Crystal and Molecular Structure of Chloro-(2-methoxycyclo-octa-1,5-dienyl)pyridineplatinum

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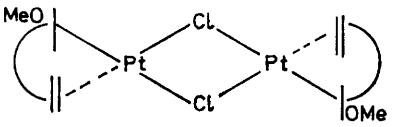
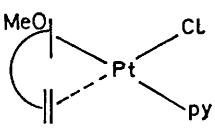
Crystals of the title compound are monoclinic, $a = 9{\cdot}84 \pm 0{\cdot}01$, $b = 18{\cdot}50 \pm 0{\cdot}02$, $c = 8{\cdot}15 \pm 0{\cdot}01$ Å, $\beta = 104° \pm 10'$, $Z = 4$, space-group $P2_1/c$. The structure was determined from photographic data by conventional Patterson and Fourier methods and refined by least-squares techniques to R 0·086 for 1445 independent reflections. The structure consists of monomeric units in which the central atom is in an essentially square planar configuration. The cyclo-octadienyl ligand is bonded to the platinum atom by both a π-olefinic bond and a σ-bond, the pyridine being *trans* to the latter. The long Pt–N distance [2·02(2) Å] results from the large *trans*-influence of the σ-bonded carbon atom.

Previous investigations on dimers of the type $[PtLCl]_2$ [L = methoxy-cyclo-octa-1,5-diene (codOMe) and -cyclopentadiene dimer (cpdOMe)] have shown that these compounds undergo bridge-splitting reactions by treatment with neutral ligands such as pyridine, *p*-toluidine, *etc.*, giving monomeric products.[1,2]

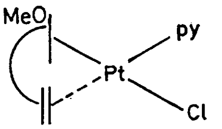
The determination of the crystal structure of the chloro-bridged dimer $[Pt(cpdOMe)Cl]_2$ (I) has established[3] that the central atom is linked to the organic moiety through both a σ and a π olefinic bond. In this structure the two metal–chlorine distances are significantly different (2·51 and 2·34 Å), the longer bond being *trans* to the carbon atom σ-bonded to the platinum. If a similar structure is assumed for the $[Pt(codOMe)Cl]_2$, it seems reasonable that in the corresponding monomer [Pt(codOMe)(py)Cl] the pyridine ligand occupies the position *trans* to the σ-bonded carbon atom as in (II), although the possibility of (III) should not be excluded.



(I)



(II)



(III)

The crystal-structure determination of [Pt(codOMe)(py)Cl] was therefore undertaken in order to verify the position of the pyridine relative to the two ' teeth ' of the bidentate ligand. Preliminary results have already been published.[4]

EXPERIMENTAL

Crystal Data.—$C_{14}H_{20}ClNOPt$, $M = 448{\cdot}9$, Monoclinic, $a = 9{\cdot}84 \pm 0{\cdot}01$, $b = 18{\cdot}50 \pm 0{\cdot}02$, $c = 8{\cdot}15 \pm 0{\cdot}01$ Å, $\beta = 104° \pm 10'$ (the errors given are three times the standard errors of the means of several measurements), $U = 1439$ Å^3, $D_m = 2{\cdot}05$ g. cm^{-3} (by flotation), $Z = 4$, $D_c = 2{\cdot}07$ g. cm^{-3}, $F(000) = 856$. Space-group $P2_1/c$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 202·2 cm^{-1}.

The crystals are colourless needles elongated along *a*. The unit-cell dimensions were evaluated from precession photographs.

Intensity data for the layers 0—8*kl* were collected by means of equi-inclination multiple-film Weissenberg photographs and for the *h*0*l* layers by the precession method.

The intensities of 1445 independent reflections were measured with a Joyce–Loebl Flying-Spot integrating microdensitometer and corrected for Lorentz and polarization factors. The Weissenberg data were scaled to a common scale by comparison with the precession data. The compound decomposed during irradiation, three crystals being required for the data collection, but in all cases very small fragments (mean dimension 0·05 mm) were chosen in order to minimize absorption effects.

Structure Solution.—The platinum atom was located from an unsharpened three-dimensional Patterson synthesis and the chlorine atom from a subsequent heavy-atom phased Fourier synthesis. R was 0·24 for a structure-factor calculation based on the platinum and chlorine atom co-ordinates. A difference Fourier synthesis revealed all the remaining non-hydrogen atom positions. The structure was then refined by least-squares methods using a block-diagonal approximation. Isotropic temperature factors were used for all atoms, the function minimized being $\sum w(|F_o|-|F_c|)^2$ with weights calculated by the Cruickshank scheme.[5]

Three cycles of refinement gave R 11·1%. Refinement was then continued with three more cycles, the Mills and Rollet weighting scheme being used: $w = 1/\{1 + [(kF_o - b)/a]^2\}$ with $a = 128$, $b = 80$, $K = 1{\cdot}78$, and $w = 1$ for $F_o = 56$. Finally, two cycles of full-matrix least-squares refinement were carried out with anisotropic thermal parameters for the platinum and chlorine atoms and isotropic thermal parameters for all other atoms. R converged to the final value of 8·6% when the mean shift in any parameter was 0·05 σ.

In all calculations the scattering factors for neutral atoms were used and were taken from ref. 6. A correction for the real part of the anomalous dispersion was applied to the

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[1] J. Chatt, M. L. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, pp. 2496, 3413.

[2] J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, *J. Amer. Chem. Soc.*, 1965, **87**, 3282.

[3] W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Comm.*, 1966, 350.

[4] C. Panattoni, G. Bombieri, E. Forsellini, and B. Crociani, and U. Belluco, *Chem. Comm.*, 1969, 187.

[5] D. W. J. Cruickshank and D. E. Pilling in ' Computing Methods and the Phase Problems in *X*-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961, p. 42.

[6] ' International Tables for *X*-Ray Crystallography,' vol. II, Kynoch Press, Birmingham, 1959.

platinum atom.[7] All calculations were performed on the IBM 7040—7094 system using the programs of ref. 8.

TABLE 1

Atomic positional ($\times 10^4$) and thermal parameters, with estimated standard deviations in parentheses

	x	y	z	B/Å^2
Pt	2239(1)	−0067(1)	0982(1)	*
Cl	1565(8)	619(4)	−1493(9)	*
O	4196(19)	−1705(9)	−1405(25)	3·7(3)
N	1919(22)	906(10)	2389(26)	2·9(4)
C(1)	904(31)	859(15)	3318(39)	4·1(5)
C(2)	693(39)	1452(20)	4236(51)	5·9(8)
C(3)	1292(37)	2064(17)	4156(46)	5·1(7)
C(4)	2307(37)	2106(17)	3257(46)	5·2(7)
C(5)	2631(34)	1490(16)	2312(42)	4·5(6)
C(6)	3631(25)	−501(11)	3227(31)	2·7(4)
C(7)	2276(30)	−869(15)	2944(39)	4·0(5)
C(8)	1932(31)	−1589(15)	2211(40)	4·1(5)
C(9)	1705(32)	−1596(15)	332(42)	4·3(6)
C(10)	2425(27)	−973(12)	−401(32)	2·9(4)
C(11)	4045(23)	−1115(11)	−248(29)	2·3(4)
C(12)	4897(33)	−1363(16)	1484(41)	4·5(6)
C(13)	4991(31)	−770(15)	2843(39)	4·1(5)
C(14)	3686(42)	−1516(21)	−3199(55)	6·3(8)

* Anisotropic thermal parameters ($\times 10^4$) in the form:

$$T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	87(1)	18(1)	129(2)	3(1)	30(1)	2(1)
Cl	107(10)	27(2)	173(15)	4(3)	38(9)	17(4)

TABLE 2

Bond distances and angles with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Pt–Cl	2·341(8)	C(6)–C(7)	1·46(4)
Pt–N	2·20(2)	C(7)–C(8)	1·47(4)
Pt–C(6)	2·16(2)	C(8)–C(9)	1·49(5)
Pt–C(7)	2·17(3)	C(9)–C(10)	1·55(4)
Pt–C(10)	2·05(2)	C(10)–C(11)	1·59(3)
N–C(1)	1·39(4)	C(11)–C(12)	1·53(4)
N–C(5)	1·30(4)	C(12)–C(13)	1·55(4)
C(1)–C(2)	1·37(5)	C(13)–C(6)	1·53(4)
C(2)–C(3)	1·30(5)	O–C(11)	1·47(3)
C(3)–C(4)	1·38(6)	O–C(14)	1·47(5)
C(4)–C(5)	1·45(5)	Pt–M *	2·04(3)

(*b*) Bond angles (°)

Cl–Pt–M *	175(1)	C(1)–C(2)–C(3)	123(4)
Cl–Pt–N	87·7(6)	C(2)–C(3)–C(4)	119(3)
Cl–Pt–C(6)	157(1)	C(3)–C(4)–C(5)	121(3)
Cl–Pt–C(7)	163(1)	C(4)–C(5)–N	116(3)
Cl–Pt–C(10)	91(1)	C(6)–C(7)–C(8)	127(3)
M *–Pt–C(10)	86(1)	C(7)–C(8)–C(9)	113(2)
N–Pt–C(6)	90(1)	C(8)–C(9)–C(10)	115(2)
N–Pt–C(7)	99(1)	C(9)–C(10)–C(11)	113(2)
N–Pt–C(10)	177(1)	Pt–C(10)–C(9)	107(2)
N–Pt–M *	96(1)	Pt–C(10)–C(11)	108(1)
C(6)–Pt–C(10)	92(1)	C(10)–C(11)–C(12)	116(2)
C(7)–Pt–C(10)	82(1)	C(10)–C(11)–O	109(2)
C(6)–Pt–C(7)	39(1)	C(12)–C(11)–O	105(2)
Pt–N–C(1)	116(2)	C(11)–C(12)–C(13)	112(2)
Pt–N–C(5)	121(2)	C(12)–C(13)–C(6)	118(2)
C(1)–N–C(5)	123(2)	C(13)–C(6)–C(7)	129(2)
N–C(1)–C(2)	118(3)	C(11)–O–C(14)	114(2)

* M is the mid-point of C(6)–C(7).

Positional and thermal parameters derived from the last cycle are listed in Table 1 with their standard deviations as estimated from the inverse matrix. A list of the observed and calculated structure factors is also given. Bond lengths and angles, and least-squares planes are given in Tables 2 and 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20276 (3 pp., 1 microfiche).*

TABLE 3

Equations of least-squares planes and, in square brackets, normal distances (Å) from the planes. The equations are in the form $AX + BY + CZ = D$ where X, Y, and Z are fractional co-ordinates referred to the crystallographic axes

	A	B	C	D
Plane (1): Pt, Cl, N, C(10), M	9·485	4·805	−1·493	1·951
[Pt 0·006, Cl −0·055, N 0·052, C(10) 0·058, M −0·061, C(6) −0·77, C(7) 0·65, C(8) 1·21, C(9) 1·15, C(11) −1·39, C(12) −1·82, C(13) −1·9]				
Plane (2): Pt, C(6), C(7)	−4·574	12·764	5·304	−0·589
[Cl 0·13]				

The angle between the planes is 87°.

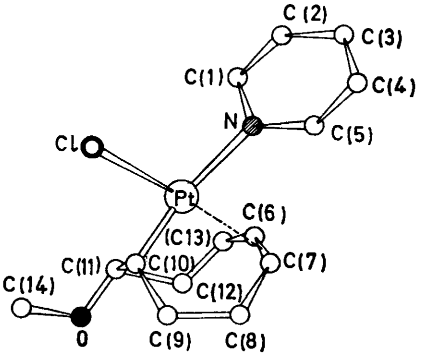

FIGURE 1 A perspective view of the molecule with numbering scheme used

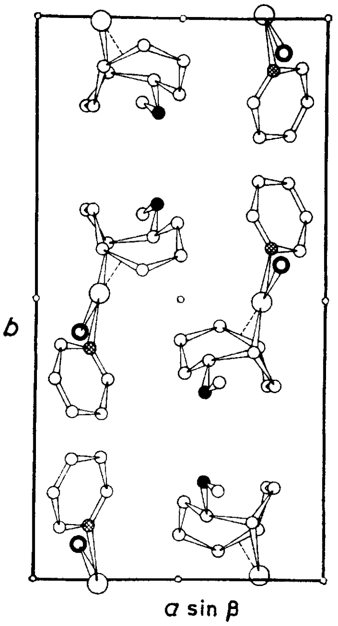

FIGURE 2 Diagrammatic projection of the structure along [001]

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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 size copies).

[7] Ref. 6, vol. III, 1962.

[8] J. M. Stewart and D. High, '*X*-Ray '63' System of Crystallographic Programs,' University of Maryland, Technical Report TR 64 6.

DISCUSSION

Description of the Structure.—A perspective drawing of the molecule together with the atom numbering scheme is shown in Figure 1, Figure 2 shows the structure viewed down *c*.

The environment of the platinum atom is essentially square planar with the chlorine atom *trans* to the π-olefinic bond and the pyridine *trans* to the Pt–C(10) σ bond. The Pt–M bond length of 2·04 Å between the platinum atom and the mid-point of C(6)–C(7) is normal for platinum–olefin bonds and comparable with the value of 2·05 Å found in a Dewar dehydrohexamethylbenzeneplatinum(II) complex,[9] $[PtCl(C_{12}H_{17})]_2$. This also applies to the Pt–C(6) and Pt–C(7) distances [2·16(2) and 2·17(3) Å] which are also comparable with the corresponding values [2·157(18) and 2·149(16) Å] found in Zeise's salt.[10]

The back-donation effect of the filled metal *d* orbitals to the empty π ligand orbitals is to lengthen the C(6)–C(7) bond to 1·46(4) Å. This is consistent with the reported values for compounds of this type.[11,12]

The Pt–Cl distance [2·341(8) Å] is comparable with the observed values for a number of *trans*-dichloro-derivatives of platinum(II), confirming the very weak *trans*-influence of a π-bonded olefin, as already pointed out.[11]

The σ-bond length Pt–C(10), [2·05(2) Å], is very similar to the corresponding distances in the dimer $[PtCl(cpdOMe)]_2$, and in the $[PtCl(C_{12}H_{17})]_2$ complex. However, the Pt–N distance of 2·20(2) Å appears to be 0·15 Å greater than expected for a normal covalent bond. This is probably due to the large *trans*-influence exercised by the σ-bonded C(10) atom because of its strong σ-donor properties. This theory is also supported by the results of the *X*-ray crystallographic-structure determination of tetrameric allyl(chloro)platinum,[13] in which the Pt–Cl distance *trans* to the σ-bonded carbon atom [2·46(1) Å] is almost 0·1 Å larger than that *trans* to the π bonded olefin [2·37(1) Å].

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[1/1064 *Received*, 28*th June*, 1971]

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[9] R. Mason, G. B. Robertson, P. O. Whimp, B. L. Shaw, and G. S. Shaw, *Chem. Comm.*, 1968, 868.

[10] M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, 1969, **B25**, 1253.

[11] R. Mason, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc.* (*A*), 1970, 535.

[12] R. Mason and G. B. Robertson, *J. Chem. Soc.* (*A*), 1969, 492.

[13] R. Raper and W. S. McDonald, *Chem. Comm.*, 1970, 655.