0.05017 (9)	0.0315 (2)
N1	0.2267 (7)	0.5322 (7)	0.0661 (8)	0.036 (2)
C2	0.3627 (8)	0.4393 (10)	0.1389 (10)	0.037 (2)
C3	0.4611 (8)	0.4192 (8)	0.0147 (9)	0.029 (2)

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

Pd—Br1	2.4422 (9)	N1—C2	1.467 (10)
Pd—Br2	2.4529 (9)	C2—C3	1.513 (11)
Pd...Br1 ⁱ	3.2712 (10)	C3—C3 ⁱⁱ	1.520 (10)
Br1—Pd—Br2 ⁱⁱⁱ	89.49 (3)	N1—C2—C3	112.4 (6)
Br1—Pd—Br2	90.51 (3)	C2—C3—C3 ⁱⁱ	113.3 (6)
N1—C2—C3—C3 ⁱⁱ	73.4 (8)	C2—C3—C3 ⁱⁱ —C2 ⁱⁱ	180.0 (6)

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

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...Br1 ⁱ	0.89	2.71	3.513 (7)	150
N1—H1B...Br1 ⁱⁱ	0.89	2.57	3.455 (6)	175
N1—H1C...Br2 ⁱⁱⁱ	0.89	2.59	3.422 (6)	156

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

Unit-cell parameters were first determined from automatic indexing with *DICVOL91* (Boultif & Lou\er, 1991) of a powder X-ray diffraction pattern recorded with a Siemens D-500 diffractometer. The cell parameters thus obtained have been confirmed by the calculation from single-crystal X-ray diffraction measurements of 25 reflections. A half sphere of reflections was recorded and the intensity data were reduced using a local program giving a *hkl* file based on F^2 . The structure was solved by the Patterson method and from subsequent difference Fourier map calculations. All non-H atoms were refined by full-matrix least squares with anisotropic displacement parameters. H atoms were idealized using the standard procedure of *SHELXL93* (Sheldrick, 1993). H-atom isotropic displacement parameters were set at $1.5U_{\text{eq}}$ of the attached C or N atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NONIUS* (unpublished). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEX* (McArdle, 1993).

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catena-Poly[diamminecopper(II)- μ -acetato-O:O'] Tetrafluoroborate

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Abstract

The crystal of the title compound, $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{NH}_3)_2]\text{BF}_4$, contains infinite chains in which the acetate groups bridge pairs of Cu^{II} ions using both *syn* and *anti* coordination modes.