

## The Crystal and Molecular Structure of Zeise's Salt, KPtCl<sub>3</sub>·C<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O

BY M. BLACK, R. H. B. MAIS AND P. G. OWSTON

I.C.I. Ltd., Petrochemical & Polymer Laboratory, P. O. Box 11, The Heath, Runcorn, Cheshire, England

(Received 3 July 1968 and in revised form 31 December 1968)

Zeise's salt K[PtCl<sub>3</sub>·C<sub>2</sub>H<sub>4</sub>].H<sub>2</sub>O forms monoclinic crystals,  $a=10.750 \pm 0.006$ ,  $b=8.405 \pm 0.003$ ,  $c=4.836 \pm 0.002$  Å,  $\beta=97.73 \pm 0.06^\circ$ , space group  $P2_1$ , with two formula units in the unit cell. A three-dimensional refinement of the structure has been carried out, with counter diffractometer data, leading to a final  $R$  value of 0.039 for 994 non-zero reflexions.

The ethylene molecule forms an approximately symmetrical  $\pi$ -type bond with the platinum atom. The C=C bond length [1.44(3) Å] shows the bond order to be reduced from 2, in free ethylene, to about  $1\frac{1}{2}$  on complexing. After correction for thermal vibration the Pt-Cl bond *trans* to ethylene [2.340(3) Å] has the same length as one of the *cis* Pt-Cl bonds [2.34(1) Å], though both are longer than Pt-Cl in K<sub>2</sub>PtCl<sub>4</sub>, [2.310(2) Å]. The other *cis*-Pt-Cl bond [2.29(1) Å] is substantially shorter. There is therefore no clear evidence for the existence of a static *trans*-effect in this compound. The inter-ionic forces in the crystal produce bond-length changes comparable with those caused by any *trans*-influence that may exist. The molecules are linked into infinite two-dimensional layers by chains of strong O-H...Cl hydrogen bonds (O-Cl=2.97 Å) parallel to *c*, ionic O-K<sup>+</sup>-O chains (O-K<sup>+</sup>=2.79 Å) parallel to *b*, and ionic forces between potassium ions and chlorine atoms, (K<sup>+</sup>-Cl=3.14-3.82 Å). The ethylene groups form the two surfaces of each layer, and the only interactions between the layers are those between the ethylene groups. The same layer coordination is found in K(PtCl<sub>3</sub>NH<sub>3</sub>).H<sub>2</sub>O in which there are additional inter-layer N-H...Cl bonds.

Zeise's salt, K[PtCl<sub>3</sub>·C<sub>2</sub>H<sub>4</sub>].H<sub>2</sub>O, is the most extensively studied example of the class of olefin-metal  $\pi$ -complexes, which are probably intermediates in many catalytic reactions involving hydrocarbons. Its structure has previously been studied by two-dimensional methods (Mellor & Wunderlich, 1954, 1955; Bokii & Kukina, 1965) and we have now carried out a three-dimensional analysis to determine (a) the mode of bonding of the ethylene group, (b) the effect of the ethylene group on the strengths of the Pt-Cl bonds, especially the *trans*-bond, and (c) the role of the water molecule, which is essential to the stability of crystalline Zeise's salt.

### Molecular structure

#### Coordination round platinum

The structure (Fig. 1 and Table 1) is essentially that derived by Bokii & Kukina (1965), though with some

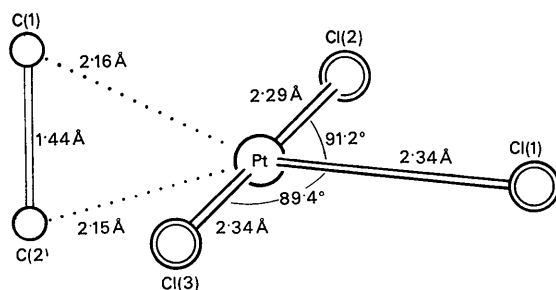


Fig. 1. Bond lengths and bond angles in the complex ion [PtCl<sub>3</sub>C<sub>2</sub>H<sub>4</sub>]<sup>-</sup>.

differences in detail. The coordination round the platinum atom is essentially square planar. The deviations from the coordination plane (*i. e.* the best plane through the platinum and three chlorine atoms) are Pt, +0.002; Cl(1), 0.000; Cl(2), -0.015; Cl(3), +0.005; centre of C-C bond, -0.15 Å. The ethylene group is bound by a  $\pi$ -type bond to the platinum atom, with the C-C bond approximately perpendicular to the coordination plane. The deviations from ideal symmetry are small, though significant: the C-C bond is inclined at  $86^\circ$  to the coordination plane instead of  $90^\circ$ , and its mid-point is 0.15 Å below the plane; in addition, C(1) is displaced from the plane perpendicular to the coordination plane and passing through Pt and Cl(1), by 0.12 Å. The Pt-C distances are effectively equal, 2.15(2) Å, and are rather longer than 2.08 Å, the distance predicted for a single Pt-C  $\sigma$ -bond. The C-C bond-length shows that coordination to the metal atom reduces the bond-order in ethylene from 2 in the uncoordinated molecule to about  $1\frac{1}{2}$  in this complex. Similar results were obtained in the substituted acetylene complex [PtCl<sub>2</sub>(Bu<sup>t</sup>C≡CBu<sup>t</sup>)(*p*-toluidine)] (Davies, Hewertson, Mais & Owston, 1967), where coordination reduces the C-C bond order by about  $\frac{1}{2}$ , and the Pt-C bond [2.19(2) Å] is also longer than expected for a single bond. These results differ from those of Baenziger, Doyle & Richards (1965) who found the C-C distance in the double bonds of norbornadiene palladium chloride to be barely significantly longer than in the uncomplexed olefin. It may be that olefins bond more strongly to platinum than to palladium.

Both Mellor & Wunderlich (1954, 1955) and Bokii & Kukina (1965) reported that the Pt-Cl bond *trans*

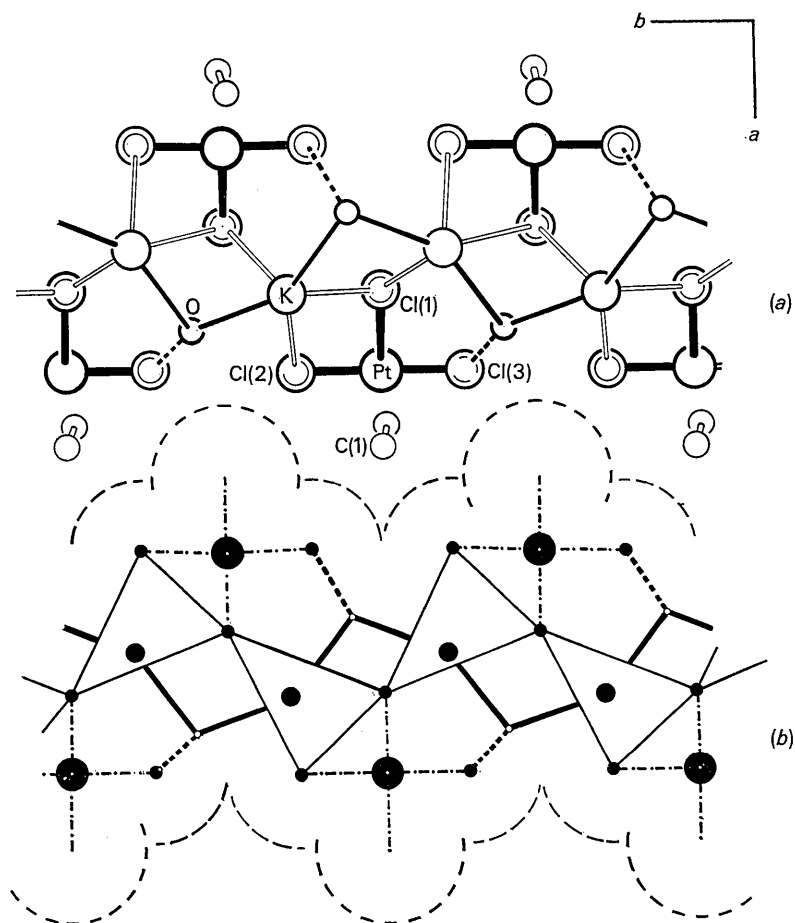
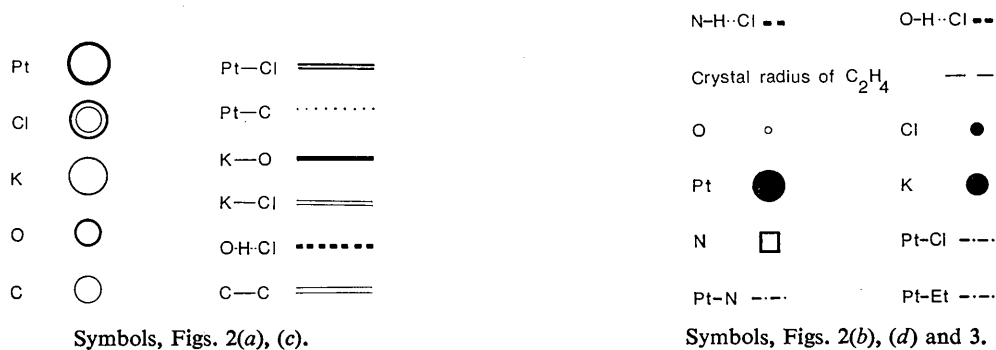


Fig. 2. The structure of Zeise's salt projected onto the  $ab$  plane, showing a cross-section through two layers, each bounded above and below by ethylene molecules. (a) In the upper layers, bonding and  $\text{K}^+-\text{Cl}$ ,  $\text{O}-\text{Cl}$ ,  $\text{O}-\text{K}^+$  coordination are shown. (b) In the lower layers, drawn in skeletal form, the triangular prismatic coordination of chlorine atoms round each potassium ion, and the chains of  $\text{O}-\text{K}^+-\text{O}$  which pass between the layers of chlorine atoms, are emphasised. Carbon atoms are not shown, but the effective boundaries of the lower layer are indicated by dashed lines representing the crystal radii of the  $\text{CH}_2=$  groups and the chlorine atoms concerned.



Symbols, Figs. 2(a), (c).

Symbols, Figs. 2(b), (d) and 3.

to ethylene is markedly longer than usual, and suggested that this was evidence for a *trans*-bond weakening effect. We find a much smaller effect, though the *trans*-bond Pt-Cl(1) is still significantly longer than in  $\text{K}_2\text{PtCl}_4$  [2.310(2) Å (Mais, Owston & Wood, 1968)]. Of the *cis* bonds, Pt-Cl(2) is significantly shorter than usu-

al, while Pt-Cl(3) is normal. However, on correcting the Pt-Cl bond lengths for thermal motion, the *trans*-Pt-Cl bond length no longer differs significantly from that of *cis*-Pt-Cl(3). As the chlorine atoms are much lighter than platinum, they were considered as 'riding' on the platinum atoms, and the corrections were cal-

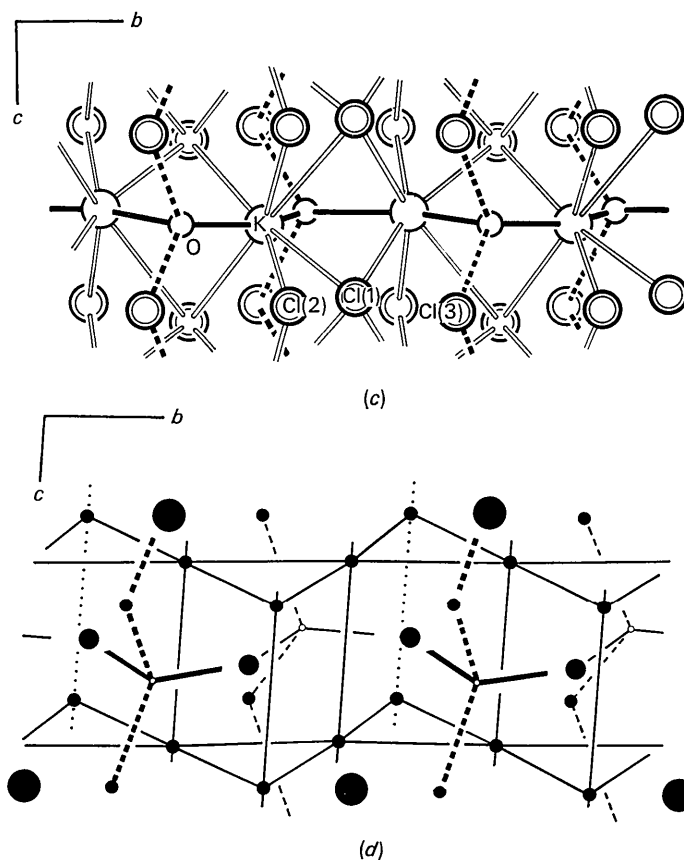


Fig. 2 (cont.). (c) Projection onto the surface of a layer, *i.e.* approximately onto the *bc* plane, using the same symbols as for (a). The ethylene molecules, Pt atoms, and the Pt-Cl bonds are omitted for clarity. One of the O-K<sup>+</sup>-O chains which run through each layer, and a number of O-H...Cl chains (hydrogen atoms not indicated) running perpendicular to the O-K<sup>+</sup>-O chains are shown. The trigonal prismatic coordination of chlorine atoms round each potassium ion is indicated. (d) A diagrammatic representation of (c) using the same symbols as for (b), showing the chlorine coordination polyhedra, and the platinum atoms. The chains of O-K<sup>+</sup>-O are shown where they emerge from the coordination polyhedra. The O-H...Cl chains running parallel to the axes of the triangular prisms of coordinated chlorine atoms are also shown.

culated from a simple 'riding motion model' (Busing & Levy, 1964).

#### Intermolecular bonding

The differences in environment of the three chlorine atoms are considerable, and may be enough to explain these differences in bond-length; Cl(1) has 4 K<sup>+</sup> neighbours, one of them particularly close; Cl(3) is hydrogen-bonded to two water molecules; Cl(2) has two K<sup>+</sup> neighbours, both relatively distant, and the Cl(2)-Pt bond length is therefore affected less than the other Pt-Cl bonds by interionic forces. These complications prevent the accurate assessment of *trans* and *cis* effects in this molecule. If the *trans* weakening influence of the ethylene group is real, it must be similar in strength to the interionic forces in the structure.

As shown in Fig. 2(a), the crystal structure is essentially ionic, and the complex ions [PtCl<sub>3</sub>C<sub>2</sub>H<sub>4</sub>]<sup>-</sup> cannot be considered independently. They are arranged in infinite double layers, with ethylene groups on both

surfaces, and held together by three main types of interaction:

(i) there are columns of alternate potassium ions and triangles of chlorine atoms parallel to the *c* axis [Figs. 2(c)(d)];

(ii) there are chains of hydrogen bonds -O-H...Cl...H-O-H...Cl... which are also parallel to the *c* axis;

(iii) these two chains are cross-linked by the coordinate bonds within the complex ions and by the ionic interactions in chains of -O-K<sup>+</sup>-O-K<sup>+</sup>- which are parallel to the *b* axis and approximately perpendicular to the other two chains.

Exactly the same structure is found in K[PtCl<sub>3</sub>NH<sub>3</sub>].H<sub>2</sub>O (Jeanin & Russell, 1968), except that there the layers are firmly bound together by chains of inter-layer NH...Cl bonds (see Fig. 3), whereas in Zeise's salt the interactions between layers consist only of van der Waals forces between the ethylene groups. The layer unit [K.H<sub>2</sub>O.PtCl<sub>3</sub>]<sub>n</sub> evidently has high stability

mainly as a result of the chain of strong  $\text{O}-\text{H} \cdots \text{Cl}$  hydrogen bonds, and this explains why the water molecule is essential to the stability of the structure. Hydrogen bonds between water molecules and chloride ions in crystals usually have  $\text{O}-\text{Cl}$  distances between 3.05 and 3.2 Å (Fuller, 1959). Here, the  $\text{O}-\text{Cl}$  distance of 2.97 Å and the  $\text{Cl}-\text{O}-\text{Cl}$  and  $\text{O}-\text{Cl}-\text{O}$  angles which are very close to the tetrahedral value provide good evidence for the existence of strong hydrogen bonds, similar to those in  $\text{HCl} \cdot \text{H}_2\text{O}$ , where  $\text{O}-\text{Cl}=2.95$  Å (Carpenter & Yoon, 1959).

Each potassium atom is eight-coordinated [Fig. 2(c), (d)], with six chlorine atoms from four different complex ions forming a distorted trigonal prism whose axis is parallel to  $c$ , and two water molecules lying approximately along the perpendiculars to two of the prism faces. Three of the six  $\text{K}^+-\text{Cl}$  distances are appreciably longer than the normal interionic distance of  $\sim 3.2$  Å [cf. 3.24 Å in  $\text{K}_2\text{PtCl}_4$  (Mais, Owston & Wood, 1968)], the other three being within  $\pm 0.1$  Å of the normal. The  $\text{K}^+-\text{O}$  distances, 2.79 Å, are close to the sum of the ionic radii, 2.73 Å, suggesting that there is only normal ionic interaction between potassium and water; on the other hand the fact that each water molecule is approximately tetrahedrally bound to two potassium ions and

two chlorine atoms might indicate that rather stronger directional forces are operating.

### Experimental

#### Crystal data

Yellow prisms or needles,  $\text{C}_2\text{H}_4\text{KPtCl}_3\text{H}_2\text{O}$ ,  $M=386.8$ , monoclinic,  $a=10.750 \pm 0.006$ ,  $b=8.405 \pm 0.003$ ,  $c=4.836 \pm 0.002$  Å,  $\beta=97.73^\circ \pm 0.06^\circ$ ;  $V=435.1$  Å<sup>3</sup>,  $D_m$  (by flotation)=2.94 g.cm<sup>-3</sup>,  $Z=2$ ,  $D_c=2.952$  g.cm<sup>-3</sup>;  $F(000)=348$ ; space group  $P2_1$ ; Mo  $K\alpha$  radiation,  $\mu=197.9$  cm<sup>-1</sup>.

A crystal of approximate dimensions  $0.04 \times 0.06 \times 0.08$  mm was used. All measurements were made on a Picker Single Crystal Four Circle Diffractometer, equipped with a scintillation counter and pulse-height analyser. The orientation and cell dimensions with their estimated standard deviations were obtained by a least-squares fit of  $\chi$ ,  $\phi$ ,  $\omega$ ,  $2\theta$  values for 10 independent planes. In these calculations the cell was assumed to be triclinic and the angles  $\alpha=89.9(4)$ ,  $\gamma=89.97(2)$  were derived and were used instead of the true values ( $90^\circ$ ) in crystal orientation calculations. The  $\theta$ - $2\theta$  scan method was used, scanning from  $0.50^\circ$  below  $\alpha_1$ , to  $0.50^\circ$  above  $\alpha_2$  at  $0.25^\circ$   $2\theta/\text{min}$ . The background was

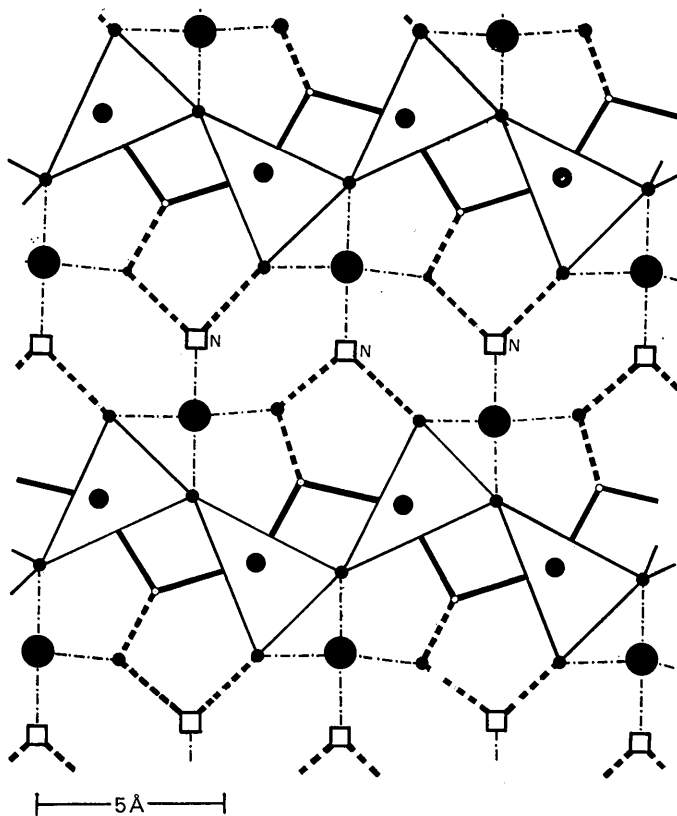


Fig. 3. The cross-section of a layer in the structure of  $\text{K}[\text{PtCl}_3] \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$  corresponding to Fig. 2(b) (drawn from parameters given by Jeannin & Russell, 1968). The central ionic 'core' of the layer,  $\{\text{K}[\text{PtCl}_3] \cdot \text{H}_2\text{O}\}_\infty$  is virtually identical with that in Zeise's salt.

measured for 20 sec at each end of the scan. Approximately every three hours the intensities of the 130 and 301 reflexions were measured, and over 14 days there was no systematic variation in the intensity of the 301 reflexion. The intensity of the 130 reflexion dropped by 4.5% of its original value, as a result of anisotropic deterioration of the crystal. A correction for deterioration was made by applying to each intensity measurement a scale factor depending on the moving average of the standard reflexion intensities.

Intensities were measured for 1278 reflexions in the quadrants  $hkl$ ,  $h\bar{k}l$ , with  $\sin \theta/\lambda \leq 0.70$ . Corrections to

the intensities were made for Lorentz and polarization factors. After rejecting 23 reflexions with discrepancies in background counts and 46 reflexions whose intensities were less than their statistical standard deviations, a correction was made to the remaining reflexions for absorption, by the method of Busing & Levy (1957), modified\* to give a more even sample-point distribution; 157 sample-points were used whose mean separation was 10 microns. By averaging the structure ampli-

\* Details of this variation on the Busing & Levy procedure are to be published elsewhere.

Table 1. *Bond lengths (Å) and angles (°) with estimated standard deviations*

The figures in parentheses represent the e.s.d. of the last significant digits.

Pt—Cl(1)	2.330 (4)	[2.331]*	[2.340]†	[2.405]‡
Pt—Cl(2)	2.251 (19)	[2.27]	[2.29]	[2.38]
Pt—Cl(3)	2.303 (20)	[2.31]	[2.34]	[2.43]
Pt—C(1)	2.157 (18)			
Pt—C(2)	2.149 (16)			
K—Cl(1)	3.146 (18)			
	3.289 (11)			
	3.331 (12)			
	3.817 (14)			
K—Cl(2)	3.574 (15)			
	3.336 (17)			
K—O	2.787 (20)			
	2.797 (25)			
O—Cl(3)	3.014 (26)			
	2.968 (22)			
C(1)—C(2)	1.44 (4)			
Cl(1)—Pt—Cl(2)	91.17 (6)		Cl(3)—O—K(1)	91.4 (4)
Cl(1)—Pt—Cl(3)	89.4 (6)		Cl(3)—O—K(1)	121.0 (8)
Cl(2)—Pt—Cl(3)	177.6 (3)		Cl(3)—O—K(1)	111.1 (7)
Cl(1)—Pt—C(1)	164.3 (7)		K(1)—O—K(1)	104.6 (6)
Cl(1)—Pt—C(2)	156.4 (6)		Pt(1)—Cl(3)—O(1)	108.8 (5)
Cl(3)—O—Cl(3)	108.2 (7)		Pt(1)—Cl(3)—O(1)	111.8 (8)
Cl(3)—O—K(1)	117.0 (5)		O(1)—Cl(3)—O(1)	108.2 (7)

\* Lower bounds of bond-lengths after correction for thermal motion based on correlated motion model.

† Estimated bond-lengths after corrections for thermal motion based on riding motion model.

‡ Upper bounds of bond-lengths after correction for thermal motion based on the uncorrelated motion model.

Table 2. *Atomic positional parameters and mean square atomic vibrations (Å<sup>2</sup>)*

	$x/a$	$y/b$	$z/c$			
Pt(1)	0.21410 (5)	0	0.33289 (10)			
Cl(1)	0.42412 (34)	0.0010 (22)	0.53116 (87)			
Cl(2)	0.2089 (12)	0.2678 (23)	0.3305 (35)			
Cl(3)	0.2149 (12)	0.7261 (24)	0.3512 (37)			
K <sup>+</sup> (1)	0.43962 (52)	0.29456 (64)	0.9342 (11)			
O(1)	0.3505 (19)	0.6061 (25)	0.8856 (31)			
C(1)	0.0121 (16)	0.0197 (63)	0.2628 (40)			
C(2)	0.0594 (16)	-0.0075 (88)	0.0015 (38)			
	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{13}$	$2U_{23}$
Pt(1)	0.0369 (2)	0.0374 (2)	0.0303 (2)	0.0124 (14)	0.0041 (3)	0.0086 (14)
Cl(1)	0.0364 (17)	0.0600 (24)	0.0604 (22)	0.016 (14)	-0.0098 (31)	0.018 (18)
Cl(2)	0.0519 (88)	0.0390 (89)	0.185 (20)	0.0114 (89)	-0.001 (19)	0.043 (13)
Cl(3)	0.069 (12)	0.0331 (78)	0.164 (18)	0.0024 (94)	0.053 (20)	0.048 (13)
K <sup>+</sup> (1)	0.0662 (29)	0.0479 (26)	0.0622 (27)	-0.0030 (47)	0.0073 (45)	-0.0155 (43)
O(1)	0.101 (13)	0.086 (13)	0.0443 (78)	0.055 (23)	0.014 (17)	0.032 (17)
C(1)	0.0400 (77)	0.051 (25)	0.0599 (92)	-0.042 (29)	-0.025 (14)	0.027 (28)
C(2)	0.0445 (83)	0.136 (25)	0.0422 (85)	-0.008 (57)	-0.026 (15)	0.084 (49)

tudes from equivalent observed reflexions, the structure amplitudes of 994 independent reflexions were then obtained and used in the analysis.

Structure determination

The atomic coordinates found by Bokii & Kukina (1965) in their two-dimensional analysis were used as a first model, and three cycles of least-squares refinement of positional and anisotropic vibrational param-

eters reduced the discrepancy index, R, to 0.086. The weighting scheme  $w^{-1} = 1 + \left(\frac{F_o - 50}{25}\right)^2$  was applied and

a further 14 cycles of full-matrix least-squares refinement were calculated, when the final R value was 0.039. The parameter shifts in the final cycle were all less than a quarter of their estimated standard deviations. The constant term in Cromer & Waber's (1965) exponential

Table 3. Observed and calculated structure factors with phase angles ( $\alpha$ )

Table with multiple columns for observed (L Fo) and calculated (L Fo) structure factors, including phase angles and various indices. The table is organized into several groups of columns, each representing different reflections.

Table 4. *Agreement analysis of observed and calculated structure factors*

Range $F(\text{obs})$	No.	$\Sigma  F_{\text{obs}} $	$\Sigma  F_{\text{calc}} $	$\Sigma  \Delta F $	Average $w \Delta F ^2$	$R$
0-6	4	23	22	5	0.39	0.219
6-12	93	898	835	208	2.20	0.232
12-18	97	1463	1330	209	2.32	0.143
18-24	142	3020	2956	222	1.97	0.074
24-30	149	4093	4107	159	1.17	0.039
30-36	101	3347	3381	107	1.23	0.032
36-42	83	3235	3229	87	1.75	0.027
42-48	68	3083	3097	61	1.26	0.020
48-54	50	2550	2541	43	1.13	0.017
54-61	44	2527	2522	33	0.87	0.013
61-73	60	3956	3919	70	1.69	0.018
73-97	54	3455	4422	70	1.30	0.015
97-182	49	5946	6021	180	2.35	0.33
$\sin \theta/\lambda$						
0.00-0.10	2	250	281	31	26.01	0.123
0.10-0.20	27	2473	2524	101	5.56	0.041
0.20-0.30	75	5639	5658	146	2.00	0.026
0.30-0.40	140	7705	7675	155	0.96	0.020
0.40-0.50	230	9454	9365	229	0.99	0.024
0.50-0.60	323	8816	8764	438	1.56	0.050
0.60-0.70	197	4260	4114	345	2.07	0.081

form-factors for Pt and K were corrected for the real part of the anomalous dispersion.

Bond lengths and angles with standard deviations derived by the method of Busing, Martin & Levy (1964) are given in Table 1. The atomic positional parameters and their standard deviations are set out in Table 2, together with the mean square atomic vibrations and their standard deviations. The observed and calculated structure factors are given in Table 3 and an analysis of their agreement in Table 4.

#### References

- BAENZIGER, N. C., DOYLE, J. R. & RICHARDS, G. F. (1965). *Acta Cryst.* **18**, 924.
- BOKII, G. B. & KUKINA, G. A. (1965). *Zh. Strukt. Khim.* **5**, 706.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *A Fortran Crystallographic Function and Error Program*. ORNL-TM-306. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CARPENTER, G. B. & YOON, Y. K. (1959). *Acta Cryst.* **12**, 17.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
- DAVIES, G. R., HEWERTSON, W., MAIS, R. H. B. & OWSTON, P. G. (1967). *Chem. Comm.* p. 423.
- FULLER, W. (1959). *J. Phys. Chem.* **63**, 1705.
- JEANIN, Y. P. & RUSSELL, D. R. (1968). Personal communication.
- MAIS, R. H. B., OWSTON, P. G. & WOOD, A. M. (1968). Unpublished results.
- MELLOR, D. P. & WUNDERLICH, J. A. (1954). *Acta Cryst.* **7**, 136.
- MELLOR, D. P. & WUNDERLICH, J. A. (1955). *Acta Cryst.* **8**, 57.