Compounds containing Platinum–Carbon Bonds. Part II.[1] Crystal and Molecular Structure of *cis*-Dichlorobis(phenyl isocyanide)platinum(II), *cis*-[$PtCl_2(CNPh)_2$]

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The structure crystal of the title compound has been determined from *X*-ray diffractometer data. The crystals are monoclinic, $a = 9{\cdot}936(4)$, $b = 11{\cdot}825(7)$, $c = 13{\cdot}088(4)$ Å, $\beta = 101{\cdot}75(3)°$, $Z = 4$, space-group $P2_1/c$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0·046 for 1644 independent reflexions. The arrangement of molecular units in the crystal structure is such that there is a Pt ··· Pt contact of 3·48 Å between centrosymmetrically related molecules. Co-ordination around the platinum atom is square planar. The mean Pt–C bond length [1·896(16) Å] suggests that there is appreciable metal–ligand back-donation. Pt–Cl (mean) is 2·308(5) Å.

COMPOUNDS of the type [$PtX_2(RNC)_2$], (X = Cl, Br, NO_2, or CN; R = alkyl or aryl), are among the first reported platinum(II) isocyanide complexes.[2] Some of these were isolated in two forms, presumably the *cis*- and *trans*-isomers. Following the early work, Badley[3] has prepared the compound (I) [$PtCl_2(CNPh)_2$] and suggested, on the basis of the i.r. spectrum, a *cis*-arrangement of

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[1] Part I, B. Jovanović and Lj. Manojlović-Muir, preceding paper.

[2] L. Chugaev and P. Teearu, *Chem. Ber.*, 1914, **47**, 568, 2643; L. Ramberg, *ibid.*, 1907, **40**, 2578.

[3] E. M. Badley, D.Phil. Thesis, University of Sussex, 1969.

the chlorine ligands. Further details of the molecular geometry of the complex and the mode of platinum–isocyanide bonding will be discussed here.

Structural features of the co-ordinated isocyanide in this compound supplement those, of lesser accuracy, in (II) *cis*-[$PtCl_2(CNEt)(PEt_2Ph)$].[1]

EXPERIMENTAL

Crystal Data.—$C_{14}H_{10}Cl_2N_2Pt$, $M = 472{\cdot}2$, Monoclinic, $a = 9{\cdot}936(4)$,* $b = 11{\cdot}825(7)$, $c = 13{\cdot}088(4)$ Å, $\beta = 101{\cdot}75(3)°$, $U = 1505{\cdot}5$ Å^3, D_m (by flotation) $= 2{\cdot}06$, $Z = 4$, $D_c = 2{\cdot}083$, $F(000) = 880$. Space-group $P2_1/c$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 101{\cdot}4$ cm^{-1}.

The crystals were light yellow, highly reflective thin plates, with all members of the {010}, {001}, and {10$\bar{2}$} forms present, the last form being preponderant. The distances between parallel faces of the specimen chosen for the analysis were 0·049 × 0·012 × 0·006 cm.

The unit-cell dimensions, initially obtained from Weissenberg and precession photographs, were adjusted by a least-squares treatment of the setting angles of twelve reflexions centred manually on a Hilger and Watts' Y 290 four-circle diffractometer, controlled by a PDP8 computer. To minimise the effects of multiple reflexions, the crystal was oriented so as to make an angle of *ca.* 10° between b^* and the ϕ axis of the diffractometer. Molybdenum radiation was used, in conjunction with a zirconium filter and a pulse-height analyser. The intensities were measured by the θ—2θ scan technique, with a scan step in 2θ of 0·02° and a counting time for each step of 1s. Each reflexion was scanned through a 2θ range, centred on the Mo-K_α peak, of 1·6°. The local background was measured for 20s at each end of the scan range, using the stationary-crystal–stationary-counter technique. To monitor the crystal and electronic stability, the intensities of two strong reflexions were measured periodically throughout the experiment, but only random fluctuations of up to ±3% in their mean values were observed.

TABLE 1

Final fractional co-ordinates and thermal parameters [a] of atoms

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0·4536(1)	0·0363(1)	0·1169(1)	93(1)	75(1)	59(1)	−5(1)	20(1)	−3(1)
Cl(1)	0·2310(4)	−0·0178(5)	0·0441(4)	102(4)	118(6)	84(3)	−14(4)	9(3)	11(3)
Cl(2)	0·5055(4)	−0·1436(4)	0·1803(3)	121(5)	77(5)	90(3)	14(4)	26(3)	13(3)
N(1)	0·7411(14)	0·1276(15)	0·2069(11)	125(18)	138(21)	76(11)	−31(16)	12(12)	−4(12)
N(2)	0·3743(14)	0·2746(15)	0·0387(11)	138(19)	87(18)	83(12)	−18(15)	12(12)	7(12)
C(1)	0·6341(19)	0·0823(18)	0·1748(12)	158(25)	98(21)	62(13)	7(18)	26(15)	−9(12)
C(2)	0·4062(18)	0·1860(19)	0·0671(13)	117(21)	114(24)	59(12)	16(19)	19(13)	−17(14)
C(3)	0·8670(16)	0·1764(15)	0·2427(13)	116(20)	46(15)	76(13)	15(13)	14(13)	−3(11)
C(4)	0·9805(18)	0·1443(16)	0·1993(13)	146(24)	74(19)	87(14)	−7(17)	11(15)	−26(12)
C(5)	1·1053(18)	0·1972(21)	0·2349(16)	116(22)	127(27)	99(17)	−4(19)	37(16)	15(16)
C(6)	1·1188(16)	0·2774(19)	0·3086(15)	97(20)	100(24)	93(16)	−10(16)	7(15)	15(15)
C(7)	1·0099(18)	0·3079(15)	0·3481(14)	147(24)	52(17)	102(16)	−13(16)	−8(16)	−11(12)
C(8)	0·8805(15)	0·2556(19)	0·3156(13)	86(18)	119(23)	84(14)	5(17)	15(14)	3(14)
C(9)	0·3230(19)	0·3783(18)	0·0041(13)	160(25)	90(21)	66(13)	15(19)	8(15)	−2(13)
C(10)	0·3661(20)	0·4244(18)	−0·0792(16)	176(27)	85(21)	98(16)	−11(19)	40(17)	−4(14)
C(11)	0·3146(29)	0·5366(23)	−0·1089(18)	288(43)	102(27)	107(18)	26(29)	43(23)	27(19)
C(12)	0·2268(33)	0·5853(23)	−0·0646(20)	411(60)	130(32)	107(21)	130(36)	74(29)	33(20)
C(13)	0·1841(33)	0·5356(24)	0·0152(20)	417(62)	125(31)	118(22)	104(36)	98(30)	26(22)
C(14)	0·2324(29)	0·4280(27)	0·0556(17)	298(46)	223(44)	86(18)	59(36)	78(24)	23(21)

[a] The atoms were assigned anisotropic temperature factors of the form: $exp[-10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

The integrated intensities and their standard deviations were derived as described previously [4] and corrected for Lorentz, polarization, and absorption effects. The transmission factors on F, calculated as in Part I,[1] ranged from 0·36—0·76.

All independent reflexions in the sphere with 2θ(Mo-K_α) $\leqslant 50°$ were measured, of which 1644 having $I \geqslant 3\sigma(I)$, were included in the subsequent analysis.

Structure Analysis.—The position of the platinum atom was found from a Patterson function, and the positions of the other non-hydrogen atoms from the subsequent difference syntheses.

The structure was refined by full-matrix least-squares. The function minimised, the least-squares weights, w, and the conventional and weighted agreement factors, R and R' respectively, were as defined previously.[4] The atomic scattering factors, except that of hydrogen,[5] and the dispersion corrections for platinum and chlorine were the same as in Part I.

The refinement of positional and isotropic thermal parameters of all non-hydrogen atoms terminated at R 0·060 and R' 0·074. An allowance was then made for the anisotropic thermal vibrations of atoms and the R and R' decreased to 0·048 and 0·060, respectively. A low-angle difference synthesis, based on terms with $\sin\theta/\lambda < 0{\cdot}35$ Å^{-1} revealed the positions of seven out of ten hydrogen atoms. All hydrogen atoms were included in the subsequent structure-factor calculations, but their positional parameters, deduced from the known stereochemistry of the benzene ring, and their isotropic thermal parameters, assumed to be equal to those of the carbon atoms to which they are bonded, were not refined. The refinement converged at R 0·046 and R' 0·056.

In the last cycle of refinement all parameters shifted by $< 0{\cdot}17\sigma$. The adequacy of the weighting scheme was confirmed by use of the same procedure as in Part I. The

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* Throughout the paper, and in the other papers of the series, limits of error are estimated standard deviations derived from the appropriate least-squares matrix. For the mean quantities they were calculated both from the appropriate estimated standard deviations and from the range of individual measurements and the higher value was taken.

[4] Lj. Manojlović-Muir, *J. Chem. Soc.* (*A*), 1971, 2796.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

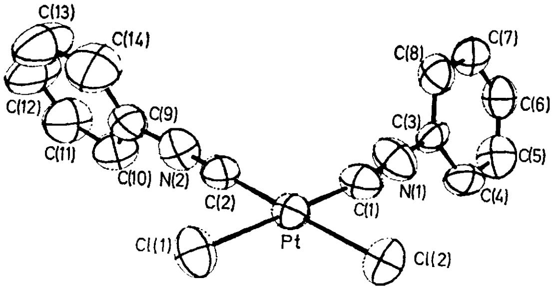
function values in the final difference synthesis were in the range +1·6 to −1·1 eÅ^{-3}, all peaks >0·80 eÅ^{-3} being associated with the position of the platinum atom. The final position and thermal parameters of atoms are shown in Table 1.

The root-mean-square amplitudes of thermal vibrations of atoms reveal no unexpected features (Table 2). Approximate directions of the principal axes of vibration can be discerned from the Figure.*

TABLE 2

Root-mean-square amplitudes of vibration (Å) along principal axes of thermal ellipsoids

Atom	Axis(1)	Axis(2)	Axis(3)
Pt	0·205	0·219	0·234
Cl(1)	0·217	0·259	0·303
Cl(2)	0·218	0·244	0·281
N(1)	0·23	0·26	0·32
N(2)	0·23	0·25	0·29
C(1)	0·22	0·26	0·28
C(2)	0·20	0·23	0·30
C(3)	0·17	0·24	0·26
C(4)	0·20	0·27	0·30
C(5)	0·22	0·28	0·31
C(6)	0·21	0·25	0·30
C(7)	0·18	0·25	0·32
C(8)	0·20	0·27	0·29
C(9)	0·23	0·24	0·29
C(10)	0·24	0·27	0·30
C(11)	0·24	0·31	0·38
C(12)	0·23	0·29	0·49
C(13)	0·25	0·28	0·48
C(14)	0·23	0·34	0·43



The molecular structure. The thermal-motion ellipsoids enclose 50% of probability

The computer programmes used were those listed previously.[1,4]

DISCUSSION

The arrangement of molecular units in the crystal structure is such that there is a Pt ··· Pt contact 3·48 Å between molecules related by centres of symmetry at $\frac{1}{2}$,0,0 and $\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$. The corresponding Pt ··· Pt vector is approximately normal to the square planes of the two molecules involved. This may indicate a weak platinum–platinum interaction reminicent of that in Magnus' Green Salt[6] and analogous compounds.[7] The other intermolecular contacts are of the van der Waals type (Table 3).

TABLE 3

Intermolecular distances ⩽3·60 Å

C(6) ··· C(9$^{\mathrm{I}}$)	3·46	Cl(1) ··· C(8$^{\mathrm{V}}$)	3·55
Pt ··· Pt$^{\mathrm{II}}$	3·48	C(13) ··· C(8$^{\mathrm{VI}}$)	3·56
C(5) ··· C(10$^{\mathrm{I}}$)	3·48	C(2) ··· Cl(2$^{\mathrm{II}}$)	3·56
C(1) ··· Cl(1$^{\mathrm{II}}$)	3·49	C(6) ··· N(2$^{\mathrm{I}}$)	3·58
C(10) ··· C(10$^{\mathrm{III}}$)	3·51	N(1) ··· Cl(1$^{\mathrm{II}}$)	3·60
C(10) ··· C(6$^{\mathrm{IV}}$)	3·52		

The superscripts refer to the following transformations of the atomic co-ordinates x, y, z:

I $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
II $1 - x, -y, -z$
III $1 - x, 1 - y, -z$
IV $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$
V $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
VI $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

The molecular structure of the complex (I) is illustrated in the Figure. Co-ordination around the platinum atom is square planar and of approximate C_{2v} symmetry. The chlorine ligands are mutually *cis*.

TABLE 4

Molecular geometry

(*a*) Bond lengths (Å)

Pt–Cl(1)	2·313(4)	Pt–Cl(2)	2·303(5)
Pt–C(1)	1·880(18)	Pt–C(2)	1·912(22)
C(1)–N(1)	1·19(2)	C(2)–N(2)	1·14(3)
N(1)–C(3)	1·37(2)	N(2)–C(9)	1·37(3)
C(3)–C(4)	1·41(3)	C(9)–C(10)	1·36(3)
C(4)–C(5)	1·38(3)	C(10)–C(11)	1·45(3)
C(5)–C(6)	1·34(3)	C(11)–C(12)	1·28(4)
C(6)–C(7)	1·34(3)	C(12)–C(13)	1·34(4)
C(7)–C(8)	1·41(2)	C(13)–C(14)	1·42(4)
C(8)–C(3)	1·33(3)	C(14)–C(9)	1·36(4)

(*b*) Bond angles (°)

Cl(1)–Pt–Cl(2)	91·1(2)	C(1)–Pt–C(2)	91·0(8)
Cl(1)–Pt–C(2)	88·1(5)	Cl(2)–Pt–C(1)	89·8(6)
Cl(1)–Pt–C(1)	179·1(6)	Cl(2)–Pt–C(2)	178·1(6)
Pt–C(1)–N(1)	170·0(18)	Pt–C(2)–N(2)	177·8(17)
C(1)–N(1)–C(3)	177·9(20)	C(2)–N(2)–C(9)	174·5(18)
N(1)–C(3)–C(4)	120(2)	N(2)–C(9)–C(10)	118(2)
N(1)–C(3)–C(8)	120(2)	N(2)–C(9)–C(14)	117(2)
C(8)–C(3)–C(4)	121(1)	C(14)–C(9)–C(10)	125(2)
C(3)–C(4)–C(5)	118(2)	C(9)–C(10)–C(11)	116(2)
C(4)–C(5)–C(6)	121(2)	C(10)–C(11)–C(12)	122(2)
C(5)–C(6)–C(7)	120(2)	C(11)–C(12)–C(13)	121(3)
C(6)–C(7)–C(8)	122(2)	C(12)–C(13)–C(14)	123(3)
C(7)–C(8)–C(3)	119(2)	C(13)–C(14)–C(9)	114(2)

(*c*) Equations of mean planes in the form $Ax + By + Cz = D$ and displacements (Å) of relevant atoms from the planes.

	A	B	C	D
Plane (A): Pt, Cl(1), Cl(2), C(1), C(2)	−4·644	2·791	12·162	−0·573
[Pt 0·011, Cl(1), 0·013, Cl(2) −0·018, C(1) 0·016, C(2) −0·022, N(1) −0·004, C(3) 0·009, N(2) −0·072, C(9) −0·179]				
Plane (B): C(3)—(8)	1·010	−8·239	8·828	1·564
[C(3) 0·000, C(4) 0·004, C(5) −0·001, C(6) −0·005, C(7) 0·008, C(8) −0·005, N(1) 0·040, C(1) 0·059, Pt 0·373]				
Plane (C): C(9)—(14)	6·378	5·050	6·450	3·991
[C(9) −0·006, C(10) 0·023, C(11) −0·024, C(12) 0·005, C(13) 0·014, C(14) −0·012, N(2) −0·033, C(2) 0·028, Pt 0·161]				

Dihedral angles (°) between planes: (B)–(A) 67; (C)–(A) 70.

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* Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20366 (8 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[6] M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1957, **79**, 3017; S. Yamada, *ibid.*, 1951, **73**, 1579.

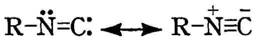
[7] M. E. Cradwick, D. Hall, and R. K. Phillips, *Acta Cryst.*, 1971, **B27**, 480.

The two Pt–Cl distances (Table 4) are equal with experimental error and their mean value of 2·308(5) Å agrees with that of 2·314(10) Å in (II).[1]

The two Pt–C bond lengths are also equal, mean 1·896(16) Å, and in agreement with equivalent distances of 1·83(4) in (II) and 1·87(3) Å in *cis*-[$PtCl_2$(CNPh)-(PEt_3)].[3] However, they are significantly shorter than the Pt–C(*sp*) single bond of 2·02 Å, predicted from the Pt–C(sp^3) distance of 2·079(14) Å in *trans*-[PtCl(CH_2SiMe_3)(PMe_2Ph)$_2$] [8] and the covalent radii of sp^3- and *sp*-carbon atoms (0·77 and 0·71 Å, respectively). This contraction suggests an appreciable platinum–isocyanide π-interaction, arising from a transfer of electron density from the metal *d* orbitals into π^* orbitals of the ligand.

The Pt–C(isocyanide) distances may also be compared with Pt–C(carbonyl) distances of 1·75(9) in *cis*-[$PtCl_2$(CO)(PEt_3)][3] and 1·74(4) Å in *trans*-[$PtCl_2$(CO)-(ONC_6H_4OMe)].[9] Despite the low accuracy of the Pt–C (carbonyl) bond lengths, this comparison suggests that in platinum(II) complexes the isocyanide ligand is a weaker π-acceptor than the isoelectronic carbon monoxide.

The (CN) stretching frequencies of (I) and (II) are *ca.* 100 cm^{-1} higher than those of the corresponding free isocyanides.[3,10] The increase in ν(CN) is commonly observed on co-ordination of isocyanide to metals in oxidation state +1 or higher, and it is generally regarded as diagnostic of pure σ-character of the metal–isocyanide bonding.[11,12] This view is in apparent conflict with our observation of the Pt–C(isocyanide) bond length. In terms of the valence-bond theory, free isocyanide may be considered as a resonance hybrid of the structures (A) and (B), with a smaller but significant contribution of (A).[13]



$$R{-}\ddot{N}{=}C\!: \longleftrightarrow R{-}\overset{+}{N}{\equiv}\overset{-}{C}$$

(A) (B)

On co-ordination to a positively charged metal ion, contribution of the structure (B) becomes further increased. The i.r. and crystallographic evidence for platinum(II)–isocyanide complexes can be reconciled if it is assumed that the observed increase in ν(CN) indicates that the decrease in the CN bond order, arising from Pt→C back-donation, is insufficient to counterbalance the effect of the increased contribution of the canonical structure (B).

The mean C(*sp*)–N and N–C(sp^3) distances of 1·16(3) and 1·37(2) Å, respectively, are comparable with those in (II) and reveal no unexpected features.

The Pt–C–N angles of 177·8(17) and 170·0(18)° show that only one isocyanide ligand is considerably bent at the *sp*-carbon atom. This bending is probably the result of the crystal-packing forces, rather than of some electronic effect; the later would be expected, in view of molecular symmetry, to affect both angles equally. The two C–N–C angles are equal, mean 176·5(15)°. In (II), the Pt–C–N and C–N–C angles are 174(4) and 172(3)°. It is therefore apparent that the pronounced non-linearity observed in *cis*-[$PtCl_2$(CNPh)(PEt_3],[3] where the C–N–C angle is 165·5(30)°, is not a general feature of the Pt–C–N–R system.

Both benzene rings are accurately planar (Table 4). The mean C–C distance and C–C–C angle are 1·369(14) Å and 120·0(9)°, respectively. Deviations of the individual C–C bond lengths and C–C–C angles from the respective mean values are not significant.

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