IBERS, J. A. (1969). *Acta Cryst.* **B25**, 1667.
MITCHELL, J. & BOEYENS, J. C. A. (1970). *Acta Cryst.* **B26**, 1121.
PHILLIPS, J. N. (1967). Private communication.
PORTER, S. K. & JACOBSON, R. A. (1970). *J. Chem. Soc.* (*A*), p. 1356.
RÉRAT, C. (1962). *Acta Cryst.* **15**, 427.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
TAKEUCHI, Y. & PEPINSKY, R. (1957). *Z. Kristallogr.* **109**, 29.
TRUTER, M. R. (1967). *Acta Cryst.* **22**, 556.
VERHOEF, L. H. W. & BOEYENS, J. C. A. (1968). *Acta Cryst.* **B24**, 1262.
VERHOEF, L. H. W. & BOEYENS, J. C. A. (1969). *Acta Cryst.* **B25**, 607.
VICKERY, B. L. (1970). *Full-matrix Isotropic Refinement Program for the IBM 1130 Computer.*

Acta Cryst. (1972). **B28**, 393

The Crystal Structure of K_2PtCl_4 and K_2PdCl_4: with Estimates of the Factors Affecting Accuracy

BY R. H. B. MAIS, P. G. OWSTON* AND AILSA M. WOOD

Imperial Chemical Industries Limited, Petrochemical & Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire, England

(*Received* 26 *August* 1971)

The structures of K_2PtCl_4 and K_2PdCl_4 have been determined with improved accuracy. The Pt–Cl distance is 2·308 (2) Å, or 2·316 Å after correction for thermal motion; the corresponding values for Pd–Cl are 2·313 (2) Å and 2·318 Å. In both compounds the K–Cl distances are 2·40 Å and the closest Cl–Cl distances 3·27 Å. After correcting for absorption and some minor causes of variation, and after allowing for statistical counting errors, there remained a variation of about 2% between the measured amplitudes of symmetry-related reflexions. This variation is approximately equal to the conventional *R*-value, and has no obvious explanation. Corrections for absorption and for anomalous dispersion have little effect on the calculated positions of the atoms, but have large effects on the e.s.d.'s and on the thermal parameters; they are therefore essential if corrections for thermal vibration are to be calculated.

Introduction

This work was undertaken to determine accurate interatomic distances in K_2PtCl_4 and K_2PdCl_4 as part of studies of the effects of substitution in square planar complexes of Pt(II) and Pd(II). The structures of K_2PtCl_4 and K_2PdCl_4 are known (Dickinson, 1922; Theilacker, 1937), but accurate coordinates have not previously been determined. The experimental results for K_2PtCl_4 were used to make estimates of various sources of error, including errors due to absorption, under the conditions normally used for data-collection, in order to decide how the accuracy can best be improved.

PART I: K_2PtCl_4

Experimental

Crystal data: K_2PtCl_4, $M=415·3$; tetragonal, $a=b=7·025$ (3), $c=4·144$ (2) Å, $V=204·5$ Å^3; space group $P4/mmm$ (D^1_{4h}, No. 123), $Z=1$, $D_c=3·350$, $F(000)=184$; Mo $K\alpha$ radiation ($\lambda=0·7107$ Å), $\mu=220$ cm^{-1}; Zr filter; Picker automatic four-circle diffractometer.

Unit cell

Measurements were made of the diffractometer setting angles χ, φ, ω, 2θ for 16 reflexions. The crystal was in a random orientation and the following cell dimensions, assuming triclinic symmetry, were obtained by a least-squares analysis:

$a=$ 7·0275 (26) $b=$ 7·0218 (24) $c=$ 4·1444 (13) Å
$\alpha=$ 89·973 (24) $\beta=$ 90·048 (27) $\gamma=$ 89·996 (27)°

The tetragonal unit-cell dimensions given in the crystal data above and used in the subsequent crystal structure analysis were derived from these values by taking the mean of *a* and *b*.

Intensity measurements

2434 observations were made of reflexions in the ranges $\sin\theta/\lambda \le 0·904$ for $\bar{h}kl$ and $\bar{h}\bar{k}l$ and $\sin\theta/\lambda \le 0·897$ for hkl and $h\bar{k}l$. The measurements of intensity were made using a θ–2θ continuous scan from 0·6° below α_1 to 0·7° above α_2 at a rate of 0·5° 2θ/min; the background was measured for 20 sec at each end of the scan range. 400 and 040 were used as standard reflexions, the intensity of each being remeasured after every 40 reflexions (*i.e.* every 5 hours). The moving average of these standard reflexions was used to calculate a local

---

* Present address: Department of Inorganic, Physical & Industrial Chemistry, The University, Liverpool, England.

scale factor by which the neighbouring intensities were multiplied, so as to correct for drift. The Lorentz and polarization correction factors were then applied. Two sets of 411 independent structure amplitudes were obtained by averaging the observed amplitudes from equivalent reflexions, one set before and the other after correction for absorption.

Absorption corrections

Absorption corrections were made by a modification of the method proposed by Busing & Levy (1957) which for randomly oriented crystals gives a more favourable distribution of sampling points (see Appendix). 557 points were used with a mean separation of 15μ. The crystal dimensions were 0·11 × 0·13 × 0·18 mm.

Structure refinement

The approximate coordinates reported by Dickinson (1922) were confirmed from the Patterson synthesis. The independent positional and anisotropic thermal parameters were refined twice; first using structure amplitudes not corrected for absorption, to an R value of 0·045 with statistical weights calculated from the equation $1/w=1+(F_o-15)^2/144$; second, using structure amplitudes correct for absorption, to an R value of 0·015 with the weighting scheme $1/w=(F-25)^2/400$. Finally, the second set was refined after correction for the anomalous dispersion of the platinum atom, using the values of Cromer & Waber (1965), to an R value of 0·018.

The three sets of refined parameters are in Table 1, the principal interatomic distances before and after correction for absorption are in Table 3, and the observed and calculated structure factors for the final refinement are analysed in Table 4 and listed in Table 6.

PART II: K_2PdCl_4

Experimental

Crystal data: K_2PdCl_4, $M=327·0$; tetragonal, $a=b=7·075$ (5), $c=4·112$ (3) Å; $V=203·2$ Å^3; space group $P4/mmm$ (D^1_{4h}, No. 123), $Z=1$, $F(000)=152$; D_m (by flotation) = 2·67, $D_c=2·67$; Mo $K\alpha$ radiation ($\lambda=0·7107$ Å); $\mu=40·9$ cm^{-1}; Picker four-circle automatic diffractometer.

Intensity measurements

518 observations were made of reflexions in the range $\sin\theta/\lambda\le0·683$ with indices hkl, $hk\bar{l}$. The measurements of intensity were made using a θ–2θ continuous scan from 0·5° below α_1 to 0·5° above α_2 at a rate of 1° 2θ/min; the background was measured for 20 sec at each end of the scan range. The 400 reflexion was measured after every 20 reflexions and remained constant within ±1 %. Six reflexions were rejected because their intensity was less than twice the statistical standard deviation. After correction for absorption using 197 sample points with mean separation 12μ, and after averaging equivalent reflexions, 191 independent structure amplitudes were obtained. The crystal dimensions were 0·06 × 0·06 × 0·10 mm.

Table 1. *Final atomic parameters* (× 10^4) *for* K_2PtCl_4 *with the e.s.d. of the final digit in parentheses*

(*a*) Before absorption correction

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$
Pt	0	0	0	146 (1)	U_{11}	183 (2)	–
K	0	½*	½*	392 (16)	260 (12)	230 (10)	–
Cl	2325·7 (22)	x/a	0	192 (5)	U_{11}	366 (10)	–59 (12)

(*b*) After absorption correction

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$
Pt	0	0	0	187 (1)	U_{11}	212 (1)	–
K	0	½*	½*	438 (8)	301 (6)	251 (5)	–
Cl	2324·4 (10)	x/a	0	232 (2)	U_{11}	388 (5)	–57 (6)

(*c*) After anomalous dispersion and absorption correction

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$
Pt	0	0	0	180 (1)	U_{11}	206 (1)	–
K	0	½*	½*	451 (8)	313 (6)	261 (5)	–
Cl	2324·5 (10)	x/a	0	242 (2)	U_{11}	401 (5)	–57 (6)

* Parameters given as fractions are not multiplied by 10^4.

Table 2. *Final atomic parameters* (× 10^4) *for* K_2PdCl_4 *with e.s.d.'s of the final digit in parentheses*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$
Pd	0	0	0	151 (3)	U_{11}	180 (5)	–
K	0	½*	½*	410 (19)	220 (15)	199 (13)	–
Cl	2311·8 (25)	x/a	0	199 (7)	U_{11}	323 (11)	–43 (17)

* Parameters given as fractions are not multiplied by 10^4.

Structure refinement

Refinement of the independent positional and anisotropic thermal parameters gave an R value of 0·041 with the weighting scheme $1/w = 1 + (F_o - 13)^2/225$. No corrections were made for the anomalous dispersion in K_2PdCl_4. The refined parameters are in Table 2, an analysis of the agreement between observed and calculated structure factors is in Table 5 and a list of observed and calculated structure factors is given in Table 7.

Crystal structures

Both compounds have the same structure-type, as was previously reported. The $[MCl_4]^{2-}$ units are exactly square planar by symmetry and are held together by ionic forces between the chlorine and potassium atoms. Each potassium is surrounded by eight chlorine neighbours at the corners of a rectangular prism (3·26 × 3·76 × 4·14 Å in the case of K_2PtCl_4) and each chlorine has four potassium neighbours. The M–Cl distances are, within experimental error, the same in the two compounds (see Table 3), 2·311 (2) Å before correction for thermal motion. After correction, using the 'riding motion' model (Busing & Levy, 1964) which is appropriate for atoms strongly bonded together, the length is 2·317 (2) Å in both compounds. (The correction for 'uncorrelated motion', which is inappropriate in this case, would make the 'corrected' M–Cl distance 2·335 Å.) The K–Cl distances are also the same in the two compounds, 3·241 (2) Å (uncorrected for thermal vibration); this is somewhat longer than the sum of the ionic radii, 3·14 Å (Wells, 1962, p. 71).

PART III

Errors in the structure factors for K_2PtCl_4

The equipment had been shown, in preliminary tests, to be capable of measuring intensities with a reproducibility of about 0·1%. It was decided to use the data for this structurally simple compound (which has only one variable positional parameter) to form estimates of the errors involved in measuring structure factors and in deriving atomic coordinates. We therefore measured:

1. The slow drift of intensity in a standard reflexion.
2. The reproducibility of a standard reflexion.
3. The variation between the structure factors for symmetrically equivalent reflexions after correction for absorption.
4. The R value after thorough refinement.

1. *Slow drift in intensity*

The incident and transmitted beams traverse a total air-path of 47·5 cm, and it can be calculated that this attenuates Mo $K\alpha$ radiation by 6·5% at 20°C and 760 mm.Hg pressure; an increase of 1°C increases the intensity by 0·022%, and a pressure increase of 10 mmHg reduces the intensity by 0·086%. During our experiments there was a variation in conditions between 25°C, 738 mm and 24°C, 752 mm, and most of this change took place during one period of 12 hours. This should lead to a total difference in intensity of 0·14%, and a change of this magnitude was clearly detectable in the intensities of the standard reflexions. All intensities were approximately corrected for this variation by using the moving mean intensity of the standard reflexions to compute a scale factor. This scale factor makes empirical correction for the effects of variations in atmospheric conditions, long-term variations in the output of the X-ray tube and of isotropic changes in the reflecting power of the crystal.

2. *Reproducibility*

After the correction for drift had been applied and the background subtracted, the structure amplitude of the 400 standard reflexion was found to be constant with a standard deviation of 0·24%. The standard deviation expected from counting statistics only was 0·11%, the remaining error being attributable to deficiencies in the corrections for drift and for the background intensity. (Because the instrument digitizers record only to the nearest 0·01°, there is a mean error of 0·004° in the angle of scan; if this angle is 1·00°, there will be a mean error of 0·4% in the background intensity correction).

3. *Variations between symmetry-related reflexions*

For every independent reflexion except {00*l*} at least four, and in most cases eight, equivalent reflexions were

Table 3. *Principal interatomic distances in* K_2PtCl_4 *and* K_2PdCl_4

(*a*) Uncorrected,
(*b*) Corrected for absorption (anomalous dispersion corrections had no significant effect),
(*c*) Corrected for absorption,
(*d*) 'Riding motion' approximation,
(*e*) 'Uncorrelated motion' approximation.

	As calculated			Corrected for thermal motion (*d*)		Corrected for thermal motion (*e*)	
	M = Pt		M = Pd	M = Pt	M = Pd	M = Pt	M = Pd
	(*a*)	(*b*)	(*c*)				
M–Cl	2·310 (2)	2·308 (2)	2·313 (2)	2·316	2·318	2·334	2·335
K–Cl	2·239 (2)	3·239 (2)	3·243 (2)				
Cl–Cl	2·268 (2)	3·266 (2)	3·271 (2)				
	3·757 (2)	3·757 (2)	3·804 (2)				
	4·144 (2)	4·144 (3)	4·112 (2)				

measured. The root mean square deviation of each set was calculated, after correction for absorption; it varied considerably from one reflexion to another but was, on the average, 2% of the structure amplitude. Possible causes of this type of variation are:

(*a*) inaccuracy in the absorption corrections,
(*b*) anisotropic variations in extinction effects caused by anisotropic differences in crystal perfection,
(*c*) errors in centring the crystal in the diffractometer and in setting the crystal orientation.

In a few cases the difference in structure amplitude between symmetry-related reflexions was considerably larger than 2%. In particular, the 400 and 040 standard reflexions were each measured 48 times, giving structure amplitudes after correction for absorption of 100·6 (mean deviation 0·2) and 113·6 (mean deviation 0·4) respectively.

4. *Assessment of the errors in the structure factors*

The conventional 'reliability index', $R=\sum||F_o|-|F_c||/\sum|F_o|$ was calculated before and after the absorption corrections were applied (Table 4). The values after correction are plotted in Fig. 1 as a function of $|F_{\text{obs}}|$, together with the corresponding index of variation between symmetry-related structure factors, S, and with the standard deviation based on counting statistics alone, C. Other random errors are smaller than R and S by an order of magnitude. No account was taken of extinction effects, which are probably the cause of the slight increase in R for high values of $|F|$; errors in measuring the X-ray background, which is particularly strong and non-uniform near the strong low angle reflexions are also a possible cause. Neither of these effects should cause S to increase for high values of $|F|$, in agreement with our observations. Over the middle range, where both these effects and the statistical counting errors are negligible, R and S are approximately equal. S is in fact slightly larger than R, and it seems probable that at least part of S is systematic error which is in some way accidentally compensated during the refinement procedure, leading to systematic errors in the atomic parameters.

We cannot at present estimate how much of the residual R is to be attributed to the uncompensated part of S and other errors, and how much to errors in the tabulated atomic scattering factors and in the calculated atomic parameters which would affect R but not S.

The effect of absorption on the structural parameters of K_2PtCl_4

The effect of absorption corrections on the one positional parameter is negligible (Table 2) in this case. Errors due to absorption will already have been partly reduced by the averaging of four or more different reflexions to give each structure amplitude; in other experiments where a less complete set of data is measured the effect of absorption corrections might be

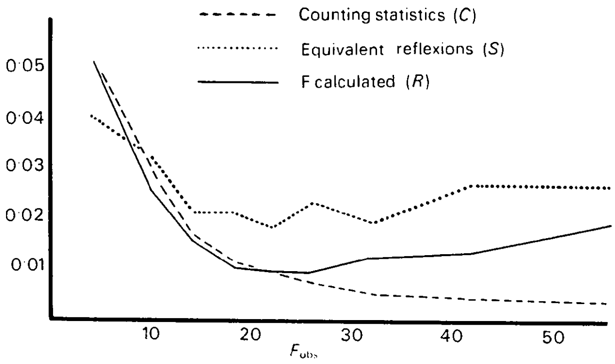

Fig. 1. The variation of different estimates of error with $|F_{\text{obs}}|$.

Table 4. *The variation with* $|F|$ *for* K_2PtCl_4 *of various measures of accuracy*

R^* is the R-value before correction for absorption and anomalous dispersion. R, S and C are defined in the text.

Range of $\|F_o\|$	No.	$\sum\|F_o\|$	$\sum\|F_c\|$	R	S	C	R^*
0–8	30	208	213	0·051	0·040	0·055	0·108
8–12	92	915	923	0·025	0·032	0·029	0·055
12–16	71	996	997	0·015	0·021	0·017	0·041
16–20	49	886	882	0·010	0·021	0·011	0·017
20–24	38	837	833	0·009	0·018	0·009	0·023
24–28	28	729	726	0·009	0·023	0·007	0·027
28–36	34	1076	1067	0·012	0·019	0·005	0·027
36–48	37	1527	1516	0·013	0·026	0·004	0·040
48–120	32	2160	2217	0·030	0·025	0·002	0·070

$\sin\theta/\lambda$	No.	$\sum\|F_o\|$	$\sum\|F_c\|$	$\sum\Delta$	Mean $w\Delta^2$	R
0–0·2	9	539	552	30	4·05	0·056
0·2–0·3	15	959	979	35	1·22	0·037
0·3–0·4	26	1149	1146	22	0·58	0·019
0·4–0·5	35	1272	1267	11	0·14	0·009
0·5–0·6	53	1440	1443	13	0·08	0·009
0·6–0·7	69	1434	1424	16	0·08	0·011
0·7–0·8	94	1410	1415	16	0·04	0·011
0·8–0·9	110	1132	1148	24	0·05	0·022

greater. The effect on the thermal vibration parameter is, however, quite marked. The other main result of the absorption corrections is to reduce the estimated standard deviations by a factor of about two.

Anomalous dispersion in K_2PtCl_4

The corrections for anomalous dispersion for the platinum atom also have negligible effect on the calculated

Table 5. *Agreement between observed and calculated structure factors for* K_2PdCl_4

$\|F_o\|$	No.	$\sum\|F_o\|$	$\sum\|F_c\|$	$\sum\Delta$	Mean $w\Delta^2$	R
3–9	31	193	174	27	0·94	0·140
10–14	44	505	504	19	0·25	0·037
15–20	41	709	707	22	0·50	0·031
21–29	31	770	767	15	0·21	0·048
29–87	44	1931	1957	87	0·67	0·043

$\sin\theta/\lambda$	No.	$\sum\|F_o\|$	$\sum\|F_c\|$	$\sum\Delta$	Mean $w\Delta^2$	R
0–0·2	8	310	330	31	1·23	0·100
0·2–0·3	16	641	665	38	1·20	0·059
0·3–0·4	24	698	682	22	0·62	0·032
0·4–0·5	34	782	766	19	0·24	0·025
0·5–0·6	48	815	798	25	0·46	0·030
0·6–0·7	61	862	868	33	0·38	0·038

Table 6. *Observed and calculated structure factors for* K_2PtCl_4

l	fo	fc	
h=0	k=0		
1	88	94	+
2	107	116	+
3	51	51	+
4	56	56	+
5	24	24	+
6	24	24	+
7	9	9	+
h=0	k=1		
0	71	81	+
1	73	73	+
2	59	59	+
3	45	45	+
4	33	32	+
5	23	23	+
6	15	15	+
7	10	10	+
h=0	k=2		
0	45	44	+
1	13	9	−
2	41	39	+
3	8	6	+
4	26	26	+
5	7	7	+
6	14	14	+
7	5	5	+
h=0	k=3		
0	45	45	+
1	45	44	+
2	38	38	+
3	31	31	+
4	23	23	+
5	18	18	+
6	12	12	+
7	8	8	+
h=0	k=4		
0	94	101	+
1	60	61	+
2	76	78	+
3	39	39	+
4	43	43	+
5	19	19	+
6	19	19	+
7	8	8	+
h=0	k=5		
0	57	58	+
1	57	57	+
2	47	47	+
3	38	38	+
4	28	28	+
5	20	20	+
6	13	13	+
h=0	k=6		
0	30	30	+
1	11	10	+
2	26	26	+
3	9	9	+
4	18	18	+
5	7	7	+
6	10	10	+
h=0	k=7		
0	18	18	+
1	20	19	+
2	16	16	+
3	16	15	+
4	12	12	+
5	10	10	+
6	6	7	+
h=0	k=8		
0	41	41	+
1	29	28	+
2	36	35	+
3	21	20	+
4	22	21	+
5	11	11	+
h=0	k=9		
0	30	30	+
1	31	31	+
2	26	25	+
3	22	22	+
4	16	16	+
5	12	12	+
h=0	k=10		
0	16	16	+
1	10	10	+
2	14	14	+
3	8	8	+
4	10	10	+
h=0	k=11		
0	6	7	+
1	8	8	+
2	6	6	+
3	7	7	+
h=0	k=12		
0	13	13	+
1	10	10	+
2	12	12	+
h=1	k=1		
0	41	39	+
1	90	95	+
2	34	33	+
3	55	56	+
4	21	21	+
5	29	28	+
6	11	10	+
7	12	12	+
h=1	k=2		
0	61	60	+
1	57	56	+
2	47	47	+
3	37	37	+
4	28	28	+
5	20	20	+
6	14	14	+
7	9	9	+
h=1	k=3		
0	36	34	+
1	72	74	+
2	30	30	+
3	47	48	+
4	19	19	+
5	25	25	+
6	9	10	+
7	11	11	+
h=1	k=4		
0	54	55	+
1	51	51	+
2	44	45	+
3	35	35	+
4	26	27	+
5	19	19	+
6	13	13	+
h=1	k=5		
0	32	32	+
1	55	55	+
2	27	27	+
3	38	38	+
4	17	17	+
5	21	21	+
6	9	9	+
h=1	k=6		
0	36	36	+
1	33	33	+
2	30	30	+
3	24	24	+
4	20	19	+
5	14	14	+
6	10	10	+
h=1	k=7		
0	22	22	+
1	36	36	+
2	20	19	+
3	27	26	+
4	13	13	+
5	15	15	+
6	7	7	+
h=1	k=8		
0	28	28	+
1	23	23	+
2	24	24	+
3	19	19	+
4	16	16	+
5	10	11	+
h=1	k=9		
0	18	18	+
1	25	25	+
2	16	16	+
3	19	19	+
4	10	10	+
5	11	11	+
h=1	k=10		
0	17	17	+
1	15	15	+
2	15	15	+
3	11	12	+
4	10	10	+
h=1	k=11		
0	11	11	+
1	14	14	+
2	9	10	+
3	11	11	+
h=1	k=12		
0	11	11	+
1	10	10	+
2	10	10	+
h=2	k=2		
0	121	129	+
1	71	73	+
2	90	93	+
3	44	44	+
4	49	49	+
5	22	21	+
6	21	21	+
7	8	8	+
h=2	k=3		
0	67	67	+
1	63	63	+
2	52	52	+
3	41	41	+
4	30	30	+
5	22	21	+
6	14	14	+
7	9	9	+
h=2	k=4		
0	38	37	+
1	9	6	+
2	32	32	+
3	9	8	+
4	22	21	+
5	7	7	+
6	12	12	+
h=2	k=5		
0	28	28	+
1	29	28	+
2	24	24	+
3	21	21	+
4	17	17	+
5	13	13	+
6	9	9	+
h=2	k=6		
0	60	61	+
1	41	40	+
2	50	50	+
3	28	28	+
4	30	30	+
5	15	15	+
6	14	14	+
h=2	k=7		
0	40	41	+
1	41	41	+
2	35	34	+
3	29	29	+
4	21	21	+
5	15	15	+
6	10	10	+
h=2	k=8		
0	21	21	+
1	11	11	+
2	19	19	+
3	9	9	+
4	13	13	+
5	6	6	+
h=2	k=9		
0	11	10	+
1	12	12	+
2	10	10	+
3	10	10	+
4	8	8	+
5	6	7	+
h=2	k=10		
0	23	23	+
1	17	17	+
2	20	20	+
3	13	12	+
4	13	13	+
h=2	k=11		
0	19	18	+
1	19	19	+
2	16	16	+
3	14	14	+
h=2	k=12		
0	11	11	+
1	8	8	+
h=3	k=3		
0	38	36	+
1	65	66	+
2	31	30	+
3	43	44	+
4	19	19	+
5	24	23	+
6	8	9	+
h=3	k=4		
0	37	36	+
1	35	34	+
2	31	31	+
3	25	25	+
4	20	20	+
5	15	15	+
6	10	10	+
h=3	k=5		
0	25	25	+
1	44	44	+
2	21	21	+
3	31	32	+
4	14	14	+
5	13	13	+
6	7	8	+
h=3	k=6		
0	39	39	+
1	37	36	+
2	33	33	+
3	26	26	+
4	21	21	+
5	14	14	+
6	10	10	+
h=3	k=7		
0	25	25	+
1	36	36	+
2	21	21	+
3	27	26	+
4	14	14	+
5	15	15	+
h=3	k=8		
0	21	21	+
1	19	19	+
2	18	18	+
3	15	15	+
4	12	12	+
5	9	9	+
h=3	k=9		
0	13	13	+
1	20	20	+
2	12	12	+
3	15	15	+
4	8	8	+
h=3	k=10		
0	18	18	+
1	16	16	+
2	15	15	+
3	12	12	+
4	10	10	+
h=3	k=11		
0	12	12	+
1	16	15	+
2	11	11	+
3	11	12	+
h=3	k=12		
0	9	10	+
1	8	8	+
h=4	k=4		
0	71	71	+
1	45	46	+
2	57	58	+
3	31	31	+
4	34	34	+
5	16	16	+
6	16	15	+
h=4	k=5		
0	45	45	+
1	44	43	+
2	37	37	+
3	31	31	+
4	23	23	+
5	16	16	+
6	11	11	+
h=4	k=6		
0	25	25	+
1	11	11	+
2	22	22	+
3	10	9	+
4	15	15	+
5	7	7	+
6	9	9	+
h=4	k=7		
0	15	15	+
1	16	15	+
2	14	14	+
3	13	13	+
4	10	11	+
5	8	9	+
h=4	k=8		
0	32	32	+
1	23	23	+
2	28	27	+
3	17	17	+
4	17	17	+
5	9	9	+
h=4	k=9		
0	25	25	+
1	25	25	+
2	21	21	+
3	18	18	+
4	13	13	+
h=4	k=10		
0	14	14	+
1	9	9	+
2	12	12	+
3	7	8	+
h=4	k=11		
0	7	6	+
1	7	7	+
2	6	6	+
h=5	k=5		
0	27	28	+
1	41	41	+
2	23	24	+
3	30	30	+
4	15	15	+
5	16	15	+
6	7	8	+
h=5	k=6		
0	20	20	+
1	19	19	+
2	18	18	+
3	15	15	+
4	12	13	+
5	9	10	+
h=5	k=7		
0	14	14	+
1	23	23	+
2	13	13	+
3	18	18	+
4	9	9	+
5	10	11	+
h=5	k=8		
0	24	24	+
1	22	22	+
2	20	21	+
3	16	16	+
4	13	13	+
h=5	k=9		
0	17	17	+
1	21	21	+
2	14	14	+
3	16	16	+
4	9	9	+
h=5	k=10		
0	11	11	+
1	10	10	+
2	10	10	+
3	8	8	+
h=5	k=11		
0	7	7	+
1	9	9	+
2	6	6	+
h=6	k=6		
0	36	36	+
1	26	26	+
2	31	31	+
3	13	13	+
4	19	19	+
5	10	10	+
h=6	k=7		
0	27	27	+
1	26	26	+
2	23	23	+
3	19	19	+
4	14	14	+
5	10	10	+
h=6	k=8		
0	16	16	+
1	10	10	+
2	14	14	+
3	8	8	+
4	10	10	+
h=6	k=9		
0	9	9	+
1	9	9	+
2	8	8	+
3	8	8	+
h=6	k=10		
0	15	15	+
1	11	11	+
2	13	13	+
h=6	k=11		
0	12	12	+
h=7	k=7		
0	18	19	+
1	24	24	+
2	16	16	+
3	18	17	+
4	10	10	+
h=7	k=8		
0	11	11	+
1	10	11	+
2	10	10	+
3	8	9	+
h=7	k=9		
0	7	8	+
1	10	11	+
2	7	7	+
3	8	9	+
h=7	k=10		
0	12	12	+
1	13	12	+
h=8	k=8		
0	17	16	+
1	12	13	+
2	14	14	+
3	9	9	+
h=8	k=9		
0	13	14	+
1	13	13	+
2	12	12	+

atomic positions, but affect the thermal vibration parameters in the way expected, *i.e.* by reducing the apparent amplitudes for platinum and increasing those for the other atoms.

Conclusion

These results show that structure amplitudes measured carefully on good modern equipment are subject to uncertainties which are much larger than the expected experimental error. The next step in improving accuracy evidently must be to find the reasons for this, at present unexplained, variation.

Corrections for absorption and for anomalous dispersion are seen to be important in improving the accuracy of the positional parameters, and essential when calculating the values of the vibrational parameters. The correction of bond-lengths for vibrational effects depends on accurate values of these parameters; it is also seen to depend very much on the exact model used for calculating the vibrational correction. It seems probable that errors in bond-lengths caused by inadequacies in the vibrational correction procedure exceed errors from most other sources. Really accurate bond-lengths can thus be obtained only by work at low temperatures where vibrational effects are small compared with other causes of error.

APPENDIX

Calculation of absorption corrections

Busing & Levy (1957) calculate the absorption correction for each reflexion by integrating the absorption at a number of points in the crystal, using the Gauss quadrature procedure. The points are specified by taking a set of reference axes (one of them coincident with the axis of the crystal mount) and specifying the number of points to be used along each axial direction; these numbers are made approximately proportional to the dimensions of the specimen along the axes. As illustrated (in two dimensions) in Fig. 2(*a*), this gives an even distribution of points when the principal dimensions of the crystal coincide with the reference axes; but in other cases [Fig. 2(*b*)] a markedly uneven distribution, and a poorer estimate of the absorption correction, is obtained. Difficulties thus arise when the principal dimensions of the crystal do not coincide with the reference axes, or when mounting methods are used in which the crystal axes are not aligned precisely with the axis of the mount (*e.g.* the simple and

Table 7. *Observed and calculated structure factors for* K_2PdCl_4

l	fo	fc
h=o k=o		
1	62	66 +
2	87	93 +
3	34	33 +
4	46	45 +
5	15	15 +
h=o k=1		
0	37	52 +
1	47	47 +
2	37	36 +
3	28	26 +
4	19	19 +
5	13	14 +
h=o k=2		
0	17	17 +
1	40	36 −
2	18	17 +
3	17	15 −
4	12	12 +
5	5	5 −
h=o k=3		
0	17	19 +
1	20	20 +
2	15	16 +
3	14	14 +
4	10	10 +
5	0	8 +
h=o k=4		
0	77	81 +
1	40	39 +
2	62	61 +
3	25	25 +
4	34	35 +
5	12	12 +
h=o k=5		
0	42	40 +
1	42	40 +
2	33	32 +
3	28	27 +
4	19	19 +
h=o k=6		
1	9	8 −
2	13	13 +
4	10	10 +
h=o k=7		
1	5	5 +
2	5	2 +
3	5	5 +
h=o k=8		
0	32	32 +
1	17	17 +
2	26	27 +
3	12	12 +
h=o k=9		
0	24	23 +
1	25	25 +
2	19	19++
h=1 k=1		
0	10	11 +
1	64	69 +
2	10	10 +
3	39	38 +
4	7	6 +
5	19	20 +
h=1 k=2		
0	32	33 +
1	32	30 +
2	26	25 +
3	20	19 +
4	15	15 +
5	11	11 +
h=1 k=3		
0	9	9 +
1	52	52 +
2	9	8 +
3	33	32 +
4	6	6 +
5	17	18 +
h=1 k=4		
0	35	34 +
1	31	30 +
2	28	27 +
3	21	20 +
4	16	16 +
5	10	11 +
h=1 k=5		
0	12	12 +
1	39	39 +
2	11	10 +
3	27	27 +
4	7	6 +
h=1 k=6		
0	20	20 +
1	16	16 +
2	17	17 +
3	12	12 +
4	11	11 +
h=1 k=7		
0	8	7 +
1	24	24 +
2	7	7 +
3	18	18 +
h=1 k=8		
0	18	18 +
1	14	14 +
2	15	15 +
3	11	11 +
h=1 k=9		
0	10	9 +
1	18	18 +
2	8	8 +
h=2 k=2		
0	85	104 +
1	49	49 +
2	73	74 +
3	29	28 +
4	39	39 +
5	13	13 +
h=2 k=3		
0	45	45 +
1	43	42 +
2	35	34 +
3	28	27 +
4	19	19 +
5	14	14 +
h=2 k=4		
0	17	16 +
1	18	16 −
2	15	14 +
3	9	8 −
4	10	11 +
h=2 k=5		
0	7	8 +
1	9	10 +
2	7	7 +
3	8	8 +
4	6	6 +
h=2 k=6		
0	47	47 +
1	25	25 +
2	39	39 +
3	17	17 +
4	23	24 +
h=2 k=7		
0	30	29 +
1	31	31 +
2	25	25 +
3	22	22 +
h=2 k=8		
0	12	12 +
1	4	1 −
2	11	11 +
h=2 k=9		
1	5	3 +
h=3 k=3		
1	47	47 +
2	13	12 +
3	32	31 +
4	8	7 +
5	16	17 +
h=3 k=4		
0	17	47 +
1	15	12 +
2	32	31 +
3	8	7 +
4	16	17 +
h=3 k=4		
0	17	16 +
1	15	15 +
2	14	14 +
3	11	11 +
4	9	9 +
h=3 k=5		
0	6	6 +
1	29	28 +
2	5	5 +
3	21	21 +
4	5	4 +
h=3 k=6		
0	26	26 +
1	23	23 +
2	22	22 +
3	17	17 +
4	14	14 +
h=3 k=7		
0	13	13 +
1	26	27 +
2	11	11 +
3	20	20 +
h=3 k=8		
0	11	11 +
1	9	9 +
2	10	10 +
h=3 k=9		
1	11	12 +
h=4 k=4		
0	56	55 +
1	29	29 +
2	46	45 +
3	20	19 +
4	27	27 +
h=4 k=5		
0	32	31 +
1	31	30 +
2	26	26 +
3	21	21 +
4	15	16 +
h=4 k=6		
0	13	13 +
1	5	3 −
2	12	12 +
h=4 k=7		
1	5	5 +
2	5	3 +
3	5	5 +
h=4 k=8		
0	24	25 +
1	13	14 +
2	20	21 +
h=5 k=5		
0	16	15 +
1	31	30 +
2	12	12 +
3	22	22 +
h=5 k=6		
0	7	8 +
1	7	7 +
2	7	7 +
3	6	6 +
h=5 k=7		
1	13	13 +
2	5	2 +
h=6 k=8		
0	16	17 +
1	15	15 +
h=6 k=6		
0	28	28 +
1	15	16 +
2	23	24 +
h=6 k=7		
0	19	20 +
1	18	19 +

stable mounts that we use in preference to adjustable goniometer heads (Davies, Jarvis, Kilbourn, Mais & Owston, 1970). The errors are particularly serious for highly absorbing crystals.

The difficulties are reduced by first specifying an average separation, A, between neighbouring sample points. At every stage during the calculation of the positions of the sample points, whenever the limits of integration are determined, the number of Gaussian points used is now chosen to make the average separation equal to A. In all other respects Busing and Levy's method is used. The result of this procedure, illustrated in Fig. 2(*c*), is a distribution of sample points which, for a given amount of calculation, gives a better approximation to the absorption correction than the use of a fixed number of Gaussian points.

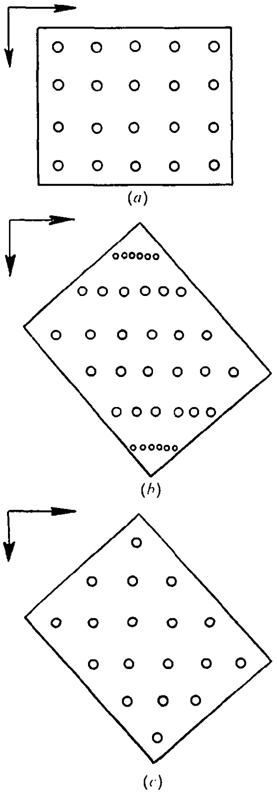

Fig. 2. The distribution of sampling points used for absorption corrections, (*a*) for a favourable orientation, using either Busing & Levy's method or its new modification, (*b*) for an unfavourable orientation, using Busing & Levy's method, (*c*) for the same orientation as (*b*), using the new modified method.

Measurements of the crystal dimensions are made by transferring the crystal and its mount from the diffractometer to a microscope (magnification ×125) whose stage is fitted with a φ-spindle and standard I.U.Cr. mount perpendicular to the line of sight. Each corner of the crystal is given a serial number, and its two coordinates in the field of view are measured with a precision of 0·01 mm, by a micrometer eyepiece; this is done for at least two values of φ, which is measured to 0·1°.

Each face is defined by the serial numbers of its corners, and the equations of the faces and the lengths of their normals from the arbitrarily chosen origin are computed. The coordinates of the corners are calculated from these equations and compared with the observed values, in order to detect mistakes. Finally the χ and φ values required to bring the faces into their reflecting positions on the diffractometer are calculated, and the indices of the faces found by comparing these with the setting angles used during data collection.

References

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.
Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.
Davies, G. R., Jarvis, J. A. J., Kilbourn, B. T., Mais, R. H. B. & Owston, P. G. (1970). *J. Chem. Soc.* (*A*), p. 1275.
Dickinson, R. G. (1922). *J. Amer. Chem. Soc.* **44**, 2404.
Theilacker, W. (1937). *Z. Anorg. Allgem. Chem.* **234**, 161.
Wells, A. F. (1962). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.