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Bis(4-bromoimidazolium) Tetrachloropalladate(II)

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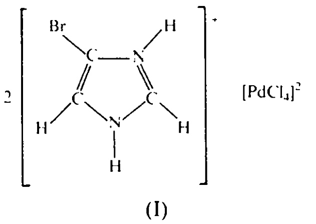
Abstract

The structure consists of discrete $C_3H_4BrN_2^+$ and $PdCl_4^{2-}$ ions in a network of N—H···Cl hydrogen bonds. Bond lengths and angles for the imidazolium ring do not change appreciably upon halogenation.

Comment

This report extends work on halogenated nitrogen bases (Casellato, Ettorre & Graziani, 1993; Valle & Ettorre, 1992; Valle, Sánchez González & Ettorre, 1991, 1993). The structure, (I), consists of discrete $C_3H_4BrN_2^+$ and $PdCl_4^{2-}$ ions. Bond lengths and angles for the $PdCl_4^{2-}$ anion are normal. The $C_3H_4BrN_2^+$ cation is planar with the largest deviation from the ring plane being that of the Br atom, 0.018 (2) Å. The dihedral angle between the plane through N(1), C(2), N(3), C(4) and C(5) and the plane through Pd, Cl(1), Cl(2), Cl(1′) and Cl(2′) is 73.2 (3)°.



(I)

Each cation is hydrogen bonded to two anions through HN(1) and HN(3), respectively. The N(1)···Cl and N(3)···Cl contact distances are equal. As displayed in Fig. 1, each anion is hydrogen bonded to four cations. The closest Br···Cl contacts between the ions are 3.475 (4) Å. It may be noted that Cl···Cl contacts of 3.285 (2) and 3.407 (6) Å, and Cl···Br contacts of 3.442 (2) Å have been found between 2-chloroimidazole and halogens bonded to Cu (Valle & Ettorre, 1992; Valle, Sánchez González & Ettorre, 1991, 1993). The distances Cl···Cl of 3.16–3.56 Å and Cl···Br of 3.12–3.62 Å are calculated from van der Waals radii for halogens bonded to C atoms (Nyburg & Faerman, 1985). Differences of ring bond lengths and angles between 4-bromoimidazolium or 2-chloroimidazolium (Valle & Ettorre, 1992) and imidazolium (Levasseur & Beauchamp, 1991) are not appreciably larger than e.s.d. values. Effects of halogenation have been observed for protonated cytosine (Casellato, Ettorre & Graziani, 1993).

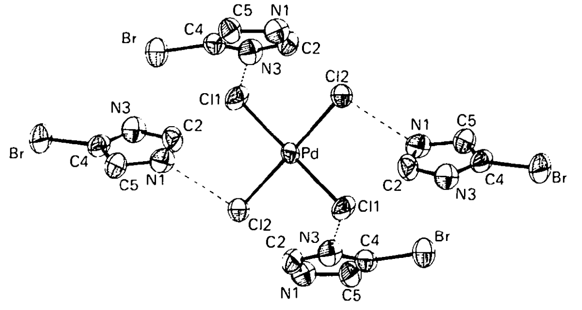


Fig. 1. Drawing of the anion and four cations with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystal data

$[C_3H_4BrN_2]_2[PdCl_4]$
$M_r = 544.2$
Monoclinic
$C2/c$
$a = 16.465$ (2) Å
$b = 7.413$ (2) Å
$c = 14.152$ (2) Å
$\beta = 115.2$ (1)°
$V = 1562.9$ (14) Å^3
$Z = 4$
$D_x = 2.31$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 6$–15°
$\mu = 6.91$ mm^{-1}
Room temperature
Needle
0.3 × 0.3 × 0.3 mm
Brick red

Data collection

Philips PW1100 diffractometer
θ–2θ scans
Absorption correction: none
2309 measured reflections
1316 independent reflections
1191 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.104$
$\theta_{\rm max} = 28°$
$h = -21 \rightarrow 18$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 180 min
intensity variation: 10%

Refinement

Refinement on F
$R = 0.074$
$wR = 0.077$

$(\Delta/\sigma)_{\rm max} = 0.273$
$\Delta\rho_{\rm max} = 1.78$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.89$ e Å^{-3}

$S = 1.2$
1191 reflections
79 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0065F^2]$

Atomic scattering factors from *SHELX*76 (Sheldrick, 1976); *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Pd	3/4	1/4	1/2	0.0360 (4)
Cl(1)	0.6820 (2)	0.4682 (3)	0.3745 (2)	0.059 (1)
Cl(2)	0.8315 (2)	0.4726 (3)	0.6177 (2)	0.0497 (9)
Br	0.4478 (1)	0.7017 (2)	0.35312 (8)	0.0735 (6)
C(2)	0.6605 (8)	0.720 (1)	0.6263 (9)	0.058 (4)
N(1)	0.6012 (7)	0.788 (1)	0.6583 (7)	0.055 (4)
C(5)	0.5170 (9)	0.798 (2)	0.5731 (8)	0.058 (5)
C(4)	0.5292 (8)	0.731 (1)	0.4899 (7)	0.049 (4)
N(3)	0.6174 (6)	0.686 (1)	0.5244 (6)	0.051 (3)

Table 2. *Selected geometric parameters* (Å, °)

Pd—Cl(1)	2.309 (3)	N(3)—C(2)	1.33 (1)
Pd—Cl(2)	2.323 (3)	N(3)—C(4)	1.36 (2)
Br—C(4)	1.839 (9)	C(4)—C(5)	1.37 (2)
N(1)—C(2)	1.33 (2)	N(3)···Cl(1)	3.19 (1)
N(1)—C(5)	1.40 (1)	N(1)···Cl(2^{i})	3.19 (1)
Cl(1)—Pd—Cl(2)	89.8 (1)	Br—C(4)—N(3)	122 (1)
C(2)—N(1)—C(5)	109 (1)	Br—C(4)—C(5)	130 (1)
C(2)—N(3)—C(4)	110 (1)	N(3)—C(4)—C(5)	108 (1)
N(1)—C(2)—N(3)	108 (1)	N(1)—C(5)—C(4)	105 (1)

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

The Pd atom was first located from a Patterson map using *SHELXS*86 (Sheldrick, 1985) and then a difference Fourier map revealed the other atoms (*SHELX*76; Sheldrick, 1976). The relatively large R and R_{int} values are a result of the quality of the crystal and its decay.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triethylammonium Hydrogen Dichlorotris(diphenylphosphinito-*P*)rhodium(III)–Tetrahydrofuran (1/1)

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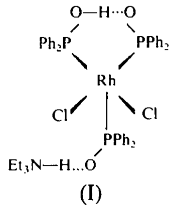
Abstract

The title complex, triethylammonium dichlorobis{hydrogen bis[oxodiphenylphosphato(1−)-*P*]}[oxodiphenylphosphato(1−)-*P*]rhodium(III)–tetrahydrofuran (1/1), $[C_6H_{16}N][RhCl_2(C_{12}H_{10}OP)\{(C_{12}H_{10}OP)_2H\}].C_4H_8O$, has square-pyramidal geometry which is unusual for rhodium(III) complexes. It occurs as an ion pair with the Et_3NH^+ ion hydrogen bonded to the O atom [2.631 (23) Å] of the unique apical Ph_2PO ligand. The basal Ph_2PO ligands are connected by an O···O hydrogen bond [2.411 (23) Å].

Comment

During the course of studies on the coordination chemistry of mixed anhydrides of acrylic and diphenylphosphinous acids $Ph_2PO_2CCR{=}CR'R''$ (Borowski *et al.*, 1990; Iraqi *et al.*, 1991), we discovered that under some circumstances, *e.g.* reaction with $[RhCl(PPh_3)_3]$ (Irvine, Cole-Hamilton, Barnes & Hodgson, 1989; Irvine, Glidewell, Cole-Hamilton, Barnes & Howie, 1991), $Ph_2PO_2CCH{=}CH_2$ was transformed into coordinated Ph_2POPPh_2. Since, in solution $Ph_2PO_2CCH{=}CH_2$ slowly converts to $Ph_2PP(O)Ph_2$, we studied the reaction of $[RhCl(PPh_3)_3]$ with $Ph_2PP(O)Ph_2$ (Irvine, 1990). The major product was $[RhCl(PPh_3)(Ph_2PPOPh_2)]$, with the title compound (I) as a minor product.



(I)

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