The Crystal and Molecular Structure of
Dichlorodi-(o-phenylenebisdimethylarsine)platinum(II)

By N. C. Stephenson*

*Crystallography Laboratory, University of Pittsburgh, Pittsburgh 13, Penna., U.S.A.*

Dichlorodi-(o-phenylenebisdimethylarsine)platinum(II), crystallizes in the space group $Pcan$, with four molecules in the unit cell of dimensions

$$a = 9.66, \quad b = 16.60, \quad c = 18.02 \text{ Å (all to 0.5\%) .}$$

The crystal structure has been determined from three-dimensional Fourier functions and has been refined by cycles of differential syntheses. Each platinum atom is in approximately square-planar configuration, being bonded to four arsenic atoms from two diarsine ligands. There are chlorine atoms completing an octahedral arrangement about each platinum atom and the Pt–Cl bond distance indicates an electrostatic interaction. Each chloride ion is cushioned on four methyl groups and the approach distances of 4.16 ± 0.01 Å do not indicate strong interactions with the metal atoms in the plane. There is an appreciable shortening of the Pt–As bond length from the normal single covalent bond distance.

Introduction

The present detailed investigation of the molecular and crystal structure of the compound

$$Pt(C_6H_4[As(CH_3)_2]_2)_2Cl_2$$
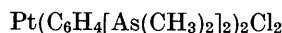
was undertaken for the following reason. Harris, Nyholm & Phillips reported in 1960 that the ditertiary arsine chelate o-phenylenebisdimethylarsine (diarsine) forms complexes of divalent platinum, palladium and nickel which exist as five-coordinate cations of the type $[M^{II}(diarsine)_2 \text{ halogen}]^+$ in solution. In the cases of the diiodides, $M^{II}(diarsine)_2I_2$, the crystal structure analyses (Stephenson, 1962, 1964) have shown that in the solid state the transition metal atom M^{II} has a coordination number of six; four arsenic atoms are strongly bonded to the metal atom in the form of a square plane whilst the iodine atoms are found in octahedral sites. The metal–iodine bond is considered to be essentially covalent in character. There is no information concerning the metal–chlorine bond in these diamagnetic d^8-complexes. In the present paper we present the details of our study and indicate that the Pt–Cl bond is essentially electrostatic in nature, which is in keeping with the greater electronegativity and smaller size of the chloride ion as compared with the iodide ion.

Experimental

Single crystals of $Pt(C_6H_4[As(CH_3)_2]_2)_2Cl_2$ were grown from aqueous solution. The colourless crystals grow

* On leave from the Chemistry Department, University of New South Wales, Sydney, Australia.

as needles elongated along the [100] axis. The following unit-cell dimensions were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation and zero layer precession photographs taken with Mo $K\alpha$ radiation; $a = 9.66$, $b = 16.60$, $c = 18.02$ Å (accurate to 0.5%).

The space group was uniquely determined as $Pcan$ from the systematically absent reflexions. Four formula units (M.W. $= 838$) per unit cell ($U = 2890$ Å³) give a calculated density of 1.93 g.cm⁻³, which agrees well with densities reported for similar diarsine complexes (Stephenson 1962, 1963). The molecular symmetry is $\bar{1}$.

The intensity data were collected on multiple-film equi-inclination Weissenberg photographs (Cu $K\alpha$) taken around [100], ($h = 0, 1, \ldots, 6$). The Weissenberg data about the b and c axes were difficult to obtain because of the experimental difficulties associated with the long b and c axes and the heavy absorption associated with the crystal shape. For these reasons separate scale factors as variates were carried for the seven layers $0kl$ through $6kl$. The use of separate scale factors to some extent hinders the determination of the anisotropic thermal parameters of the heavy atoms, but may compensate partially for absorption errors which would otherwise have been introduced.

The intensities were estimated visually with the aid of a calibration strip and the Lorentz and polarization corrections were applied on an IBM 1620 computer with the programs of Shiono (1963). Neither extinction corrections nor absorption corrections were applied to these data. The structure amplitudes were

not scaled initially; the final scaling (Table 1)* is based on the calculated structure amplitudes.

Solution of the structure

The initial trial model placed platinum atoms at the symmetry centres $(0, 0, 0)$, $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. Despite the heavy scattering power of these atoms they are not phase determining so that y and z parameters for the arsenic and chlorine atoms were obtained from the $(0kl)$ Patterson projection. Reasonable x coordinates were calculated for the arsenic atoms with the use of the above y and z parameters and accepted platinum–arsenic bond distances. In order to place the chlorine atoms in octahedral sites with respect to the platinum and arsenic atoms the platinum–chlorine bond must be much longer than would be expected in a six coordinate covalent complex. The coordinates of the platinum and arsenic atoms, together with a rough isotropic thermal parameter, were next used to calculate structure amplitudes, against which the observed structure amplitudes were scaled. The initial reliability index was $R = 0.67$. The resultant values of $F_o - F_c$ were used in the calculation of a three-dimensional difference Fourier synthesis. In this Fourier synthesis the position of the chlorine atom was evident and corrections were made to the coordinates of the arsenic atoms. Structure factors calculated with these new coordinates and an isotropic temperature factor of $B = 2.80$ Å^2 were used to scale each level of the observed data. The reliability index at this stage was $R = 0.31$.

Three cycles of refinement of these heavy atom positions together with isotropic thermal parameters for each atom were carried out with the differential synthesis IBM 7070 programs of Shiono (1961). After each cycle the observed structure amplitudes were scaled against the calculated structure amplitudes with the use of the interlayer scaler program of McMullan (1962). The reliability index at this stage was $R = 0.26$ and the standard deviation in electron density was 0.97 e.A^{-3}. The resultant values of $F_o - F_c$ were used in the calculation of a three-dimensional difference Fourier synthesis. Six of the ten carbon atoms were identified with peaks appearing on this electron density distribution. Three further cycles of differential syntheses refined the atomic coordinates and isotropic thermal parameters of these carbon atoms and the heavier atoms to a stage where $R = 0.18$. The remaining four carbon atoms were then located by computing a difference Fourier synthesis.

_____

* Table 1 has been deposited as Document number 7822 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document number and by remitting $5.00 for photoprints, or $2.25 for 35 mm microfilm. Advance payment is required. Make cheques or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Refinement of the structure

Refinement of the structure was carried out almost entirely by differential synthesis techniques. At the completion of the refinement a program for full-matrix least-squares refinement on the IBM 7070 computer became available (Shapiro, 1962). One cycle of least-squares (1649 data, 124 parameters, anisotropic thermal parameters) gave parameter shifts which were less than the estimated standard deviations in the respective parameters.

For the calculation of structure factors the atomic scattering factors for Pt, As and C, and Cl of Thomas & Umeda (1957), Thomas & Fermi (1935), & Dawson (1960) were used. A correction for anomalous dispersion was applied to the platinum atom scattering factor (Dauben & Templeton, 1955; Templeton, 1962).

The initial refinement was based on all the observed reflexions, on separate scale factors for individual layers, and on individual isotropic thermal parameters for all atoms. The scale factors and the β_{11} of the heavy atoms depend only on h, and since the heavy atoms are the principal contributors to the structure amplitudes, the situation for anisotropic refinement is equivalent to having nearly a singular least-squares matrix of normal equations. In the succeeding anisotropic refinement the scale factors from the isotropic refinement were used and were not varied. The anisotropic refinement (124 parameters) converged to a reliability index of 0.12. The final positional parameters from this refinement are listed in Table 2. The values of F_c based on these data, together with the values of F_o for observed and non-observed reflexions, are listed in Table 1. The F_c values accordingly do not include the contributions from hydrogen atoms. The F_o values have been scaled absolutely with the use of the scale factors from the isotropic refinement. Table 3 shows the final values, referred to the orthogonal axes, for the tensor components describing the anisotropic vibration of the atoms. The tensor components U_{ij} are those occurring in the temperature factor

$$\exp\left[-2\pi^2(h^2 a^{*2} U_{11} + 2hk a^* b^* U_{12} + \ldots)\right]$$

Table 2. Final fractional coordinates and standard deviations (Å)

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Pt(1)	0·0000	0·0000	0·0000	0·000	0·000	0·000
As(2)	0·5179	0·3886	0·0824	0·005	0·003	0·003
As(3)	0·2044	0·0450	0·4400	0·005	0·003	0·003
Cl(4)	0·2252	0·3626	0·3749	0·013	0·008	0·010
C(5)	0·279	0·040	0·116	0·02	0·02	0·03
C(6)	0·401	0·037	0·151	0·05	0·04	0·03
C(7)	0·195	0·098	0·198	0·05	0·04	0·03
C(8)	0·242	0·111	0·126	0·04	0·02	0·02
C(9)	0·242	0·169	0·175	0·07	0·05	0·03
C(10)	0·368	0·165	0·211	0·05	0·04	0·03
C(11)	0·006	0·218	0·043	0·06	0·02	0·03
C(12)	0·155	0·129	0·362	0·18	0·05	0·06
C(13)	0·380	0·392	0·169	0·04	0·04	0·02
C(14)	0·347	0·090	0·497	0·04	0·02	0·02

so that, for instance, U_{11} is the mean-square amplitude of vibration of the atom parallel to the a^* axis. The vibrations of the platinum atoms are essentially isotropic, which is reasonable on the basis of the molecular structure. The chlorine atoms are vibrating with considerably greater amplitudes and they occur in the crystal as ions with no strong bonding to the platinum complex.

Table 3. *Thermal parameters* ($\times 10^3$ Å)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Pt(1)	30	30	31	3	0	1
As(2)	38	35	38	-2	3	4
As(3)	41	41	51	-7	0	8
Cl(4)	61	46	60	-2	4	-6
C(5)	16	40	15	2	5	2
C(6)	70	57	50	-26	2	0
C(7)	52	88	66	-22	42	2
C(8)	21	29	23	-13	0	0
C(9)	87	51	39	0	8	2
C(10)	54	64	43	-3	-10	-1
C(11)	94	68	65	8	-1	3
C(12)	64	44	53	9	5	6
C(13)	37	46	44	11	0	3
C(14)	24	23	4	-25	-4	8

In general the vibrations of the lighter atoms are greater than those of the heavier metal atoms. Atoms C(1), C(4) and C(9) are exceptions but we find that their peak heights are greater than the average for a carbon atom. These figures are thus concordant since the thermal parameters give a qualitative relationship between peak height and thermal spread. It is possible that the increase in peak height is due to an additive effect of diffraction ripples from the heavy atoms at the light atom position. Systematic errors in the data might possibly be the explanation for the thermal parameter of C(10). The isotropic thermal parameter ($B = 1\cdot3$ Å^2) of atom C(10) is significantly lower than the mean value derived from the individual thermal parameters of the other nine carbon atoms. The peak height is only about 61% of the theoretical peak height for a carbon atom in this position. We offer no positive reasons for these anomalous values.
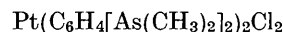
Description of the structure

The structure defined by the parameters in Table 2 and by the equivalent positions of the space group is one in which individual molecules of

$$Pt(C_6H_4[As(CH_3)_2]_2)_2Cl_2$$

of conformation depicted in Fig. 1 pack together tightly, in the manner shown in Fig. 2. Each platinum atom is in an approximately square-planar configuration being bonded to four arsenic atoms from two diarsine ligands. There are chlorine atoms completing an octahedral arrangement about each platinum atom.

The best least-squares planes through various atoms in the molecule have been calculated following Schomaker, Waser, Marsh & Bergman (1959) using a diagonal weight matrix. The equation of the plane through the platinum and arsenic atoms is

$$0\cdot554X + 0\cdot489Y - 0\cdot674Z = 0$$

where the coordinates X, Y and Z are in Å and

Table 4. *Atomic peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5})

|			$-A(HH)$	$-A(KK)$	$-A(LL)$	$A(HK)$	$A(KL)$	$A(HL)$
Pt(1)	obs.	147·7	730	1463	1354	42	20	-1
	calc.	148·4	734	1474	1362	27	17	-1
As(2)	obs.	53·8	249	501	467	-8	-5	21
	calc.	57·4	267	535	500	-7	-9	17
As(3)	obs.	49·5	234	443	397	-35	1	33
	calc.	52·0	245	470	422	-25	2	28
Cl(4)	obs.	20·2	90	178	132	0	25	1
	calc.	21·3	96	183	144	0	22	1
C(5)	obs.	7·0	34	60	45	-1	18	6
	calc.	7·7	38	70	53	-3	17	6
C(6)	obs.	6·2	22	39	43	-9	6	-1
	calc.	5·7	21	39	41	-5	5	0
C(7)	obs.	5·5	21	30	44	-1	7	0
	calc.	5·4	21	33	40	3	3	0
C(8)	obs.	7·1	32	78	72	-5	-1	2
	calc.	8·4	39	94	83	-3	-2	1
C(9)	obs.	5·5	16	30	48	2	-6	-1
	calc.	5·8	20	33	48	3	-4	-2
C(10)	obs.	6·5	24	34	49	-1	4	-3
	calc.	6·3	24	35	43	1	4	-3
C(11)	obs.	6·0	21	72	51	4	3	-1
	calc.	5·8	23	72	49	1	3	-1
C(12)	obs.	3·5	7	30	21	3	3	-10
	calc.	4·8	15	41	37	-1	3	-11
C(13)	obs.	6·4	32	36	69	1	-16	4
	calc.	7·1	36	46	77	1	-16	4
C(14)	obs.	5·7	30	73	62	-23	4	9
	calc.	9·4	47	111	85	-22	8	10
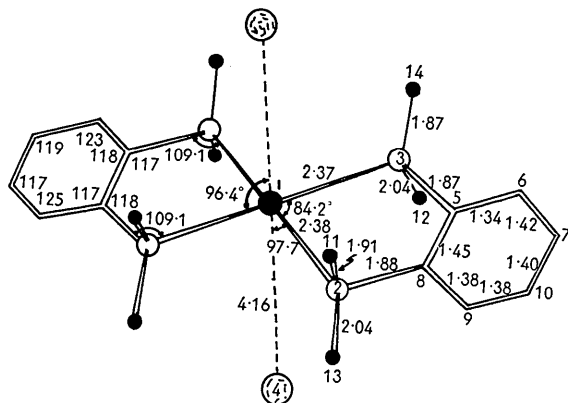
Fig. 1. Schematic depiction of the dichlorodi-(o-phenylene-bisdimethylarsine)-platinum(II) molecule. Hatched circles: chlorine. Small full circles: methyl groups. Small open circles: arsenic. Large full circle: platinum. Atoms are numbered as in Tables 2, 3, and 4.

Table 5. *Deviations* (Å) *of atoms from least-squares plane*

Atom	Deviation	Atom	Deviation
C(5)	−0·012	C(9)	−0·017
C(6)	−0·016	C(10)	−0·012
C(7)	0·028	As(2)	−0·106
C(8)	0·028	As(3)	−0·194

Equation of formal (unit weight) least-squares through the carbon atoms of the benzene ring:

$$0·437X + 0·458Y − 0·774Z + 0·123 = 0 \,.$$

refer to the crystallographic axes. The benzene ring is also planar. In Table 5 the equation of the formal (unit weight) least-squares planes is given, together with the deviations of the individual atoms from this plane. Only the deviations of the arsenic atoms are significant (at the 1% level). The dihedral angle between the benzene ring and the platinum–arsenic plane is 9° 3′.

The packing of the molecules is tight. The C–C intermolecular contacts are 3·5 Å or longer. The benzene rings of adjacent sets of molecules (e.g. I and IV) approach one another quite closely and are inclined to each other at an angle of 51·8°. There is thus more interaction between the π-electron systems of the benzene rings in this orthogonal cell than between similar neighbours in the monoclinic $M^{II}(diarsine)_2I_2$. The C–C intermolecular contacts are much longer in this latter case and the benzene rings are inclined to each other at an angle of 75°. This difference in the extent to which the π-electron systems interact can probably be traced to the nature of the solvent from which the crystals were grown. Strong interaction occurs in the crystals grown from water, a polar solvent which helps promote stability of the charge-transfer state of various molecules (Murrell, 1961). If one imagines the interaction to be a charge-transfer type then a transition from the ground state AA to a transition state A^+A^- will be stabilized by increasing the dielectric constant or polarity of the surrounding medium.

Non-bonding approach distances between a chlorine

Table 6. *Selected intramolecular bond distances* (Å) *and angles*

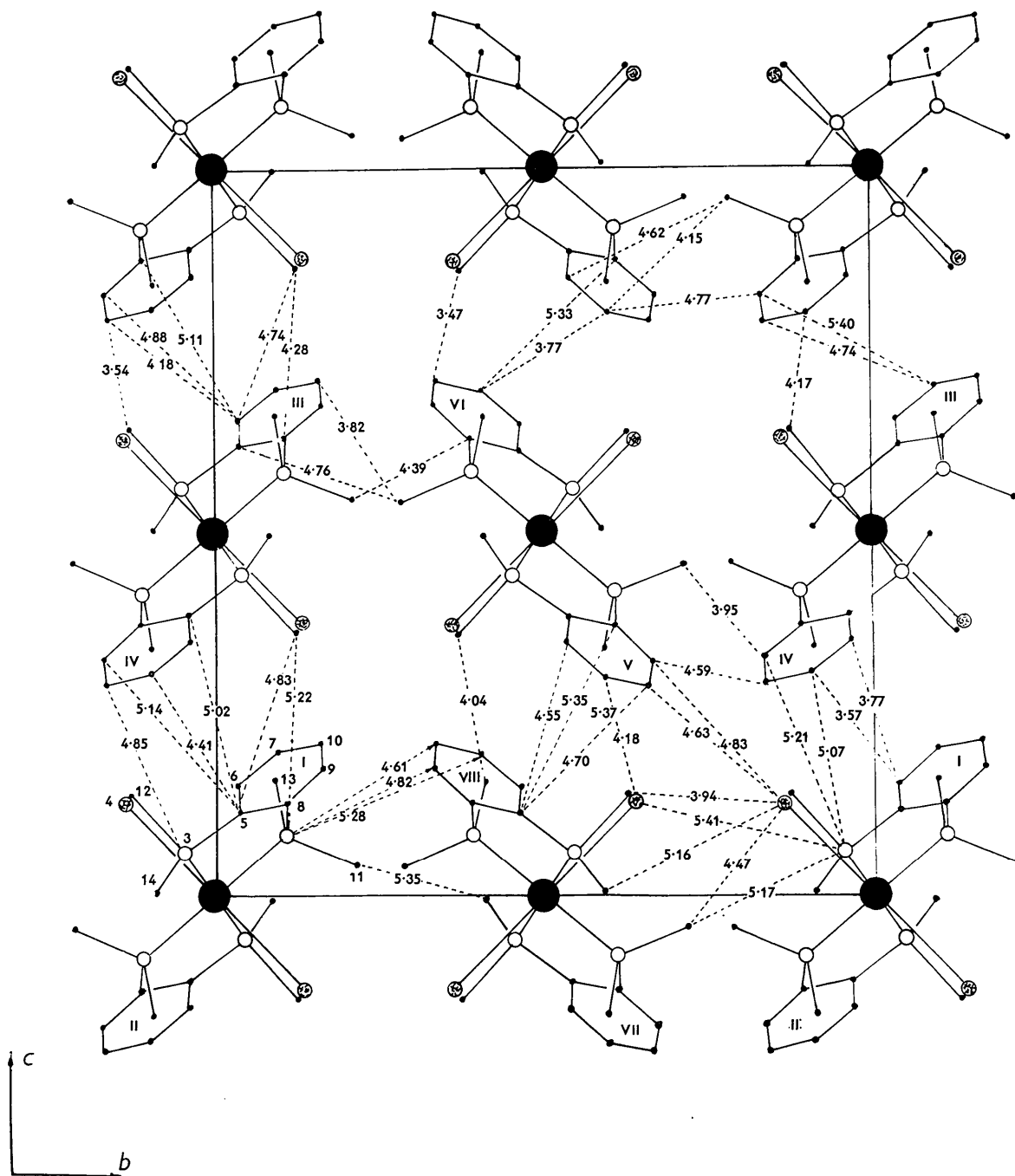| Distances A–B					Angles A–B–C				
A	B	d (A–B)	σ(d(A–B))		A	B	C	(A–B–C)	σ(A–B–C)
Pt(1)–Cl(4)		4·162	0·011		(4)	(1)	(2)	97·7°	0·2
Pt(1)–As(2)		2·378	0·004		(4)	(1)	(3)	96·4	0·2
Pt(1)–As(3)		2·372	0·004		(2)	(1)	(3)	84·2	0·1
As(2)–C(8)		1·88	0·03		(8)	(2)	(1)	109·0	0·9
	−C(11)	1·91	0·04		(8)	(2)	(13)	105·9	1·3
	−C(13)	2·04	0·04		(8)	(2)	(11)	102·3	1·3
As(3)–C(5)		1·87	0·02		(11)	(2)	(13)	105·1	1·5
	−C(12)	2·04	0·11		(11)	(2)	(1)	119·1	1·2
	−C(14)	1·87	0·03		(13)	(2)	(1)	114·1	1·2
		1·94	0·08						
					(2)	(8)	(5)	117	2
C(5)–C(6)		1·34	0·05		(8)	(5)	(3)	118	2
C(5)–C(8)		1·45	0·04		(5)	(3)	(1)	109	1
C(6)–C(7)		1·42	0·06		(5)	(3)	(14)	108	1
C(7)–C(10)		1·40	0·06		(5)	(3)	(12)	104	3
C(9)–C(10)		1·38	0·07		(12)	(3)	(1)	110	3
C(8)–C(9)		1·38	0·06		(12)	(3)	(14)	106	3
		1·38	0·03		(14)	(3)	(1)	119	1
					(5)	(8)	(9)	118	3
Cl(4)–C(11)		4·22	0·04		(8)	(9)	(10)	124	4
	−C(12)	4·16	0·11		(9)	(10)	(7)	119	4
	−C(13)	4·42	0·04		(10)	(7)	(6)	117	4
	−C(14)	4·48	0·03		(7)	(6)	(5)	125	4
		4·32	0·13		(6)	(5)	(8)	117	3

Fig. 2. Projection of the structure of dichlorodi-(o-phenylenebisdimethylarsine)platinum(II) on a plane normal to [100]. Small black circles: carbon. Large black circles: platinum. Open circles: arsenic. Hatched circles: chlorine. Atoms are numbered as in Tables 2, 3, and 4. Dashed lines represent intermolecular approach distances. Dashed lines ending in an arrowhead indicate that the distance is associated with the atom translated one unit in the a direction.

Molecule:

(i)	x, y, z	(ii)	$\bar{x}, \bar{y}, \bar{z}$	(iii)	$\bar{x}, y, \frac{1}{2}+z$	(iv) $x, \bar{y}, \frac{1}{2}-z$
(v)	$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$	(vi)	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$	(vii)	$\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$	(viii) $\frac{1}{2}+x, \frac{1}{2}-y, z$

atom and surrounding carbon atoms are generally greater than 4·3 Å. There are some Cl–C inter-molecular contacts as short as 3·94 Å. Such close packing may be the explanation for the small deviations of the chlorine atoms from precise octahedral positioning.

Table 6 lists selected intramolecular bond distances and angles. The standard deviations attached to individual distances and angles do not include the effects of correlation between variables. The Pt–As distance of $2·375 \pm 0·015$ Å (99% level) compares well with the Pt–As distance of 2·38 Å in the compound Pt(diarsine)$_2$I$_2$. This distance is appreciably shorter than the sum of the square covalent radius for platinum(II) and the tetrahedral covalent radius for arsenic $(1·31 + 1·18 = 1·49$ Å) (Pauling, 1948). The shortening is probably due to interaction between the less stable and unfilled ligand d orbitals and the filled metal d orbitals. If we suppose that the dative σ-bond is first formed, then this confers a positive charge on the ligand and a negative one on the metal. These respectively increase and decrease the exponents for the ultimate $d\pi$ and penultimate $d\pi$ orbitals on the two atoms. Consequently these two orbitals become more nearly matched, and overlap between them is improved. If a dative π-bond from metal to ligand is now formed the charges will be partly neutralized. This double bonding is thus responsible for an appreciable shortening of the Pt–As bond length from the normal single covalent bond distance.

The Pt–Cl bond can be considered to be electrostatic in nature. This bond distance $(4·16 \pm 0·03$ Å) exceeds the sum of the ionic radius of chlorine and the van der Waals' radius of divalent platinum $(1·81 + 2·07 = 3·88$ Å). The van der Waals' radius of the platinum atom is taken as one half of the separation distance of PtCl$_4$ ions (2·07 Å) in the compound K$_2$PtCl$_4$ (Theilacker, 1937). The chloride ion approaches the platinum–arsenic plane from a position of minimum electrostatic potential energy. It is cushioned on the four methyl groups C(11), C(12), C(13) and C(14), and the non-bonding approach distance to these atoms is in each case a little greater than the sum of the van der Waals' radii for a methyl group and a chlorine atom. The estimated mean standard deviation in the Pt–As–CH$_3$ angle is 1·2° so that the distortions from the normal tetrahedral angle are significant. There is a 'pushing aside' of these methyl groups as the negative charged chlroide ion is attracted towards the cation. However the resulting distortions

of tetrahedral configuration about the arsenic atoms are not as great as when the anion is an iodide ion (Stephenson, 1964), in which case the attractive force is somewhat greater than purely electrostatic in nature.

When due account has been taken of the anisotropic nature of the heavy atom vibrations the ring geometry is fairly well defined. The six aromatic bonds average 1·39 $(\sigma = 0·03)$ Å with no significant variations from this mean. The mean As–CH$_3$ bond distance is 1·94 $(\sigma = 0·08)$ Å and this agrees well with the distance of $1·98 \pm ·02$ Å reported for the compound As(CH$_3$)$_3$ (Sutton, 1958).

References

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

HARRIS, C. M., NYHOLM, R. S. & PHILLIPS, D.J. (1960). *J. Chem. Soc.* p. 4379.

MURRELL, J. N. (1961). *Quart. Rev. Chem. Soc., Lond.* **15**, 191.

McMULLAN, R. K. (1962). Private communication.

PAULING, L. (1948). *The Nature of the Chemical Bond* p. 179. Ithaca: Cornell Univ. Press.

SCHOMAKER, V., WASER, J., MARSCH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

SHAPIRO, P. (1962). Private communication.

SHIONO, R. (1961). I. U. Cr. *World List of Crystallographic Computer Programs.* Programs Nos. 330 and 376.

SHIONO, R. (1963). Technical Report No. 43, The Crystallography Laboratory, Univ. of Pittsburgh.

STEPHENSON, N. C. (1962). *J. Inorg. Nuclear Chem.* **24**, 791.

STEPHENSON, N. C. (1964). *Acta Cryst.* **17**, 592.

SUTTON, L. E. (1958). London: Chemical Society Special Publication No. 11.

TEMPLETON, D. H. (1962). *International Tables for X-ray Crystallography.* Vol. III. Section 3. 3. 2.

THEILACKER, W. (1937). *Z. anorg. Chem.* **234**, 161.

THOMAS, L. H. & FERMI, E. (1935). *Internationale Tabellen zur Bestimmung von Kristallstrukturen.* Berlin: Borntraeger.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.