the atomic numbering scheme used. The figure was designed by *KPLOT* (Hundt, 1979) and executed with *ORTEP* (Johnson, 1965).

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Bis(5-bromocytosinium) Tetrachloropalladate(II)

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Abstract

The structure consists of discrete $C_4H_5BrN_3O^+$ and $PdCl_4^{2-}$ ions in a network of N—H⋯Cl hydrogen bonds with the crystal packing being different from that of the analogous compound bis(cytosinium) tetrachloropalladate(II). The largest deviations from bond lengths and angles of 5-bromocytosine [4-amino-5-bromo-2(1H)-pyrimidinone] observed upon protonation are analogous to those found for cytosine.

Comment

This report extends work on halogenated nitrogen bases (Valle & Ettorre, 1992; Casellato, Graziani & Sánchez González, 1992).

The structure consists of discrete $C_4H_5BrN_3O^+$ and $PdCl_4^{2-}$ ions in a network of N—H⋯Cl hydrogen bonds. The $PdCl_4^{2-}$ anion is planar with the metal atom located at the origin of the centrosymmetric triclinic cell. Coordination bond lengths and angles are normal. The largest deviations from bond lengths and angles of 5-bromocytosine (Kato, Takenaka & Sasada, 1979) observed upon protonation are the decrease of C(4)—N(4) (*ca* 0.04 Å, 4σ), C(2)—O(2) (*ca* 0.05 Å, 4σ), N(3)—C(4)—C(5) (*ca* 4°, 5σ) and N(1)—C(2)—N(3) (*ca* 5°, 6σ), and the increase of C(2)—N(3)—C(4) (*ca* 6°, 8σ) [$\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$]. Analogous effects have been observed for cytosine (Bagieu-Beucher, 1990).

The crystal packing is different from that of bis-(cytosinium) tetrachloropalladate(II) (Kindberg & Amma, 1975) where, for example, the planes of the anions have two orientations.

The O(2)⋯Br ($x, y-1, z$) contact of 2.972 (4) Å is remarkably close in relation to reported van der Waals radii for O (1.54 Å) and Br atoms (1.54–1.84 Å) (Nyburg & Faerman, 1985).

As shown in Table 2, each coordinated Cl(1) atom forms hydrogen bonds with the H—N(1) groups of two different cations, and Cl(2) is involved in bifurcated hydrogen bonds with the H—N(3) and H—N(4)H groups of a third cation, so that each centrosymmetric $PdCl_4^{2-}$ anion is hydrogen bonded to six cations, which gives compactness and stability to the crystal packing.
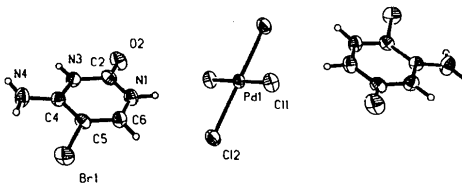

Fig. 1. Plot of the anion and two cations of the title compound showing the atomic numbering scheme.

Experimental

Crystal data

$[C_4H_5BrN_3O]_2[PdCl_4]$	Mo $K\alpha$ radiation
$M_r = 630.2$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 30
$P\bar{1}$	reflections
$a = 9.146$ (4) Å	$\theta = 6$–$12°$
$b = 8.650$ (4) Å	$\mu = 5.987$ mm^{-1}
$c = 6.622$ (3) Å	Room temperature
$\alpha = 109.05$ (4)°	Plates
$\beta = 71.05$ (4)°	$0.2 \times 0.2 \times 0.2$ mm
$\gamma = 109.03$ (5)°	Brick red

$V = 453.9$ (4) Å^3
$Z = 1$
$D_x = 2.305$ Mg m^{-3}

Crystal source: chemical synthesis

the electron density map and refined with a fixed temperature factor ($U_{iso} = 0.07$ Å^2). All calculations were performed on a MicroVAX using *SHELX*76 (Sheldrick, 1976)

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.890$, $T_{max} = 0.995$
4279 measured reflections
4001 independent reflections

2435 observed reflections
$[F > 12\sigma(F)]$
$\theta_{max} = 25°$
$h = -13 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 10$
2 standard reflections monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F
Final $R = 0.031$
$wR = 0.031$
$S = 0.777$
2435 reflections
121 parameters
Only coordinates of H atoms refined

$w = 1$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 1.2$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Pd	0.0	0.0	0.0	0.0255 (1)
Cl(1)	−0.1585 (1)	0.1833 (1)	0.2099 (2)	0.0357 (4)
Cl(2)	0.1108 (1)	0.1579 (1)	−0.2580 (2)	0.0417 (4)
N(1)	0.4893 (4)	0.1183 (4)	−0.2567 (6)	0.034 (1)
C(2)	0.6059 (4)	0.0570 (4)	−0.2453 (6)	0.032 (1)
N(3)	0.7499 (4)	0.1744 (4)	−0.2416 (6)	0.032 (1)
C(4)	0.7826 (4)	0.3370 (4)	−0.2489 (6)	0.029 (1)
C(5)	0.6573 (4)	0.3896 (4)	−0.2686 (6)	0.029 (1)
C(6)	0.5147 (4)	0.2776 (5)	−0.2725 (7)	0.033 (1)
O(2)	0.5860 (4)	−0.0862 (3)	−0.2390 (6)	0.047 (1)
N(4)	0.9248 (4)	0.4340 (5)	−0.2375 (7)	0.044 (2)
Br	0.69082 (6)	0.60824 (5)	−0.29450 (8)	0.0449 (2)

Table 2. *Geometric parameters* (Å, °)

Pd—Cl(1)	2.302 (2)	C(4)—C(5)	1.419 (7)
N(1)—C(2)	1.368 (7)	C(6)—N(1)	1.354 (6)
N(3)—C(4)	1.353 (5)	C(4)—N(4)	1.309 (5)
C(5)—C(6)	1.349 (5)		
C(2)—O(2)	1.205 (5)	N(1)···Cl(1)^i	3.291 (4)
C(5)—Br	1.871 (4)	N(3)···Cl(2)^{ii}	3.316 (4)
Pd—Cl(2)	2.304 (2)	N(4)···Cl(2)^{ii}	3.302 (5)
C(2)—N(3)	1.378 (5)	N(4)···Cl(1)^{iii}	3.287 (4)
Cl(1)—Pd—Cl(2)	90.3 (1)	N(1)—C(2)—N(3)	113.9 (3)
C(2)—N(3)—C(4)	126.3 (4)	N(3)—C(4)—C(5)	116.5 (4)
C(4)—C(5)—C(6)	118.6 (4)	C(5)—C(6)—N(1)	121.5 (4)
C(6)—N(1)—C(2)	123.1 (4)	N(1)—C(2)—O(2)	123.6 (4)
O(2)—C(2)—N(3)	122.5 (4)	N(3)—C(4)—N(4)	118.8 (4)
N(4)—C(4)—C(5)	124.7 (4)	C(4)—C(5)—Br	120.6 (3)
Br—C(5)—C(6)	120.9 (3)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 + x, y, z$; (iii) $1 - x, 1 - y, -z$.

Intensities were corrected for Lp and for absorption (North, Phillips & Mathews, 1968). The structure was solved by the heavy-atom method and final scale factors, atomic coordinates and anisotropic thermal parameters were obtained by full-matrix least-squares refinement. H-atom positions were obtained from

2-(η²-Dithioformato)-2-(triphenylphosphine)-1,7-dicarba-2-rhoda-*closo*-dodecaborane(12)

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Abstract

The asymmetric unit has two independent molecules which have very similar conformations. The dithioformato ligand is bonded asymmetrically with Rh—S distances of 2.355(1) and 2.432(1) Å in one molecule and 2.347(1) and 2.423(1) Å in the other; in each case, the shorter Rh—S bond is *trans* to a C atom and the longer one *trans* to a B atom. The Rh—P bond [2.314(1) and 2.320(1) Å, respectively, in the two molecules] is *trans* to the second C atom in the C$_2$B$_9$ cage.