Crystal and Molecular Structure of Chloro{methyldi-[(6-methyl-2-pyridyl)methyl]amine}palladium(II) Chloride

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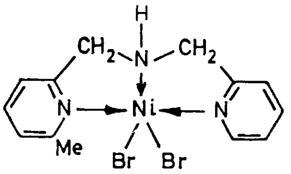
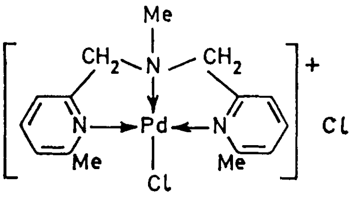
Crystals of the title compound are orthorhombic, space-group $Cmc2_1$, $Z = 4$, in a unit cell of dimensions a = 13·648(9), b = 13·156(11), c = 8·772(8) Å. The intensities of 1115 independent reflections above background collected by counter methods were refined to R 0·042. The palladium atom is in a distorted square planar environment, the chlorine atom being 0·93 Å out of the plane containing the palladium and three nitrogen atoms. The Pd–Cl bond distance is 2·331(3) Å. The Pd–N(tertiary) bond distance [2·018(8) Å] is significantly shorter than the Pd–N(pyridine) distances [2·068(6) Å]. The preparation of the analogous bromo-complex is also given together with i.r. and n.m.r. spectral data for the two complexes.

It is well known that relatively small structural modifications in a multidentate ligand can produce significant changes in the geometry of its transition-metal complexes, sometimes resulting in a change in co-ordination number. Such an example is to be found in the series of ligands derived from di-[(2-pyridyl)methyl]amine (dpma). With Fe^{II} and Ni^{II}, this gives[1] octahedral complex ions of the form $[M(dpma)_2]^{2+}$. However, either by extending the aliphatic chain between donor nitrogen atoms, as in di-[(2-pyridyl)ethyl]amine (dpea), or by introducing methyl substituents in the pyridine rings, as in di-[(6-methyl-2-pyridyl)methyl]amine (Me$_2$-dpma), high-spin five-co-ordinate complexes are formed with co-ordinated halide ions.[2,3] An X-ray structural investigation of one of these, NiBr$_2$(Me$_2$dpma) (I), has shown[4] that the distorted trigonal bipyramidal geometry adopted can be satisfactorily explained by steric arguments. An additional interesting observation was that the approach of a fourth co-ordinating group in the (Me$_2$dpma) molecular plane appeared to be effectively blocked by the two methyl groups; thus it appeared that regular square planar and octahedral complexes would be sterically unlikely. Accordingly we attempted to prepare compounds with these two symmetries using palladium(II) and titanium(III) as the metal atoms. We chose the former because, although its complexes are predominately four-co-ordinate square planar, five-co-ordinate complexes can be prepared in particular


(I)


(II)

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circumstances. The structures of several five-co-ordinate complexes of both palladium(II) and platinum(II) have been established through *X*-ray diffraction, and the metal atom found to be in an environment which is either trigonal bipyramidal [as in $Pt(SnCl_3)_5$ (ref. 5)] or square pyramidal (as in the $[Pd(tpas)Cl]^+$ cation where tpas is *o*-phenylenebis{[(*o*-dimethylarsino)phenyl]methylarsine}[6]). We used the ligand methyldi-[(6-methyl-2-pyridyl)methyl]amine (Me_3dmpa) to prepare $PdCl_2(Me_3dpma)$ and here report its crystal structure which contains a very distorted square planar $[PdCl(Me_3dpma)]^+$ cation, as in (II), rather than a five-co-ordinate species analogous to the $NiX_2(Me_2dpma)$ series. The crystal structure of $TiCl_3(Me_3dpma)$, in which the titanium atom has a distorted octahedral environment, will be reported subsequently.[7]

EXPERIMENTAL

Preparation and Characterisation of the Complexes.—The preparation of the ligand has been described previously.[3] (II) was prepared by shaking $PdCl_2$ (2·0 g, 11·3 mmol) with an aqueous solution of Me_3dpma (2·8 g, 11·6 mmol in 30 ml) for 3 days. The filtered solution was evaporated to dryness (70%), and orange crystals were obtained by a slow recrystallisation from ethanol (Found: C, 42·9; H, 4·6; N, 10·0; Pd, 25·3. $C_{15}H_{19}Cl_2N_3Pd$ requires C, 43·0; H, 4·6; N, 10·0; Pd, 25·4%).

The bromo-complex, $PdBr_2(Me_3dpma)$, was prepared similarly (Found: C, 35·8; H, 3·9; N, 8·3; Pd, 21·0. $C_{15}H_{19}Br_2N_3Pd$ requires C, 35·4; H, 3·7; N, 8·3; Pd, 21·0%). *X*-Ray powder diffraction patterns show the chloro- and bromo-complexes to be isomorphous.

The molar conductivities of the chloro- and bromo-complexes ($10^{-3}m$) in nitromethane were measured by use of a Pye conductance bridge 11700 and found to be 81·6, 84·5 mhos cm^2 respectively. These values are typical for a 1 : 1 electrolyte in nitromethane.[8]

The i.r. spectra (as Nujol or hexachlorobutadiene mulls; Perkin-Elmer 457 spectrometer) of both compounds show two strong bands at 1592 and 1628 cm^{-1} and no absorption in the region 2760—2820 cm^{-1}. Two strong bands in the region 1560—1650 cm^{-1} are found for complexes in which the two pyridyl groups are co-ordinated. When one of the pyridyl groups is not co-ordinated, three strong bands appear in this region.[3] The absence of absorption in the 2760—2820 cm^{-1} region suggest that the central nitrogen atom is bonded, since a non-bonded $\rangle$NMe grouping would show a number of strong peaks in this region.[9,10]

Further evidence of the terdentate nature of the ligand comes from ^{1}H n.m.r. shifts of the ligand and of (II) (Table 1). In the complex the aromatic protons and pyridylmethyl protons have shifted downfield by *ca.* τ 0·25, and 0·42 respectively, confirming that the pyridyl groups are co-ordinated. That the central nitrogen atom is also co-ordinated is shown by the downfield shift of *ca.* τ 0·44 of the methyl protons. N.m.r. spectra were run on a Perkin-Elmer R 10 spectrometer.

Crystal Data.—$C_{15}H_{19}Cl_2N_3Pd$, $M = 418·6$, Orthorhombic, $a = 13·648(9)$, $b = 13·156(11)$, $c = 8·772(8)$ Å, $U = 1575·0$ Å^3, $D_c = 1·76$, $Z = 4$, D_m (by flotation) $= 1·74$, $F(000) = 840$. Space-group $Cmc2_1$ from systematic absences: hkl for $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$. Mo-K_α radiation, $\lambda = 0·7107$ Å; μ(Mo-K_α) $= 14·9$ cm^{-1}.

TABLE 1

^{1}H N.m.r. chemical shifts [a]

Compound		
Free ligand	(II)	Assignment
2·00—2·75	1·75—2·55	Aromatic multiplet
6·32	[b]	$-CH_2-$
7·48	7·06	2-pyridylmethyl
7·67	7·23	NMe

[a] τ Values; D_2O solution with the sodium salt of 3-(trimethylsilyl)propanesulphonic acid as internal reference. [b] Peaks obscured by H_2O peak.

A crystal with dimensions 0·20 × 0·15 × 0·10 mm was mounted with the *c* axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter, and pulse-height analyser. A molybdenum tube was used with a zirconium filter at the receiving slit. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were measured repeatedly during the course of the experiment, but no significant change in intensity was detected. 1272 independent reflections were measured with $2\theta < 60°$. No absorption or extinction corrections were applied. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0·03I^2)]^{\frac{1}{2}}$, where I is the intensity and E the estimated background of the reflection. 1115 reflections with $I > 3\sigma(I)$ were used in the subsequent calculations.

Structure Determination.—The position of the palladium atom was determined from a Patterson function and Fourier syntheses were then used to determine the positions of the remaining atoms. The structure was refined by full-matrix least squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$ was $\sqrt{w} = 1$ for $F_o < 30$ and $\sqrt{w} = 30/F_o$ for $F_o > 30$. Calculations were made on an ATLAS computer at S.R.C. Chilton, Berkshire, with the programs described in ref. 11 and on an Elliott 4130 with some of our own programs. Atomic scattering factors for palladium were taken from ref. 12 and chlorine, nitrogen, carbon, and hydrogen from ref. 13, together with corrections for the real and imaginary part of the anomalous dispersion for the palladium and chlorine atoms. The anisotropic temperature factor is defined as $\exp(-0·25\sum_i\sum_j h_ih_jb_ib_jB_{ij})$ where $i,j = 1, 2, 3$, and b_i is the ith reciprocal cell dimension: the isotropic temperature

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factor is exp $(-B \sin^2 \theta/\lambda^2)$. The palladium and chlorine atoms were refined anisotropically and the carbon and nitrogen atoms isotropically. The approximate positions of the 10 independent hydrogen atoms were found from the difference Fourier map; these positions were idealised at 1·075 Å from the carbon atoms to which they were attached in trigonal or tetrahedral positions. These hydrogen atoms were included in the refinement, but their parameters were not refined. In the structure, the *z* direction is indeterminate. We therefore refined two models, in which the effect of the imaginary part of the anomalous dispersion is reversed (*i.e.* with opposing signs for the *z* co-ordinates). There were no significant differences in dimensions between the two models. The model with the lowest *R* value (0·042) was assumed to be correct. The atomic parameters and thermal parameters for this model are given in Table 2. The bond distances and angles are given in Table 3. The final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20257 (7 pp., 1 microfiche).*

TABLE 2

Atomic parameters and thermal parameters of (II), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B/\text{Å}^2$
Pd	0 [a]	0·1562(1)	0 [a]	*b*
Cl(1)	0 [a]	0·0796(2)	−0·2428(4)	*b*
Cl(2)	0 [a]	0·4692(2)	−0·1620(4)	*b*
N(1)	0·1498(4)	0·1585(4)	0·0338(6)	2·29(8)
N(2)	0 [a]	0·2559(6)	0·1686(9)	2·09(9)
C(1)	0·2193(5)	0·0878(5)	0·0112(12)	2·68(9)
C(2)	0·3147(6)	0·1038(6)	0·0635(11)	3·18(12)
C(3)	0·3394(7)	0·1935(7)	0·1397(11)	3·51(13)
C(4)	0·2662(6)	0·2626(6)	0·1670(9)	3·02(12)
C(5)	0·1724(5)	0·2453(5)	0·1125(8)	2·31(9)
C(6)	0·0900(5)	0·3169(6)	0·1373(9)	2·50(9)
C(7)	0·1942(6)	−0·0092(7)	−0·0637(11)	3·54(14)
C(8)	0 [a]	0·2180(8)	0·3266(14)	2·95(15)
H(2)	0·3697	0·0466	0·0451	*c*
H(3)	0·4133	0·2079	0·1759	*c*
H(4)	0·2817	0·3304	0·2310	*c*
H(6—1)	0·1058	0·3653	0·2330	*c*
H(6—2)	0·0793	0·3627	0·0372	*c*
H(7—1)	0·2536	−0·0547	−0·1064	*c*
H(7—2)	0·1547	−0·0540	0·0182	*c*
H(7—3)	0·1470	0·0085	−0·1582	*c*
H(8—1)	0	0·2736	0·4164	*c*
H(8—2)	0·0643	0·1718	0·3408	*c*

[a] Parameter not refined. [b] Anisotropic thermal parameters, $B_{11}, B_{22}, B_{33}, B_{23}$ are: for Pd, 2·00(3), 1·69(2), 2·63(2), −0·35(3); for Cl(1), 3·63(7), 3·93(7), 3·25(6), −1·16(6); and for Cl(2), 3·41(6), 2·88(6), 3·42(7), and 0·21(7). [c] Hydrogen atoms were given temperature factors equivalent to those of the atoms to which they were bonded, but their parameters were not refined.

TABLE 3

Bond distances (Å) and angles (deg.), with estimated standard deviations in parentheses for (II)

(*a*) Distances

Pd–N(1)	2·068(6)	C(4)–C(5)	1·385(10)
Pd–N(2)	2·018(8)	C(5)–C(6)	1·483(10)
Pd–Cl(1)	2·331(3)	C(6)–N(2)	1·493(9)
N(1)–C(1)	1·343(8)	N(2)–C(8)	1·474(15)
C(1)–C(2)	1·397(11)	C(1)–C(7)	1·474(12)
C(2)–C(3)	1·398(12)	N(1)–C(5)	1·371(8)
C(3)–C(4)	1·371(12)		

(*b*) Angles

C(5)–C(6)–N(2)	108·3(6)	C(1)–N(1)–C(5)	119·3(6)
C(6)–N(2)–C(8)	110·7(6)	N(1)–C(1)–C(2)	120·4(7)
C(6)–N(2)–C(6^{I})	110·8(7)	N(1)–C(1)–C(7)	119·4(7)
Cl(1)–Pd–N(1)	98·5(2)	C(2)–C(1)–C(7)	120·2(7)
Cl(1)–Pd–N(2)	161·0(2)	C(1)–C(2)–C(3)	120·1(8)
N(2)–Pd–N(1)	82·3(3)	C(2)–C(3)–C(4)	118·7(9)
N(1)–Pd–N(1^{I}) *	162·8(4)	C(3)–C(4)–C(5)	119·7(8)
Pd–N(1)–C(1)	130·2(4)	C(4)–C(5)–N(1)	121·7(7)
Pd–N(1)–C(5)	109·6(4)	C(4)–C(5)–C(6)	123·2(7)
Pd–N(2)–C(6)	103·5(4)	N(1)–C(5)–C(6)	115·1(6)
Pd–N(2)–C(8)	117·3(7)		

* Atoms N(1^{I}) and C(6^{I}) are in equivalent positions $-x, y, z$ relative to the reference set at x, y, z.

DISCUSSION

The configuration of the [PdCl(Me_3dpma)] cation of (II) is shown in Figure 1, together with the atomic numbering scheme and the bond distances. Atoms Pd, Cl(1), N(2), and C(8), of the cation and the chloride ion Cl(2) lie on a crystallographic mirror plane. In (II) the Pd–N(1) bonds [2·068(6) Å] are significantly longer than the corresponding Pd–N(2) bond [2·018(8) Å]. Pd^{II}–N distances found in square planar palladium(II) complexes, in which the Pd–N bond is neither sterically hindered nor *trans* to a very strong metal–ligand bond are in the range 1·99—2·04 Å.[14] The Pd–N(2) bond length falls in this range while the Pd–N(1) bond is slightly longer. A similar disparity between the Ni–N(1) and Ni–N(2) bond lengths has been noted[4] in the five-co-ordinate nickel complex (I) and the elongation of the M–N(1) bonds in both structures can therefore be ascribed to steric effects.

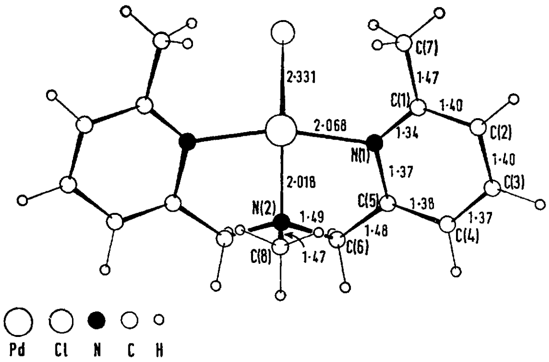

FIGURE 1 A view of the [PdCl(Me_3dpma)] cation

Pd^{II}–Cl and Pt^{II}–Cl distances[15,16] have been found in the range 2·294—2·422 Å, the lengths being dependent upon the steric nature of the ligands and the type of *trans*-bond. The range 2·29—2·33 Å is found in non-sterically hindered structures with no particularly strong *trans*-group such as dichloro(tetrahydrogen ethylenediaminetetra-acetato)palladium(II) pentahydrate,[17] 2·30(1) Å, and norbornadienepalladium(II) chloride,[18]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full page copies).

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2·323 and 2·310 Å. The Pd$^{\text{II}}$–Cl bond distance in (II) of 2·331(3) Å is therefore at the top of the range of such distances in similar compounds. In (II), the major influences on the stereochemistry of the cation are the short contacts between the Cl(1) atom [*trans* to N(2)] and the methyl groups C(7) and C(7$^{\text{I}}$). The Cl(1) · · · C(7) contact distances have been increased to acceptable values by distortions from ideal square planar symmetry around the palladium atom and by variations in the ligand conformation. The slight increase in Pd–N(1) and Pd–Cl(1) bond lengths, from values to be expected in an unstrained molecule, will have only a minor effect on such contacts.

It is pertinent to compare the configuration of (II) with that of (I)[4] in which there is no atom *trans* to N(2).* Thus, the Br · · · C(7) contacts ($\geqslant$3·78 Å) are considerably less important in fixing the geometry of (I) than are the Cl(1) · · · C(7) contacts (3·29 Å) in (II).† In (II), the chlorine atom Cl(1) is bent to one side of the Pd, N(1), N(1$^{\text{I}}$), N(2) plane [plane (2), Table 4] by 0·93 Å, the Cl(1)–Pd–N(2) angle being 161·0(2)°.

TABLE 4

Equations of least-squares planes for (II) in the form $Ax + By + Cz = D$ where x, y, z are the crystallographic fractional co-ordinates of the atoms. Distances (Å) of the relevant atoms from the planes are given in square brackets

	A	*B*	*C*	*D*
Plane (1):				
N(1), C(1)—(5)	−3·18	−5·88	7·58	−1·14
[N(1), C(1)—(5) 0·00, C(6) * 0·03, C(7) * 0·09, N(2) * 0·91]				
Plane (2):				
Pd, N(1), N(1$^{\text{I}}$), N(2)	0·00	9·28	−6·21	1·31
[Pd −0·09, N(1) 0·05, N(1$^{\text{I}}$) 0·05, N(2) −0·01, Cl(1) * −0·93, C(7) * 1·00]				

* Atoms given zero weight in the calculation of the plane. Angle between the two pyridine rings is 27·0°; angle between planes (1) and (2) is 22·0°.

We have described the conformation of the ligand by the least-squares planes listed in Table 4. In both structures the pyridine rings are planar within experimental error and the dimensions of the ligands are comparable. In (II), the pyridine rings are twisted out of plane by 22·0° leaving C(7) 1·00 Å from plane (2) on the opposite side to Cl(1). This distance is increased slightly by C(7) being 0·09 Å out of the pyridine ring plane. In addition, the Pd–N(1)–C(5) angle (130·2°) is greater than the Pd–N(1)–C(1) angle (109·6°); this feature also increases the Cl · · · C(7) distances.

In (I), the ligand is, as expected, considerably less distorted than in (II) as there is no atom in a position *trans* to N(2). The two pyridine rings are twisted out of plane (2) by 12·5°, while C(7) is only −0·30 and −0·42 Å from that plane. C(7) is coplanar with the pyridine ring and the difference between the Pd–N(1)–C(5) and Pd–N(1)–C(1) angles (mean 127·0 and 113·6°) is less than in (II).

In (II), there are few significant intermolecular contacts: among them being C(3) · · · Cl(2$^{\text{II}}$) ‡ 3·52, C(2) · · · Cl(2$^{\text{II}}$) 3·62, C(2) · · · Cl(2$^{\text{III}}$) 3·67, C(6) · · · Cl(2$^{\text{IV}}$) 3·54, Pd · · · Cl(1$^{\text{V}}$) 3·79 Å. A packing diagram of the unit cell is given in Figure 2.

From a comparison of the configurations of (I) and (II), it is clear that (II) is under more steric strain than would be found in the comparable five-co-ordinate trigonal bipyramidal PdCl$_2$(Me$_3$dpma) molecule. However, structural data on Pd$^{\text{II}}$ and Pt$^{\text{II}}$ five-co-ordinate complexes has been interpretated[6] as showing that, in the absence of steric requirements of the ligands or of very strong metal–ligand bonds, the preferred symmetry is square pyramidal. This is illustrated by the square pyramidal [Pd(tpas)Cl]$^+$ cation, in which the relative configuration of the four donor arsenic atoms is sufficiently flexible to participate in either geometry. The preferred symmetry of nickel(II) high-spin five-co-ordinate complexes is also square pyramidal[20] and the distorted trigonal bipyramidal structure found in (I) is presumably a consequence of the steric requirements of the Me$_2$dpma ligand. It follows that a five-co-ordinate PdCl$_2$(Me$_3$dpma) would be forced into the less favoured of the two ideal symmetries, trigonal bipyramidal. It is not surprising, therefore, that in the present case the four-co-ordinate distorted square planar structure (II) is found.

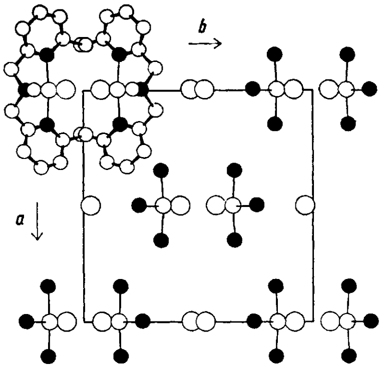

FIGURE 2 The unit cell of (II) in the *c* projection

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* The environment of the nickel atom in NiBr$_2$(Me$_2$dpma) (I) can best be described as distorted trigonal bipyramidal, with N(1), N(1$^{\text{I}}$) in axial positions and N(2), Br(1), and Br(2) in equatorial positions.

† Van der Waals radii[19] are: CH$_3$ 2·00, Cl 1·80, and Br 1·95 Å.

‡ Roman numerals in superscripts refer to atoms in the following equivalent positions relative to the reference set at x, y, z:

I (see Table 3) $-x, y, z$; II, $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; III, $\frac{1}{2} + x, -\frac{1}{2} + y, z$; IV, $x, 1 - y, \frac{1}{2} + z$; and V, $x, -y, \frac{1}{2} + z$.

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