

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)°.

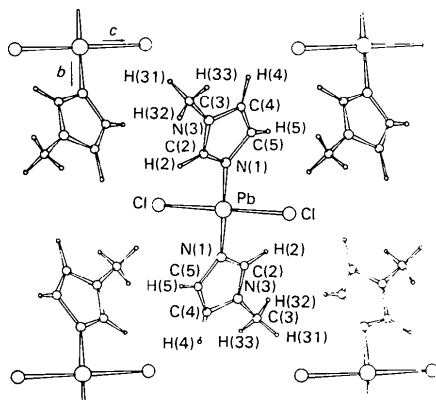


Fig. 2. A projection of the crystal structure along a.

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(C₄H₆N₂)₂Cl₂]

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Abstract. $M_r = 341.52$, triclinic, $P\bar{1}$, $a = 7.312(2)$, $b = 7.558(6)$, $c = 7.413(6)$ Å, $\alpha = 123.85(5)$, $\beta = 113.04(3)$, $\gamma = 66.40(3)^\circ$, $V = 304.0(4)$ Å³, $Z = 1$, $D_x = 1.865$ Mg m⁻³, $\mu(\text{Ag } K\alpha) = 9.85$ cm⁻¹,

$F(000) = 168$, $T = 298$ 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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Bond distances and angles are normal. The structure consists of discrete molecules linked by van der Waals interactions and hydrogen bonds.

Introduction. Complex formation between imidazole groups and metal ions plays an important role in both molecular biology and technology (Hughes, 1972; Sundberg & Martin, 1974; Welleman, Hulsbergen, Verbiest & Reedijk, 1978).

Studies have been made of the interactions between Pd and nitrogen bases (*L*) (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1983). Many *cis*-[PdL₂X₂] (*X* = halogen) compounds isomerize to give *trans* isomers. Since *trans*-[PdL₂X₂] compounds have no antitumour activity the study of these isomerization reactions is important.

Both *cis*- and *trans*-[Pd(2MeIm)₂Cl₂] have been synthesized, but only the *trans* isomer gave suitable crystals.

Experimental. Crystals obtained as needles by suspending palladium chloride and 2-methylimidazole (2MeIm) (ratio Pd/2MeIm = 1/2.3) in absolute methanol and evaporating an acetone/dimethylformamide solution at room temperature; crystal used: 0.3 × 0.1 × 0.2 mm; unit-cell parameters by least-squares refinement of 33 reflections, 3° < θ < 25°, Philips PW 1100 four-circle diffractometer, graphite-monochromated Ag Kα radiation (λ = 0.5608 Å); intensity data (maximum *h*, *k*, *l* 10,10,10) recorded in ω-scan mode for 2° < θ < 27°; 2162 independent reflections, 2077 with *I* > 2σ(*I*); absorption corrected using ORABS from the XRAY 70 system (Stewart, Kundell & Baldwin, 1970); scattering factors, including real and imaginary anomalous-dispersion corrections, from *International Tables for X-ray Crystallography* (1974); *E* statistics showed crystal to be non-centrosymmetric, but there being no evidence of a pyroelectric effect the structure was refined in P $\bar{1}$; Pd and Cl positions from three-dimensional Patterson synthesis; remaining non-hydrogen atoms from three-dimensional difference syntheses; isotropic full-matrix least-squares refinements with unit weights gave *R* 0.035; H atoms from difference maps; final refinement by full-matrix least squares, anisotropic for non-hydrogen atoms and isotropic for H atoms (the H atoms being assigned the isotropic temperature factor of their carrier atoms), gave *R* = 0.031 and *R*_w = 0.035 with *w* = 1.0; final difference map showed no maxima greater than 0.3 eÅ⁻³; calculations carried out with the XRAY System (Stewart, Kundell & Baldwin, 1970), on a Univac 1100/80 computer.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38193 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

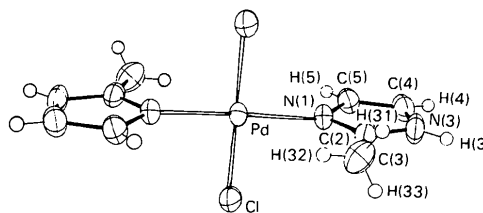


Fig. 1. ORTEP view of the molecule with the labelling of atoms.

Table 1. Atomic parameters (*U*_{eq} are × 10⁴) for *trans*-dichlorobis(2-methylimidazole)palladium(II)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
C(5)	0.2042 (5)	0.2639 (5)	0.4767 (5)	384 (15)
C(2)	0.2160 (4)	-0.0617 (5)	0.4056 (5)	353 (14)
C(3)	0.1971 (7)	-0.2891 (6)	0.2934 (7)	491 (21)
C(4)	0.3026 (5)	0.2510 (6)	0.6668 (5)	432 (16)
N(1)	0.1505 (3)	0.0666 (4)	0.3142 (4)	323 (12)
N(3)	0.3083 (4)	0.0475 (5)	0.6200 (4)	422 (14)
Cl	-0.3065 (1)	0.1868 (2)	0.1120 (1)	440 (5)
Pd	0.0000	0.0000	0.0000	290 (2)

Table 2. Bond lengths (Å) and angles (°) involving non-H atoms with e.s.d.'s in parentheses

Pd-Cl	2.307 (1)	Cl-Pd-N(1)	90.4 (1)
Pd-N(1)	2.005 (3)	Pd-N(1)-C(2)	128.0 (3)
N(1)-C(2)	1.317 (6)	Pd-N(1)-C(5)	124.5 (3)
C(2)-N(3)	1.344 (4)	N(1)-C(2)-N(3)	108.7 (3)
N(3)-C(4)	1.362 (6)	C(2)-N(3)-C(4)	109.4 (3)
C(4)-C(5)	1.347 (5)	N(3)-C(4)-C(5)	106.1 (3)
C(5)-N(1)	1.388 (4)	C(4)-C(5)-N(1)	108.3 (4)
C(2)-C(3)	1.474 (6)	C(5)-N(1)-C(2)	107.5 (3)
		N(1)-C(2)-C(3)	126.4 (3)
		N(3)-C(2)-C(3)	124.9 (4)

Discussion. Fig. 1 shows an ORTEP plot (Johnson, 1965) of the molecule with the H atoms. The final atomic parameters are given in Table 1. Table 2 shows the interatomic distances and angles. Coordination around the Pd atom is *trans* square-planar. The Pd-N(1) and Pd-Cl bond distances of 2.005 (3) and 2.307 (1) Å, respectively, are comparable with values found in related complexes (Fronczek, 1981). The imidazole ring is planar. Bond lengths and angles in the 2-methylimidazole ligand are similar to those reported for a variety of metal complexes and derivatives (Craven, McMullan, Bell & Freeman, 1977; Lundberg, 1966; Phillips, Shreeve & Skapski, 1976; Graves, Hodgson, van Kralingen & Reedijk, 1978). The dihedral angle between the plane of the imidazole ring and the coordination plane is 99.0 (1)°.

The main cohesive forces between the complex molecules arise from hydrogen bonds of type N-H...Cl. Every N(3) atom in the structure forms one of these bonds, and the Cl atom is involved only in one hydrogen bond. There are no other significant interactions, as shown by the packing diagram (Fig. 2). The distance Cl...N(3)($\bar{x}, \bar{y}, 1-z$) is 3.323 (5) Å.

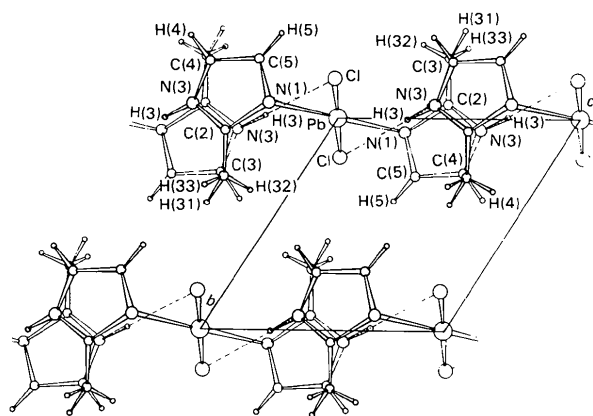


Fig. 2. A projection of the crystal structure along the *a* axis.

The compounds *trans*-dichlorobis(1-methylimidazole)palladium(II) (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1983) and *trans*-dichlorobis(2-methylimidazole)palladium(II) show very similar structural relations in molecular geometry.

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Structure of a Cubic Form of Tetraethylammonium Octakis(thiocyanato-*N*)thorate(IV), $[N(C_2H_5)_4]_4[Th(NCS)_8]$

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Abstract. $M_r = 1217.7$, cubic, $Pm\bar{3}m$, $a = 11.589(5) \text{ \AA}$, $V = 1556(2) \text{ \AA}^3$, $Z = 1$, $D_x = 1.300(2) \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu(\text{Mo } K\alpha) = 2.74 \text{ mm}^{-1}$, $T = 294 \text{ K}$. The structure solved from intensities measured on a single crystal was refined to a final $R = 0.039$. The Th atom is eight-coordinated in a strictly cubic configuration. The structure is disordered in the sense that occupancy

factors of the tetraethylammonium positions are less than unity given with equal probability. These tetraethylammonium ions are of two kinds: three sandwiched between the faces of adjacent cubic anions occupy two positions related by a unique fourfold axis, while the fourth lies at the center of the cell with six positions given by the three fourfold axes. The cubic structure differs from the tetragonal one in the packing of consecutive layers of cubic anions, which are not translated.

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