

distance closer than 6.7 Å. The coordination geometry about Pt is planar but distorted from square planarity. The Pt, S(1), S(2), P(1) and P(2) atoms all lie within 0.092 (4) Å of the best least-squares plane through those atoms. The respective bond angles S(1)—Pt—S(2), P(1)—Pt—P(2), S(1)—Pt—P(1) and S(2)—Pt—P(2) are 87.7 (1), 99.0 (1), 85.1 (1) and 88.4 (1)°. The S(1)—Pt—S(2) bond angle of 87.7 (1)° is significantly larger than the S—Pt—S angle of 83.14 (8)° in the compound *cis*-Pt(SH)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The difference is likely due to the conformational requirements of the thia-platinacycle. This thia-platinacycle is a five-membered ring with the C atoms in a staggered conformation. The angles about the two ring C atoms, S(1)—C(1)—C(2) and S(2)—C(2)—C(1), are both 112 (1)° as expected for saturated hydrocarbons. The C(1)—C(2) bond distance of 1.45 (2) Å is considerably shorter than the usual value of 1.54 Å for such bonds. Thermal motion may be contributing to this apparent shortening.

The deviation of the P(1)—Pt—P(2) bond angle of Pt(SCH<sub>2</sub>CH<sub>2</sub>S)(PPh<sub>3</sub>)<sub>2</sub> from 90° can be accounted for by steric interactions of the triphenylphosphine groups. The P(1)—Pt—P(2) angle of 99.0 (1)° is larger than 97.65 (7)° found in *cis*-Pt(SH)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The bond-angle difference between S(1)—Pt—P(1) of 85.1 (1)°, and S(2)—Pt—P(2) of 88.4 (1)° is unanticipated, but all non-bonded intermolecular S...phenyl hydrogen interactions are too long to cause any such distortions. The structure can therefore be described as a planar, monomeric, slightly distorted thiametallacycle with a puckered ring.

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## Structure of *trans*-Dichlorobis(1-methylimidazole)palladium(II), [Pd(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]

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**Abstract.**  $M_r = 341.52$ , monoclinic,  $P2_1/c$ ,  $a = 5.1278$  (1),  $b = 11.636$  (1),  $c = 10.168$  (1) Å,  $\beta = 97.402$  (4)°,  $V = 601.64$  (4) Å<sup>3</sup>,  $\lambda(\text{Ag } K\alpha) = 0.5608$  Å,  $Z = 2$ ,  $D_x = 1.885$  Mg m<sup>-3</sup>,  $\mu(\text{Ag } K\alpha) = 9.85$  cm<sup>-1</sup>,  $F(000) = 306$ ,  $T = 298$  K. Final  $R = 0.040$  for 2162 reflections. The Pd atom lies on a symmetry centre, all other atoms are in general positions.

**Introduction.** The study of imidazole complexes with transition-metal ions is of interest as the ligand is closely related to biological systems involving the histidine residue.

On the other hand, although coordination compounds of Pt<sup>II</sup> and Pd<sup>II</sup> have been known for more than a century (Kauffman, 1976), the coordination chemis-

try of palladium and platinum has recently taken on increased interest, due to the antitumour properties of certain amine-halide compounds, such as *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Stone, Kelman & Sinex, 1974; Marcellis, Canters & Reedijk, 1981; Brouwer, Van de Putte, Fichtinger-Schepman & Reedijk, 1981).

As part a programme of structural investigation of palladium complexes, in the present paper the crystal structure of *trans*-dichlorobis(1-methylimidazole)-palladium(II) is discussed. The published space group and cell dimensions are incorrect (Navarro-Ranninger, 1979).

**Experimental.** Single crystals of *trans*-Pd(NMeIm)<sub>2</sub>Cl<sub>2</sub>, NMeIm = 1-methylimidazole, grown as described previously (Navarro-Ranninger & Gayoso, 1978); long needles from alcoholic solutions of PdCl<sub>2</sub> and NMeIm; crystal used: 0.10 × 0.30 × 0.10 mm, cleaved from a larger one; crystal system, space group and approximate unit-cell parameters from Weissenberg and precession photographs; accurate unit-cell parameters by least-squares analysis of setting angles of 67 reflections, Philips PW 1100 four-circle diffractometer; intensities recorded in ω/2θ scan mode [scan width 1.7°(θ), scan speed 0.034°(θ)s<sup>-1</sup>], θ between 2 and 25° (maximum *h,k,l* 7,17,15), with graphite-monochromated Ag Kα radiation; 2162 reflections measured (*R*<sub>int</sub> = 0.017), 1466 with *I* > 2σ(*I*), σ from counting statistics; two standard reflections (060,060) measured every 90 min with no significant variation in either intensity or position; data corrected for absorption.

Pd and Cl positions from three-dimensional Patterson synthesis, remaining non-hydrogen atoms from subsequent Fourier map; refinement by full-matrix least-squares method, anisotropic thermal parameters, function minimized  $\sum_w \Delta F^2$ ; three-dimensional Fourier synthesis showed all H atoms; anisotropic (non-hydrogen) and isotropic (H) refinement gave *R* 0.040, *R*<sub>w</sub> = 0.047, with unit weights; difference syntheses showed no significant features; calculations carried out with the XRAY system (Stewart, Kundell & Baldwin, 1970), Univac 1100/80 computer; scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).\*

**Discussion.** Fig. 1 shows a view of the complex and the atom numbering. The final atomic parameters are given in Table 1, Table 2 shows interatomic distances and angles.

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38192 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The complex consists of monomeric Pd(NMeIm)<sub>2</sub>Cl<sub>2</sub> units. The imidazole ring is planar, with no atom deviating from the least-squares plane through the five atoms by more than 0.006 (6) Å; the Pd and methyl C atoms lie only 0.15 (1) and 0.08 (1) Å out of this plane, respectively. The bond lengths and angles in the 1-methylimidazole ligand are similar to those already reported (Graves, Hodgson, van Kralingen & Reedijk, 1978) and also to those in a variety of metal complexes of imidazole and its derivatives (Carmichael, Chan, Cordes, Fair & Johnson, 1972; Phillips, Shreeve & Skapski, 1976; Santoro, Mighell, Zocchi & Reimann, 1969).

The imidazole ligands were found (Freeman & Szymanski, 1967) to coordinate to metal ions *via* the pyridine N rather than the pyrrole N. The electronic 'pair' at N(1) is the only pair which can be considered

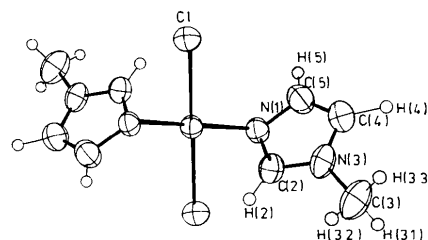


Fig. 1. View of the coordination around palladium in *trans*-Pd(NMeIm)<sub>2</sub>Cl<sub>2</sub>.

Table 1. Atomic parameters (*U*<sub>eq</sub> values are × 10<sup>4</sup>) for *trans*-dichlorobis(1-methylimidazole) palladium(II)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} \rho_i^* \rho_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
C(2)	0.3958 (10)	0.1690 (4)	-0.0718 (6)	473 (16)
C(3)	0.6814 (14)	0.3346 (7)	-0.1184 (9)	730 (27)
C(4)	0.3808 (14)	0.3167 (5)	0.0602 (6)	647 (23)
C(5)	0.2141 (13)	0.2351 (5)	0.0921 (6)	607 (21)
N(1)	0.2249 (8)	0.1421 (3)	0.0098 (4)	422 (12)
N(3)	0.4967 (9)	0.2737 (4)	-0.0438 (5)	521 (15)
Cl	-0.0822 (3)	0.0181 (1)	-0.2275 (1)	526 (4)
Pd	0.0000	0.0000	0.0000	373 (1)

Table 2. Intramolecular bond distances (Å) and angles (°)

E.s.d.'s in parentheses.			
Pd-Cl	2.307 (1)	Cl-Pd-Cl	180.0
Pd-N(1)	2.011 (4)	N(1)-Pd-N(1)	180.0
N(1)-C(2)	1.320 (7)	Cl-Pd-N(1)	90.2 (1)
C(2)-N(3)	1.340 (7)	Pd-N(1)-C(2)	125.9 (3)
N(3)-C(4)	1.372 (8)	Pd-N(1)-C(5)	127.6 (4)
C(4)-C(5)	1.345 (9)	N(1)-C(2)-N(3)	110.5 (5)
C(5)-N(1)	1.373 (7)	C(2)-N(3)-C(4)	107.6 (5)
N(3)-C(3)	1.47 (1)	N(3)-C(4)-C(5)	106.3 (5)
		C(4)-C(5)-N(1)	109.4 (6)
		C(5)-N(1)-C(2)	106.2 (4)
		C(2)-N(3)-C(3)	125.8 (5)
		C(3)-N(3)-C(4)	126.4 (5)

unshared in the imidazole molecule. Since the electrons at N(3) are part of the aromatic sextet, the bonding of N(3) to a metal ion is disfavoured and although bonding of the imidazole ring to metal ions *via* C(2) has been reported recently (Sundberg, Brian, Taylor & Taube, 1974) it can be stated as a rule that neutral imidazole and its derivatives show, as the unique coordination position, that of the electron pair at N(1), as has been observed in this compound.

The Pd atom is coordinated in a square-planar fashion to the Cl atoms and the N atoms. The Pd–N(1) and Pd–Cl distances of 2.011 (4) and 2.307 (1) Å, respectively, are comparable with values found in related complexes (Fronczek, 1981; Bell, Hall & Waters, 1966).

The dihedral angle between the plane of imidazole ring and the square plane around Pd is 134 (1)°.

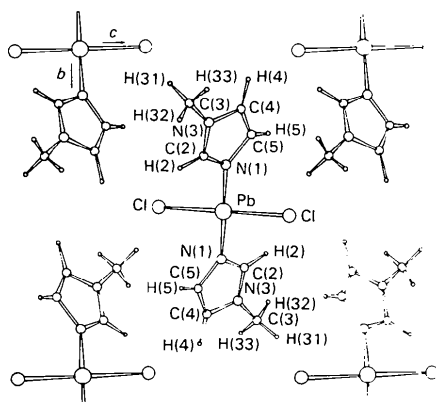


Fig. 2. A projection of the crystal structure along *a*.

The molecules are held together solely by van der Waals forces. There are no significant intermolecular interactions; the packing diagram is shown in Fig. 2.

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## Structure of *trans*-Dichlorobis(2-methylimidazole)palladium(II), [Pd(C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]

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(Received 10 June 1982; accepted 19 October 1982)

**Abstract.**  $M_r = 341.52$ , triclinic,  $P\bar{1}$ ,  $a = 7.312$  (2),  $b = 7.558$  (6),  $c = 7.413$  (6) Å,  $\alpha = 123.85$  (5),  $\beta = 113.04$  (3),  $\gamma = 66.40$  (3)°,  $V = 304.0$  (4) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.865$  Mg m<sup>-3</sup>,  $\mu(\text{Ag } K\alpha) = 9.85$  cm<sup>-1</sup>,

$F(000) = 168$ ,  $T = 298$  K. The structure was determined by heavy-atom methods and refined to  $R = 0.031$ ,  $R_w = 0.035$  based on 2162 independent non-zero reflections. The complex is *trans* square-planar.

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