

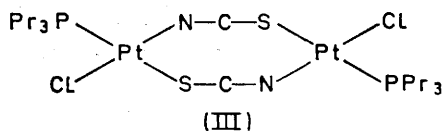
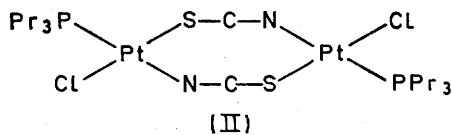
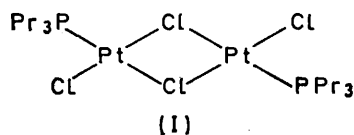
Molecular Structure of Dinuclear Complexes of Platinum(II). Part III.¹ Dichloro-bis- μ -ethanethiolato-bis(triethylphosphine)diplatinum(II)

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The title compound is orthorhombic, space group $Pbca$, $a = 20.02(1)$, $b = 21.73(1)$, $c = 15.72(1)$ Å, $Z = 4$. Least-squares refinement of X-ray diffractometer data using 2115 independent structure amplitudes converged with R 0.05.

The co-ordination round each platinum atom is strained square-planar, but the two co-ordination planes are not coplanar, having a dihedral angle of 130° between them. This conformation is partly attributed to severe steric repulsion between the alkyl groups on the phosphorus and on the sulphur atoms. The non-planarity of the (Pt_2S_2) bridge and the pyramidal configuration at the sulphur atoms are unfavourable to $d_{\pi}-p_{\pi}$ aromatic bonding in the bridge while allowing $d_{\pi}-d_{\pi}$ overlap. The Pt-S bonds *trans* to P have approximately normal lengths for single bonds [2.37(1) Å], whilst those *cis* to P and *trans* to Cl are much shorter [2.27(1) Å]; the Pt-P bonds are also short [2.26(1) Å]. The stability of the *cis*-isomer is attributed to the continuous zig-zag chain of strong *cis*-bonds P-Pt-S-Pt-P in which one of the bridging sulphur atoms is held by two strong bonds; the *trans*-isomer is inherently less stable because one Pt-S bond to each bridging sulphur atom will be weakened by the *trans*-influence of the phosphines. The bonds in the zig-zag chain in the *cis*-isomer all have appreciable π -character, and a multiple overlap of d_{π} orbitals resembling conjugation may be present.

DINUCLEAR complexes of Pt^{II} usually have the *trans*-configuration, and the eight principal atoms (two Pt^{II} , two bridging, and four terminal ligand atoms) are coplanar. The structures of three examples of *trans* complexes, (I)—(III) have been described in detail in earlier papers in this series;^{1,2} their *cis*-isomers are unknown. The trimethylarsine analogue of (I) is also *trans*.³

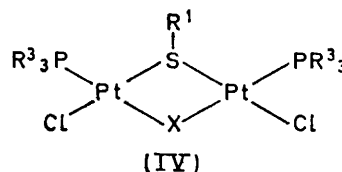


Exceptions to the general rule that the *trans* configuration is preferred have been found⁴⁻⁶ when thiol

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¹ Part II, J. A. J. Jarvis, B. T. Kilbourn, P. G. Owston, and Ursula A. Raeburn, *J. Chem. Soc. (A)*, 1970, 2770.

radicals act as bridging groups, e.g. (IV; X = Cl, Br, etc; R¹ = alkyl or aryl) and (IV; X = SR²; R¹ and R² = alkyl). Those complexes have high dipole



moments ($>10D$), and are stable in the *cis*-configuration in spite of the high electrostatic stress indicated by the dipole moment; their *trans*-isomers are labile and difficult to isolate in a pure state. Surprisingly, however, the stable form of the complex (IV; X = SR², R¹ and R² = aryl) is *trans*, whilst that of (IV; X = SR², R² = aryl, R¹ = alkyl) is *cis*. These observations led Chatt and Hart⁶ to suggest that there might be some special property in the thiol bridge, perhaps involving $d_{\pi}-d_{\pi}$ bonding and the p -orbitals of the sulphur atoms; this might make the bridge an 'inorganic aromatic ring', which could account for *cis*-directing effects in substitution and formation reactions, and also for the differing effects of conjugated aryl groups and non-conjugating alkyl groups in the thiol radical. To

² Part I, M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, 1969, B, 25, 1760.

³ S. F. Watkins, *J. Chem. Soc. (A)*, 1970, 168.

⁴ J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1953, 2363.

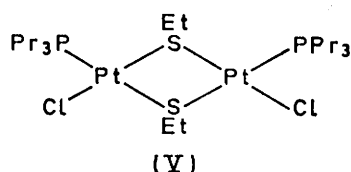
⁵ J. Chatt and F. A. Hart, *Nature*, 1952, 169, 673.

⁶ J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 2807.

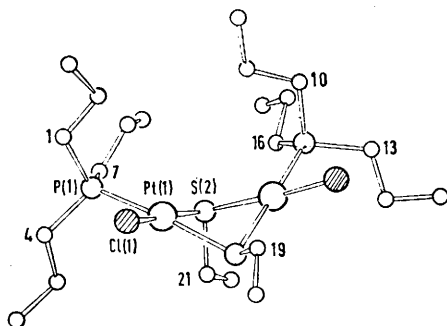
investigate the question further, we have determined the structure of the *cis*-complex (V); we were unable to prepare satisfactory crystals of the *trans*-isomer, which readily converts to a mixture of the *cis* and *trans* forms on attempted recrystallisation.

Molecular structure.—The structure of the molecule is shown in the Figure and the principal molecular dimensions are listed in Table 1.

(i) **Molecular conformation.** The co-ordination round each platinum atom is approximately square-planar, and



the molecule has the predicted *cis*-configuration. Unexpectedly, however, the central {PtS₂Pt} bridge is not planar, the dihedral angle between the two platinum



The molecular structure. For clarity, the heavy atoms have been labelled in only one half of the molecule, and only the α -carbon atoms have been numbered

co-ordination planes being 130°. This appears to be the first example of a non-planar bridge in dinuclear Pt^{II} complexes, though examples are known amongst Pd^{II} and Ni^{II} complexes, e.g. in {Pd(SPr)₂}₂,⁷ {Pd(SC₂H₄OH)₂}₂,⁸ {Ni(SC₂H₄OH)₂}₂,⁸ and {Ni(SET)₂}₂,⁹ where the dihedral angle is constrained to be 120° by the cyclic hexameric structure, and in {PdCl(CH₃·CH₂·CH₂·CH₂·CH₂·CH₃)₂} and {PdBr(C₇H₁₁)₂}, where the angles^{10,11} are 150 and 139° respectively.

The lack of planarity in the {PtS₂Pt} bridge can be attributed, at least partly, to intramolecular crowding between the alkyl groups on the two phosphorus atoms and on S(2), as shown by several short non-bonding distances (3.0–3.2 Å) between carbon atoms. The crowding is minimised by the adoption of the axial position (relative to the mean plane through the Pt, S, Cl, and P atoms) by the ethyl group on S(2), rather than the equatorial position which is adopted on S(1); in

⁷ N. R. Kunchur, *Acta Cryst.*, 1968, B, **24**, 1623.

⁸ R. O. Gould and M. M. Harding, *J. Chem. Soc. (A)*, 1970, 875.

⁹ P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, 1965, **87**, 5251.

¹⁰ G. R. Davies, R. H. B. Mais, S. O'Brien, and P. G. Owston, *Chem. Comm.*, 1967, 1151.

{Ni(SC₂H₄OH)₂}₂ also, half the hydroxyethyl groups are axial and half equatorial.⁸ The crowding is also reduced by increasing the two P–Pt–S(2) angles to 96°, rather than the usual 90°. The bond angles in the central ring

TABLE 1

Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses			
Pt(1)–P(1)	2.267(7)	S(1)–C(19)	1.89(2)
Pt(2)–P(2)	2.257(7)	S(2)–C(21)	1.86(2)
Pt(1)–Cl(1)	2.339(6)	C(1)–C(2)	1.53(3)
Pt(2)–Cl(2)	2.338(6)	C(4)–C(5)	1.54(3)
		C(7)–C(8)	1.56(3)
Pt(1)–S(1)	2.378(6)	C(10)–C(11)	1.51(3)
Pt(2)–S(1)	2.363(5)	C(13)–C(14)	1.55(4)
		C(16)–C(17)	1.58(3)
Pt(1)–S(2)	2.281(6)	Mean	1.55
Pt(2)–S(2)	2.267(6)		
		C(2)–C(3)	1.54(4)
P(1)–C(1)	1.86(2)	C(5)–C(6)	1.55(3)
P(1)–C(4)	1.85(2)	C(8)–C(9)	1.53(4)
P(1)–C(7)	1.88(2)	C(11)–C(12)	1.55(3)
P(2)–C(10)	1.83(2)	C(14)–C(15)	1.53(4)
P(2)–C(13)	1.87(2)	C(17)–C(18)	1.56(4)
P(2)–C(16)	1.85(2)	Mean	1.54
Mean	1.86		
		C(19)–C(20)	1.47(3)
		C(21)–C(22)	1.55(3)
Pt(1)–S(1)–Pt(2)	85.1(2)	Pt(1)–P(1)–C(1)	116.6(8)
Pt(1)–S(2)–Pt(2)	89.7(2)	Pt(1)–P(1)–C(4)	109.2(9)
		Pt(1)–P(1)–C(7)	116.2(8)
P(1)–Pt(1)–S(2)	96.3(2)	Pt(2)–P(2)–C(10)	111.0(8)
P(2)–Pt(2)–S(2)	95.9(2)	Pt(2)–P(2)–C(13)	114.1(8)
		Pt(2)–P(2)–C(16)	115.0(8)
		Mean	113.7
P(1)–Pt(1)–S(1)	173.2(2)		
P(2)–Pt(2)–S(1)	176.6(2)	P(1)–C(1)–C(2)	116.8(19)
		P(1)–C(4)–C(5)	113.4(16)
Cl(1)–Pt(1)–S(1)	95.2(3)	P(1)–C(7)–C(8)	111.7(17)
Cl(2)–Pt(2)–S(1)	94.8(2)	P(2)–C(10)–C(11)	111.1(17)
		P(2)–C(13)–C(14)	112.8(21)
Cl(1)–Pt(1)–S(2)	172.7(3)	P(2)–C(16)–C(17)	112.1(21)
Cl(2)–Pt(2)–S(2)	172.1(2)	Mean	112.8
S(1)–Pt(1)–S(2)	79.9(2)	C(1)–P(1)–C(4)	101.8(11)
S(1)–Pt(2)–S(2)	80.5(2)	C(1)–P(1)–C(7)	107.4(12)
		C(4)–P(1)–C(7)	104.0(11)
P(1)–Pt(1)–Cl(1)	89.1(3)	C(10)–P(2)–C(13)	102.9(13)
P(2)–Pt(2)–Cl(2)	88.8(2)	C(10)–P(2)–C(16)	106.4(11)
		C(13)–P(2)–C(16)	106.6(12)
Pt(1)–S(1)–C(19)	111.6(10)	Mean	104.9
Pt(2)–S(1)–C(19)	110.2(8)		
Pt(1)–S(2)–C(21)	104.4(7)	C(1)–C(2)–C(3)	107.5(28)
Pt(2)–S(2)–C(21)	108.3(8)	C(4)–C(5)–C(6)	108.2(22)
		C(7)–C(8)–C(9)	107.0(22)
S(1)–C(19)–C(20)	108.2(19)	C(10)–C(11)–C(12)	112.0(23)
S(2)–C(21)–C(22)	108.5(16)	C(13)–C(14)–C(15)	104.8(29)
		C(16)–C(17)–C(18)	109.1(22)
		Mean	108.1

are all smaller than expected, especially the S–Pt–S angles (80 and 81°) which give further indication of strain. Angles at bridging sulphur atoms appear to vary so widely that no firm conclusions can be drawn; values have been reported varying from 98° in {Pt₂Br₄(SMc₂)₂}¹² and {(π-C₅H₅)₂Mo(SBu)₂FeCl₂}¹³ 92° in

¹¹ B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *Chem. Comm.*, 1968, 1438.

¹² D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc. (A)*, 1968, 1852.

¹³ T. S. Cameron and C. K. Prout, *Chem. Comm.*, 1971, 161.

$[\text{Pd}_2(\text{SPh})_4(\text{PPh}_3)_2]^{14}$ and $[\text{Cd}\{\text{SC}(\text{NH}_2)\}_2(\text{HCO}_2)_2]^{15}$ 83° in $\{\text{Ni}(\text{SEt})_2\}_6$, $\{\text{Ni}(\text{SC}_2\text{H}_4\text{OH})_2\}_6$, and $\{\text{Pd}(\text{SC}_3\text{H}_7)_2\}_6$, 83° and 81° in $[(\text{C}_5\text{H}_5)_2\text{Ti}(\text{SMe})_2\text{Mo}(\text{CO})_4]^{16}$ 81 and 80° in the present compound, and 79° in $[\text{Cr}_2(\text{SPh})_2(\pi\text{-C}_5\text{H}_5)_2(\text{NO})_2]^{17}$

In each phosphine ligand, one propyl group has its α -carbon atom approximately in the platinum co-ordination plane, and as far as possible from the chlorine atom. This conformation is also found in (I)—(III), and is evidently very stable.

(ii) *Bond lengths.* The bond-lengths involving Pt^{II} are listed in Table 2 together with those from the other determinations in this series; in all cases σ is $< 0.01 \text{ \AA}$. The *trans*-weakening effects of the ligands are in the usual order, $\text{P} \gg \text{S} > \text{N} \sim \text{Cl}$, and these effects are discussed in more detail elsewhere.¹⁸

The Pt-P bonds are much shorter than the radius sum, as is usual in complexes of Pt^{II} . The Pt-S(2) bonds are considerably shorter than those in (II) and (III), presumably because they have more π -bond character.

TABLE 2
Bond lengths in dinuclear Pt^{II} complexes

Bond	<i>trans</i> -group					Radius sum
	Cl	NCS	SCN	SR	PR_3	
Pt-Cl *	2.28	2.28	2.31	2.34	2.43	2.31
Pt-NCS	1.97				2.07	1.96
Pt-SCN	2.33				2.41	2.36
Pt-SR	2.27				2.37	2.36
Pt- PR_3	2.23	2.24	2.26	2.26		2.42

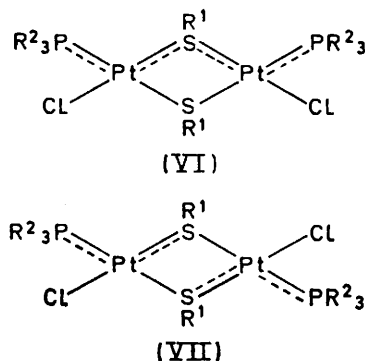
* These values are for terminal Pt-Cl bonds only.

Very short Pt-S bonds occur in other sulphur-bridged complexes, e.g. 2.21 and 2.25 \AA in $\{\text{Pt}_2\text{Br}_4(\text{SEt}_2)_2\}^{12}$ and 2.22 and 2.23 \AA in $[\text{Pt}_2\text{S}(\text{PPh}_3)_3(\text{CO})]^{19}$. The Pt-S(1) bonds, *trans* to phosphine, are much longer and have approximately the lengths expected for single bonds.

(iii) *Stability of the complex.* Though the Pt-S(2) bonds appear to have some π -character, the central $\{\text{Pt}_2\text{S}_2\}$ ring does not have the properties expected of an 'aromatic inorganic ring' involving p orbitals. It is not planar, and the four Pt-S bonds are neither equal nor alternating. The co-ordination round sulphur is pyramidal rather than planar, and therefore does not favour the formation of a $p_\pi\text{-}d_\pi$ delocalised π -system in the ring.

The principal feature of the bonding is the chain of short and presumably strong bonds, P-Pt-S(2)-Pt-P. The structure can be represented as (VI) which indicates how the second bridging ligand S(1) is held by two bonds, both of which are *trans* to phosphine and therefore relatively weak. This second ligand can readily be exchanged (e.g. for Cl, Br, etc.) without affecting the stability of the chain. This type of structure can occur only when one of the bridging ligands can form two strong bonds to the metal atoms, and when the *cis*-

conformation is adopted. The thiolate ligand can form two strong bonds, and in the *cis*-complex (VI) one of them does so. In the less stable *trans*-complex (VII) one bond from each sulphur is weakened by the *trans*-influence of the phosphines, so that the two metal centres are held together less strongly, and dissociation occurs



more readily than in the *cis*-form (VI). Chlorine, whose bonds to Pt^{II} have little or no π -character,² can form only two normal bonds, and thiocyanate can form one strong and one normal bond to platinum. Complexes (I)—(III) cannot therefore show this special effect, and thus adopt the normal *trans*-configuration.

Chatt and Hart⁶ have earlier concluded, on the basis of dipole-moment measurements, that the thiolate group S(2), *cis* to the phosphines, is firmly bound, whilst the *trans*-group S(1) is readily replaceable by other ligands; our results show the structural reasons for this difference.

As pointed out, the pyramidal co-ordination at the sulphur atoms precludes $p_\pi\text{-}d_\pi$ overlap, and the π character of the bonds of the P-Pt-S(2)-Pt-P chain must arise from $d_\pi\text{-}d_\pi$ overlap. It is probably significant that, if we regard S(2) as approximately tetrahedrally co-ordinated with the lone-pair 'E' as the fourth 'virtual ligand', then: (a) E, S(2), Pt(1), P(1), and C(7) are nearly coplanar, and (b) E, S(2), Pt(2), P(2), and C(16) are also nearly coplanar.

This geometrical arrangement is favourable to a 'multiple overlap' of π -bonding orbitals which can give the chain of short bonds some of the characteristics of a conjugated chain.¹⁸ We cannot at this stage assess quantitatively the stabilising effect of this conjugation. It may be that the steric factors and the strong π -bonding are sufficient to stabilise the *cis*-isomer and the non-planar conformation, and that conjugation is a minor effect which can occur only when the geometrical arrangement is already determined by these factors. The fact that the *trans*-isomer can be isolated though not in a pure form, indicates that the *cis*-isomer is only slightly more stable than the *trans*, and that all these possible stabilising factors must be small in magnitude.

¹⁴ R. H. Fenn and G. R. Segrott, *J. Chem. Soc. (A)*, 1970, 3197.

¹⁵ M. Nardelli, G. F. Gasparri, and P. Boldini, *Acta Cryst.*, 1965, **18**, 618.

¹⁶ G. R. Davies and B. T. Kilbourn, *J. Chem. Soc. (A)*, 1971, 87.

¹⁷ A. T. McPhail and G. A. Sim, *J. Chem. Soc. (A)*, 1968, 1853.

¹⁸ P. G. Owston, to be published.

¹⁹ A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. (A)*, 1969, 2772.

TABLE 3
Atomic and thermal parameters *

	$10^5x/a$	$10^5y/b$	$10^5z/c$	10^4U_{11}	10^42U_{12}	10^42U_{13}	10^4U_{22}	10^42U_{23}	10^4U_{33}
Pt(1)	19250(6)	8674(4)	27497(5)	1071(7)	-33(12)	-235(14)	547(5)	-31(9)	736(6)
Pt(2)	30410(5)	-1632(4)	24170(5)	824(6)	-167(11)	32(13)	613(5)	79(9)	671(5)
	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U_{11}	10^32U_{12}	10^32U_{13}	10^3U_{22}	10^32U_{23}	10^3U_{33}
Cl(1)	1634(4)	1694(3)	1871(5)	194(9)	24(10)	-82(12)	67(41)	42(8)	140(6)
Cl(2)	1271(4)	4743(3)	1223(4)	123(6)	23(8)	-67(9)	87(45)	2(8)	104(5)
P(1)	850(4)	816(3)	3196(4)	91(5)	22(9)	-30(8)	88(48)	-24(8)	88(5)
P(2)	2054(3)	3802(3)	2444(4)	95(5)	6(7)	-25(9)	62(32)	9(7)	92(4)
S(1)	3088(3)	923(2)	2455(3)	99(4)	-50(7)	3(9)	66(32)	0(7)	83(4)
S(2)	2712(3)	5017(3)	3465(4)	104(5)	-1(7)	-1(7)	57(35)	12(6)	70(4)
C(1)	198(12)	825(12)	2358(15)	85(16)	75(34)	-47(30)	168(27)	-42(38)	99(19)
C(2)	325(9)	428(15)	1570(20)	216(38)	65(56)	-50(50)	155(29)	-92(42)	126(25)
C(3)	4814(20)	620(24)	4113(21)	195(38)	22(89)	198(55)	426(64)	-69(68)	117(28)
C(4)	647(13)	1519(11)	3804(14)	121(22)	61(32)	-21(30)	91(17)	-27(27)	82(16)
C(5)	1094(13)	1613(11)	4591(14)	119(23)	-9(34)	-29(31)	98(19)	-43(28)	81(16)
C(6)	907(18)	2237(10)	5005(16)	255(37)	1(39)	-23(46)	66(15)	-17(29)	93(19)
C(7)	642(12)	172(10)	3948(15)	98(20)	-18(30)	17(30)	73(15)	13(30)	119(19)
C(8)	4370(13)	4535(12)	3485(18)	111(22)	18(34)	-8(36)	86(18)	-71(35)	143(24)
C(9)	4377(16)	4040(12)	4176(20)	183(34)	35(44)	-21(47)	93(20)	57(38)	157(27)
C(10)	2529(15)	3525(12)	1529(14)	130(22)	43(33)	58(34)	80(18)	-12(28)	93(17)
C(11)	3228(12)	3787(12)	1548(14)	83(20)	78(34)	66(29)	136(20)	-9(30)	93(17)
C(12)	3647(18)	3576(13)	769(17)	215(35)	75(49)	41(46)	121(25)	62(37)	109(22)
C(13)	1242(12)	3385(11)	2337(19)	82(16)	-65(29)	-86(38)	99(17)	70(37)	168(26)
C(14)	752(16)	3527(14)	3075(21)	131(26)	25(43)	84(47)	139(25)	100(45)	184(30)
C(15)	126(13)	3147(16)	2872(28)	57(17)	-48(39)	-25(53)	200(33)	223(71)	345(54)
C(16)	2471(14)	3487(11)	3398(13)	149(23)	50(33)	-74(34)	75(17)	31(27)	84(16)
C(17)	2583(15)	2767(11)	3333(18)	162(28)	30(37)	-22(45)	74(18)	8(33)	137(25)
C(18)	2922(17)	2536(12)	4163(20)	230(35)	29(47)	-205(57)	65(15)	75(38)	193(30)
C(19)	3253(15)	1237(11)	1356(15)	203(33)	-11(40)	64(40)	74(17)	51(29)	103(18)
C(20)	3654(17)	1803(13)	1442(19)	181(31)	-112(44)	57(47)	115(23)	115(39)	148(25)
C(21)	2740(11)	331(10)	4399(13)	100(19)	16(29)	-53(25)	97(19)	-18(25)	60(14)
C(22)	1897(18)	4795(12)	4851(16)	233(42)	-39(51)	148(50)	101(20)	31(33)	113(21)

* In the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + U_{22}h^2b^{*2} + 2U_{23}hkb^*c^* + U_{33}h^2c^{*2})]$.

These results suggest no definite reason why the compounds (IV; X = SR², R¹ and R² = aryl) should normally be *trans*, and this point requires further clarification.

EXPERIMENTAL

Crystal Data.—C₂₂H₅₂Cl₂Pt₂P₂S₂, $M = 904.1$, Orthorhombic, $a = 20.024 \pm 0.010$, $b = 21.726 \pm 0.009$, $c = 15.720 \pm 0.008$ Å, $U = 6838.5$ Å³, D_m (by flotation) = 1.758; $Z = 4$, $D_c = 1.758$, $F(000) = 1744$. Space group $Pbca$ (D_{2h}^{15} No. 61). Zirconium-filtered Mo- $K\alpha$ radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K\alpha) = 97.5$ cm⁻¹.

All measurements were made on a Picker single-crystal four-circle diffractometer equipped with a scintillation counter and a pulse-height analyser. The orientation and cell dimensions, with their estimated standard deviations, were obtained by least-squares fit of χ , ϕ , ω , 2θ values²⁰ for 12 independent planes. The θ — 2θ scan method was used for data collection scanning from 0.5° below α_1 to 0.4° above α_2 , at 1.0° 2 θ min⁻¹. The background was measured for 20 s at each end of the scan. Every 8 h the intensities of the 006 and the 800 reflections were measured; over the 23 days of data collection their intensities varied by only $\pm 3\%$.

Intensities were measured for 3325 reflections in the octant $[hkl]$ with $\sin \theta/\lambda \leq 0.5$. These were corrected for Lorentz and polarisation factors, and for absorption by use of the method of Busing and Levy modified to give a more even sample point distribution.²¹ The crystal dimensions were 0.24 × 0.29 × 0.32 mm and 558 sample points were used whose mean separation was 30 μ . By averaging struc-

ture amplitudes from equivalent observed reflections, structure amplitudes for 2115 independent reflections were obtained. The observed intensities of a further 810 independent reflections were less than their statistical standard deviations and these were omitted from the analysis.

TABLE 4

Analysis of agreement of observed and calculated structure factors

Range	N^*	$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta F $	Mean $w \Delta F ^2$	R (%)
		$ F_o $				
0—49	473	18686	17176	3882	30.0	20.8
50—99	708	50908	50440	3625	15.6	7.1
100—149	388	47015	47142	1836	20.2	3.9
150—199	222	38377	38213	1047	29.3	2.7
200—249	111	24691	24663	510	34.4	2.1
250—299	56	15317	15330	289	37.7	1.9
300—399	73	24946	25042	676	69.7	2.7
400—499	45	20209	20483	620	96.3	3.0
600—	39	25465	26428	1168	96.5	4.5
		$\sin \theta/\lambda$				
0—0.09	26	9851	10730	1054	322.2	10.7
0.10—0.19	188	39383	39228	1688	54.7	4.3
0.20—0.29	468	77111	46718	2623	20.9	3.4
0.30—0.39	781	87607	87201	3922	17.2	4.5
0.40—0.49	652	51463	50941	4367	25.8	8.5

* N is no. in ranges.

Structure Determination.—The positions of the platinum atoms were found from a three-dimensional Patterson synthesis. The independent positional and isotropic thermal parameters of these atoms, and the scale factor, were adjusted by 3 cycles of least-squares refinement, which reduced R to 0.407. Difference syntheses then revealed the positions of all the other atoms except hydrogen. After 8

²⁰ W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

²¹ R. H. B. Mais, P. G. Owston, and Ailsa M. Wood, *Acta Cryst.*, 1972, **B28**, 393.

cycles of least-squares refinement of the positional and anisotropic thermal parameters, R was 0.051. The convergence factor for the last cycle was 0.103 {the convergence factor is $[(\sum wd^2)_{n-1} - (\sum wd^2)_n]/[(\sum wd^2)_{n-1}]$ where n is the cycle number, w = weight of the observation, and $d = |\Delta F|$ }. The platinum atoms were refined in one matrix block that included both positional and anisotropic thermal parameters. The remaining atoms were refined using five matrix blocks for the positional co-ordinates, and one block-diagonal matrix for their thermal parameters. The

* For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

** D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

weighting scheme used was $[1/w = 1 + (F_o - b)^2/a^2]$ where $a = 104$ and $b = 226$.

The atomic form factors used were taken from ref. 22 with a correction for anomalous dispersion for Pt.

The final atomic parameters are listed in Table 3, and an analysis of the agreement between observed and calculated structure factors is given in Table 4. The observed and calculated structure factors are listed in Supplementary Publication No. SUP 20380 (24 pp., 1 microfiche).*

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