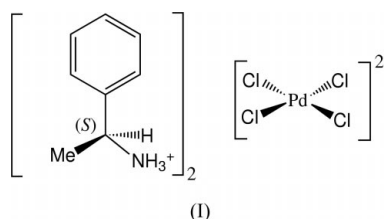


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Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
R factor = 0.028
wR factor = 0.074
Data-to-parameter ratio = 15.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis[(S)-(-)-1-phenylethylammonium]
tetrachloropalladate(II)In the title compound, $(\text{C}_8\text{H}_{12}\text{N})_2[\text{PdCl}_4]$, the ammonium functionality is involved in three bifurcated hydrogen contacts with the Cl atoms of symmetry-related tetrachloropalladate anions, with $\text{H}\cdots\text{Cl}$ separations in the range 2.48 (3)–2.95 (4) Å .

Comment

In recent years, (*S*)- and (*R*)-1-phenylethylamine have been widely employed as auxiliary chiral reagents, due to the high levels of stereoselectivity that they can induce in asymmetric synthesis (Juaristi *et al.*, 1998). These amines also have the distinction of being the most frequently used of all the synthetic basic resolving agents. Our group has recently been involved in the synthesis of chiral Pd complexes derived from optically pure α -ketoimines and α -diimines based on these amines (Vázquez García *et al.*, 2000). Following this line of research, we attempted the complexation of 3-[(*S*)-(-)-1-phenylethylimino]butan-2-one with $(\text{cod})\text{PdCl}_2$ (cod is cyclo-octa-1,5-diene). However, the expected coordination compound seems to be unstable, as our efforts failed and we obtained only the salt derived from the amine used for the synthesis of the α -ketoimine. The only crystallized compound obtained *via* this reaction (see *Experimental*) was bis[(*S*)-(-)-1-phenylethylammonium] tetrachloropalladate(II), (I), for which we report the crystal structure.The asymmetric unit of (I) contains one cation on a general position and half an anion, with the metal center lying on a twofold axis (Fig. 1). Observed geometric parameters (Table 1) are very close to expected values; the tetrachloropalladate moiety exhibits a square-planar coordination geometry, found in other complexes of this anion with small organic cations, such as guanidinium (Kiryama *et al.*, 1986) or imidazolium (Valle & Ettore, 1997). For the organic cation, the positions of the methyl and ammonium functionalities were unambiguously determined and are in agreement with the chirality of the starting material, (*S*)-(-)-1-phenylethylamine. Furthermore, bond lengths for these groups [$\text{C1}-\text{C2} = 1.519$ (6) Å and $\text{C1}-\text{N1} = 1.506$ (4) Å] are very similar to those observed, for instance, in the enantiomer of the same cation used as

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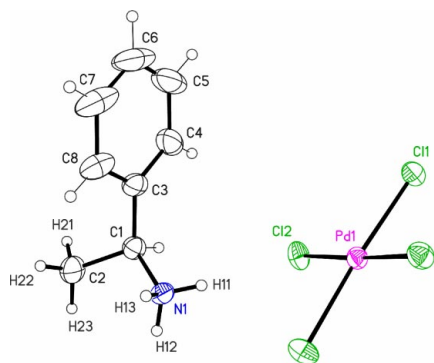


Figure 1

The cation and anion of (I), with displacement ellipsoids at the 30% probability level and the atom-numbering scheme for the asymmetric unit (thin C—H bonds indicate that the H atoms were placed in idealized positions).

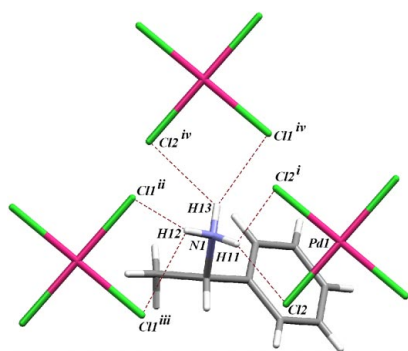


Figure 2

Contacts between the ammonium H atoms and the tetrachloropalladate anions in the crystal structure of (I). Contacts are represented as dashed lines. One cation and three anions are shown [symmetry codes: (i) $1 - x, y, 1 - z$; (ii) $1 - x, y - 1, 1 - z$; (iii) $x, y - 1, z$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$].

counter-ion in an Fe^{II} complex (Shan & Huang, 2001), *viz.* 1.53 (2) and 1.491 (8) Å, respectively.

The most interesting feature in the packing of (I) concerns the NH_3^+ group of the cation, which is prevented from rotating by six intermolecular contacts with three symmetry-related anions; each ammonium H atom bridges two *cis*-Cl atoms of a PdCl_4^- anion (Fig. 2 and Table 2). A similar scheme is observed for each H atom; one contact can be considered as very weak, based on a long $\text{H}\cdots\text{Cl}$ separation and an acute $\text{N}-\text{H}\cdots\text{Cl}$ angle, while the other contact is more effective, with a shorter $\text{H}\cdots\text{Cl}$ separation and an angle $\text{N}-\text{H}\cdots\text{Cl}$ closer to 180° . This scheme for $\text{N}-\text{H}\cdots\text{Cl}$ contacts is reminiscent of that found in systems based upon ammonium and pyridinium salts of perhalometalates, used as synthons for the design of hydrogen-bonded assemblies (Mareque Rivas & Brammer, 1998; Brammer *et al.*, 2001). Finally, no significant $\pi-\pi$ interactions between phenyl rings in the packing of (I) are observed, in agreement with the relatively low packing index calculated for this crystal (0.658; Spek, 2003).

Experimental

A solution of 3-[(S)-(-)-1-phenylethylimino]butan-2-one (0.6 g, 0.35 mmol) in acetonitrile (20 ml) was treated with (cod) PdCl_2 (0.1 g, 0.35 mmol) with stirring at room temperature for 5 min. Orange

crystals of (I) were obtained upon crystallization from an ethyl acetate–dichloromethane mixture (1:1) (yield: 27.9%).

Crystal data

$(\text{C}_8\text{H}_{12}\text{N})_2[\text{PdCl}_4]$
 $M_r = 492.57$
 Monoclinic, $C2$
 $a = 11.2280$ (11) Å
 $b = 7.2220$ (11) Å
 $c = 13.3393$ (16) Å
 $\beta = 97.80$ (1)°
 $V = 1071.7$ (2) Å³
 $Z = 2$

$D_x = 1.526$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 79 reflections
 $\theta = 4.6\text{--}13.0^\circ$
 $\mu = 1.36$ mm⁻¹
 $T = 296$ (1) K
 Plate, orange
 $0.60 \times 0.28 \times 0.08$ mm

Data collection

Bruker P4 diffractometer
 $2\theta/\omega$ scans
 Absorption correction: ψ scan
 (XSCANS; Siemens, 1996)
 $T_{\text{min}} = 0.643, T_{\text{max}} = 0.898$
 2431 measured reflections
 1904 independent reflections
 1836 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -15 \rightarrow 3$
 $k = -1 \rightarrow 10$
 $l = -18 \rightarrow 18$
 3 standard reflections
 every 97 reflections
 intensity decay: <1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.074$
 $S = 1.07$
 1904 reflections
 125 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.1903P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.17$ e Å⁻³
 Absolute structure: Flack (1983),
 227 Friedel pairs
 Flack parameter = -0.01 (4)

Table 1

Selected geometric parameters (Å, °).

Pd1—Cl1	2.3030 (17)	C1—C2	1.519 (6)
Pd1—Cl2	2.3001 (18)	C1—C3	1.497 (5)
Cl1—N1	1.506 (4)		
Cl2 ⁱ —Pd1—Cl2	89.66 (9)	C3—C1—N1	110.5 (3)
Cl2 ⁱ —Pd1—Cl1	176.08 (10)	C3—C1—C2	114.2 (3)
Cl2—Pd1—Cl1	90.84 (3)	N1—C1—C2	109.4 (4)
Cl1 ⁱ —Pd1—Cl1	88.94 (8)		

Symmetry code: (i) $1 - x, y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H11 \cdots Cl2	0.856 (19)	2.56 (3)	3.356 (5)	155 (4)
N1—H11 \cdots Cl2 ⁱ	0.856 (19)	2.83 (4)	3.419 (5)	127 (4)
N1—H12 \cdots Cl1 ⁱⁱ	0.860 (19)	2.48 (3)	3.302 (5)	160 (5)
N1—H12 \cdots Cl1 ⁱⁱⁱ	0.860 (19)	2.95 (4)	3.444 (5)	119 (4)
N1—H13 \cdots Cl1 ^{iv}	0.872 (19)	2.53 (4)	3.325 (5)	153 (7)
N1—H13 \cdots Cl2 ^{iv}	0.872 (19)	2.76 (6)	3.387 (5)	130 (6)

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

H atoms bonded to aromatic C atoms and atom C1 were placed in idealized positions and refined using a riding model, with constrained distances (0.93 Å for aromatic C—H and 0.98 Å for C1—H1A) and with U_{iso} fixed at $1.2U_{\text{eq}}(\text{C})$. Methyl and ammonium H atoms were located in difference maps. Distances were restrained to target values corresponding to the expected bond lengths: 0.85 (2) Å for the ammonium group and 0.98 (2) Å for the methyl group. For each group, U_{iso} was allowed to refine as a common value.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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