

Structure Refinement of Potassium Chloroplatinate by Powder and Single-Crystal Methods*

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The crystal structure of potassium chloroplatinate, K_2PtCl_6 , has been refined from both single-crystal and powder X-ray diffraction data. The system is cubic, space group $Fm\bar{3}m$ with $a = 9.751 \pm 0.005$ Å. The measured density is 3.47 ± 0.01 g cm⁻³ and the calculated density for $Z = 4$ is 3.478 g cm⁻³. Interatomic distances are Pt-Cl, 2.323 (1) Å, Cl-Cl, 3.285 (2) Å (in the same octahedron), 3.610 (2) Å (in adjacent octahedra) and K-Cl, 3.449 (1) Å. For the two determinations the values of the chlorine atom position parameter agree within one standard deviation and the temperature factors agree relatively; however, the powder method yielded temperature factors which were slightly larger. The results suggest that the powder method, when applied to high-symmetry systems with small numbers of variable parameters, yields refined parameters comparable in reliability to those from the single-crystal method.

Introduction

For many classes of compounds it is extremely difficult to prepare single crystals which are suitable in size and degree of perfection for the single-crystal method. Some of these compounds whose structural properties are of interest to us are the rare earth and actinide metal hydroxides, numerous hydrous oxides, and many of the heavy-metal and transition metal ferro-, ferri-, and cobalti-cyanides. In order to obtain reliable structural information concerning these materials by X-ray diffraction techniques one has to resort to the powder method. Because of the limited number of intensities available and the possibility of overlap or coincidence of some reflections, it is clear that this method would be most applicable to those compounds which exist in high-symmetry space groups with small numbers of variable parameters.

In order to get a closer evaluation of the reliability of our powder technique, we felt it necessary to test the procedure on some suitable material whose structure could also be refined using single-crystal methods. A meaningful comparison of the models and their associated e.s.d.'s could then be made. One such suitable material is potassium chloroplatinate.

Although there have been a number of early structural investigations of potassium chloroplatinate, to our knowledge no attempt has been made to refine its structure, with temperature parameters, using counter-tube data. Ewing & Pauling (1928) and Frederikse & Verweel (1928) first independently determined its structure from Laue and powder photographs. There have been several unit-cell measurements of this compound; the most recent and the one now generally accepted is that done at the National Bureau of Stan-

dards [see Swanson, Gilfrich & Ugrinic (1955) and references contained therein]. Wyckoff (1965) lists K_2PtCl_6 as a structure type for substances of the form R_2MX_6 (with close to 100 analogues) where MX_6 is a large stable ion. We have refined the structure of K_2PtCl_6 including the determination of its thermal parameters, using both single crystal and powder data independently and now report the details of this investigation.

Experimental

Single-crystal method

Chloroplatinic acid was first prepared by dissolving platinum in *aqua regia*. Most of the excess acid was removed by evaporation. Potassium chloroplatinate was then prepared by adding slightly more than the stoichiometric amount of potassium chloride to the chloroplatinic acid solution.

The resulting bright-yellow precipitate was washed with ether and then absolute alcohol and air dried. Small, octahedrally shaped single crystals, suitable for intensity measurements were grown from deionized water.

Precession photographs confirmed the earlier determinations of $Fm\bar{3}m$ as the space group. The lattice constant was obtained from a least-squares analysis of the settings of 13 high-angle reflections measured with $Cu K\alpha$ radiation ($\lambda = 1.5418$ Å) on a G.E. XRD-5 single-crystal orienter. A $\cos \theta \cdot \cot \theta$ extrapolation function was employed (Roof, 1971). The lattice constant is $a = 9.751 \pm 0.005$ Å and agrees, within the estimated standard deviation, with Swanson, Gilfrich & Ugrinic's (1955) determination, $a = 9.755$ Å. The observed density at 23°C, measured pycnometrically using a modified Culbertson & Weber (1938) method, is 3.47 ± 0.01 g cm⁻³, and the calculated density, for $Z = 4$, is 3.478 g cm⁻³.

All attempts to grind a spherical crystal failed because of a tendency of this material to flake or cleave into thin platelets. However, a small crystal in the ap-

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proximate shape of a tetragonal bipyramid with truncated apexes was found which closely approximated a sphere and was used for intensity measurements. The base of the bipyramid had dimensions of 0.025×0.040 mm and the height was 0.035 mm. Spherical absorption corrections according to Bond (1959) were applied for $\mu R = 0.864$ ($\mu = 519.3 \text{ cm}^{-1}$ for Cu $K\alpha$ radiation). The maximum possible error introduced into the value of an individual intensity by this approximation is $\sim 20\%$, but the average error is only $\sim 5\%$. This corresponds to an average error of $\sim 2.5\%$ in the value of an individual structure factor.

Intensities were measured with a G.E. XRD-5 diffractometer equipped with a three-circle goniometer using nickel-filtered copper radiation and $\theta-2\theta$ scans to a maximum 2θ of 155° . The scan rate was $2^\circ/\text{min}$, and the normal scan range was 3.33° . The background was measured for 20 sec on either side of the scan range. A standard reflection was measured approximately every 25 reflections, and the intensities were

linearly corrected between standards for instrumental drift. Estimated standard deviations for the intensities were calculated from the expression:

$$\sigma_I = [I_T + B + (0.02I)^2]^{1/2}, \quad (1)$$

where I_T is the total integrated peak intensity, B is the total normalized background count, and the factor $(0.02I)^2$ takes into account instrumental instabilities (Stout & Jensen, 1968). A total of 78 unique reflections were recorded of which 75 were considered observed according to the criterion: $(I - B) \geq 2.0\sigma_I$ where σ_I is defined in equation (1).

Crystal data

K_2PtCl_6	F.W. 486.012
$a = 9.751 \pm 0.005 \text{ \AA}$	$V = 927.14 \text{ \AA}^3$
$\rho_{\text{obs}} = 3.47 \pm 0.01 \text{ g cm}^{-3}$	$\rho_{\text{cal}} = 3.478 \text{ g cm}^{-3}$
Systematic absences	$hkl: h+k, k+l, (l+h) \neq 2n$
Space group	$Fm\bar{3}m$.

Table 1. Final calculated and observed structure factors for K_2PtCl_6

Powder data			Single-crystal data			Powder data			Single-crystal data						
<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	F_o	F_c	F_c	<i>h</i>	<i>k</i>	<i>l</i>	F_o	F_c	F_o	F_c	F_c
1	1	1	56.29	59.41	54.68	52.49	53.06	9	3	1	27.11	25.42	26.55	25.50	27.25
2	0	0	57.13	51.98	38.06	45.67	45.27	8	4	4	40.42	42.21	43.87	43.87	43.50
2	2	0	54.74	52.45	51.13	47.03	46.57	7	5	5	22.94	22.61	24.43	22.96	22.83
3	1	1	44.85	47.03	39.11	41.97	41.92	7	7	1	17.01	16.76	17.40	17.05	16.39
2	2	2	24.37	28.60	27.87	25.87	25.68	9	3	3	22.72	22.40	24.22	22.74	24.45
4	0	0	133.19	113.89	86.93	103.06	103.18	8	6	0	22.70	22.38	23.53	21.22	21.46
3	3	1	35.88	38.33	37.08	34.58	34.29	10	0	0	24.29	23.93	20.74	22.81	19.50
4	2	0	42.35	41.55	39.40	36.67	37.36	10	2	0	23.32	20.48	21.20	22.48	20.74
4	2	2	41.29	41.91	41.53	39.11	40.36	8	6	2	21.63	18.99	24.25	20.94	22.60
5	1	1	47.53	46.14	41.98	42.23	43.23	9	5	1	27.53	25.25	26.99	25.90	27.22
3	3	3	32.67	31.74	29.70	28.94	28.59	7	7	3	15.85	14.54	13.85	14.96	14.61
4	4	0	85.66	86.56	85.62	80.60	80.51	6	6	6	2.96	2.52	0.00	1.64	2.39
5	3	1	38.15	38.98	37.85	36.09	36.77	10	2	2	2.75	2.52	0.00	1.62	2.35
4	4	2	34.67	35.42	36.70	31.51	32.75	9	5	3	23.05	22.47	25.20	23.31	24.62
6	0	0	36.30	37.09	27.75	33.08	30.67	8	6	4	20.48	19.97	18.91	19.27	19.77
6	2	0	36.63	35.88	33.86	34.76	33.43	10	4	0	21.84	21.29	18.40	20.66	18.12
5	3	3	30.59	33.19	35.45	31.06	31.59	10	4	2	19.58	17.92	19.78	20.26	19.27
6	2	2	5.87	6.38	6.82	6.96	6.34	11	1	1	14.03	15.71	14.20	16.54	14.57
4	4	4	59.03	69.84	69.49	66.91	66.69	7	7	5	13.88	15.54	15.60	16.36	16.10
5	5	1	38.17	38.37	41.25	36.37	37.30	8	8	0	32.34	31.61	34.95	34.54	34.16
7	1	1	28.38	28.53	25.09	27.01	26.03	9	5	5	24.15	22.11	23.22	23.48	24.33
6	4	0	32.04	32.21	30.32	29.13	27.77	9	7	1	19.48	17.84	19.48	18.98	19.76
6	4	2	30.08	29.93	31.04	30.01	29.86	11	3	1	15.07	13.80	13.48	14.73	13.15
5	5	3	32.31	33.31	34.18	31.93	32.71	8	8	2	18.85	17.26	18.83	16.96	18.96
7	3	1	23.66	24.39	22.62	23.36	22.56	10	4	4	20.71	18.96	17.14	18.78	16.87
8	0	0	64.37	58.18	57.08	57.29	57.01	8	6	6	16.58	14.81	18.48	17.75	18.59
7	3	3	19.29	20.86	19.46	20.18	19.59	10	6	0	17.77	16.29	17.29	18.92	17.26
6	4	4	26.29	28.42	27.01	26.04	25.39	11	3	3	11.93	12.12	12.02	13.12	11.92
8	2	0	25.28	27.33	27.70	24.97	26.78	10	6	2	3.70	3.76	4.23	3.07	3.91
6	6	0	28.33	26.50	27.88	27.38	25.72	9	7	3	15.71	15.85	16.76	17.10	18.00
8	2	2	26.08	24.40	29.48	25.29	28.33	8	8	4	27.02	27.48	28.57	30.83	30.46
7	5	1	23.89	25.41	25.36	24.88	24.51	12	0	0	27.07	27.52	30.29	30.87	30.47
5	5	5	30.94	32.91	33.69	32.23	32.92	7	7	7	10.59	10.59	11.00	11.61	11.59
6	6	2	1.06	1.06	0.00	1.75	1.20	11	5	1	14.36	14.37	14.01	15.69	14.26
8	4	0	48.17	49.63	51.86	49.96	49.61	12	2	0	15.51	15.52	17.55	15.55	17.47
7	5	3	22.27	22.11	22.39	21.91	21.70	9	7	5			16.68	17.60	18.16
9	1	1	29.08	28.88	29.09	28.61	30.45	10	6	4			16.02	17.19	16.14
8	4	2	24.44	24.26	25.02	22.51	24.45	11	5	3			12.38	14.14	13.04
6	6	4	20.91	22.75	23.72	24.27	23.54	12	2	2			17.99	15.16	18.38

* Isotropic refinement.

† Anisotropic refinement.

Powder method

Potassium chloroplatinate prepared as described above was ground to 325 mesh, encased in an Epon 812 resin binder and finely polished. In this way errors in intensities due to surface effects and preferred orientation effects were minimized.

The total diffracted intensity profile was measured to $155^\circ 2\theta$ by a continuous θ - 2θ scan technique using a G.E. XRD-6 diffractometer. The radiation was copper $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) monochromatized with a diffracted beam LiF curved crystal monochromator ($\theta_M = 22.5486^\circ$) which was placed between the flat plate sample and the General Electric SPG-8 proportional counter tube. The scan rate was $0.024^\circ/\text{min}$. The entire range of reflections was recorded by three overlapping scans and the final data set was an average of the normalized runs. A linear background was fitted to each diffraction peak profile and subtracted from the total net count to yield the intensity of the peak. A total of 39 separate intensities containing 74 unique Bragg reflections was measured.

Structure refinement*Single-crystal method*

The model defined by Ewing & Pauling (1928) was used as the starting model for our refinement. This model has platinum atoms in position set 4(a); potassium atoms in position set 8(c); and chlorine atoms in position set 24(e) with $u = 0.24$ in space group $Fm\bar{3}m$. This model was refined with a full-matrix least-squares program (Stemple, 1971) with all atoms given isotropic temperature factors. Convergence was reached after six cycles of refinement and yielded disagreement indices $R = 0.067$ and $R_w = 0.0702$ where:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_w = \frac{\sum w||F_o| - |F_c||}{\sum w|F_o|}$$

A difference Fourier calculated at this point had a large peak at the Pt atom position ($2e \text{ \AA}^{-3}$) and another ($0.8e \text{ \AA}^{-3}$) elongated perpendicular to the Pt-Cl bond indicating some anisotropic thermal motion for the chlorine atom. It was decided, therefore, to refine the structure using an anisotropic model, where aniso-

tropic temperature parameters are defined by the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The Pt and K atoms must have isotropic temperature factors because of their point symmetry, but the chlorine atom has only the restrictions $\beta_{33} = \beta_{22}$ and $\beta_{12} = \beta_{23} = \beta_{13} = 0$ (Levy, 1956). Several cycles of anisotropic refinement converged to give final disagreement indices $R = 0.0499$ and $R_w = 0.0453$. A final difference Fourier had only one significant peak, $1.4 e \text{ \AA}^{-3}$ at (0,0,0), the platinum atom position.

The quantity minimized in the least-squares refinement procedure was $\sum w(|F_o| - k|F_c|)^2$, where k is a scale factor, and $w = 1/\sigma^2(F_o)$ is the weight derived from equation (1) (Stout & Jensen, 1968). For all unobserved reflections $w = 0$.

The largest $\Delta\xi_i/\sigma(\xi_i)$ after refinement was 0.063, and the average value was approximately 0.01 for all parameters. No secondary extinction corrections were made. The atomic scattering factors for Pt were from Cromer & Waber (1965) and those for K and Cl were from Ibers (1962). Both the real and the imaginary components of the anomalous dispersion corrections were applied to all scattering factors (Cromer, 1965). The final observed and calculated structure factors are given in Table 1.

Powder method

Beginning with the same starting model as above, the powder data were refined by an isotropic full-matrix least-squares technique. Because of the overlapping reflections, the function minimized in this case was

$$\sum_m w(k \sum_i I_c - I_o)^2,$$

where I_o = observed intensity of a single peak
 $\sum_i I_c$ = sum of the i calculated intensities for all reflections contained in each observation I_o

k = scale factor

w = weighting factor (Hughes, 1941)

m = number of observations

In the above expression

$$I_c = M \cdot L_p \cdot |F_{hkl}|^2,$$

where M = multiplicity of reflection I_{hkl}

F_{hkl} = structure factor for reflection I_{hkl}

L_p = Lorentz-polarization correction

$$= 1 + \cos 2\theta^2 \cdot \cos 2\theta_M^2 / \sin \theta \cdot \sin 2\theta.$$

Table 2. Final parameter values for refinements of K_2PtCl_6

Anisotropic - single-crystal method								
	x	y	z	B or β_{11}	β_{22}	β_{33}		
Pt	0.00	0.00	0.00	1.04 (7)				
K	0.25	0.25	0.25	2.89 (29)				
Cl	0.2382 (9)	0.00	0.00	0.0025 (7)	0.0085 (11)	0.0085 (11)		
Isotropic - single-crystal method				Isotropic - powder method				
	x	y	z	B	x	y	z	B
Pt	0.00	0.00	0.00	1.06 (9)	0.00	0.00	0.00	1.62 (13)
K	0.25	0.25	0.25	2.69 (32)	0.25	0.25	0.25	4.38 (66)
Cl	0.2391 (12)	0.00	0.00	2.44 (21)	0.2393 (17)	0.00	0.00	2.93 (37)

Several cycles of refinement converged and gave a final disagreement index of $R=0.056$ where $R = \frac{\sum_m |V \sum_c \bar{I}_c - V I_o|}{\sum |V I_o|}$. The same atomic scattering factors with the same anomalous dispersion corrections, as for the single-crystal refinement, were used. A list of the final observed and calculated structure factors for this refinement are given in Table 1. Reflections that overlap in the powder pattern are enclosed in brackets in this table. The original observed intensity of the given peak may be calculated from the expression

$$I_o = \sum_i M \cdot L_p \cdot F_o(hkl)^2$$

where $F_o(hkl)$ is the observed structure factor, and the summation is over the i reflections contained in the peak (indicated by the brackets). The observed structure factors for overlapping reflections are defined by:

$$F_o = \left(\frac{I_c(hkl)}{\sum_i \bar{I}_c} \cdot I_o \right)^{1/2}$$

Discussion

The final position and thermal parameters for all refinements are given in Table 2. Some significant distances from the anisotropic single-crystal refinement are: Pt-Cl=2.323 (1) Å, Cl-Cl=3.285 (2) Å (in the same octahedron), 3.610 (2) Å (in adjacent octahedra), and K-Cl=3.449 (1) Å. The longer Cl-Cl distance (3.61 Å) and the Pt-Cl distance (2.32 Å) correspond closely with the sums of the 'crystal radii' (Cl-Cl=3.62; Pt-Cl=2.36). The K-Cl distance of 3.45 Å is larger than the sum of the 'crystal radii' (3.14 Å), and is in qualitative accord with the larger temperature parameter for the K atom, and with the anisotropic character of the Cl temperature parameter.

It will be noted in Table 2 that the position parameters found by both methods agree within one standard deviation. The temperature parameters are in relative agreement, although the isotropic powder values are consistently higher than the isotropic or anisotropic single crystal values. It is concluded that the powder method when applied to crystalline systems with a small number of variable parameters can yield refined parameters comparable in reliability to those from the single crystal method.

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Structure du Diméthyl-2,6 Phénol

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The crystal structure of 2,6-dimethylphenol, initially determined at room temperature, has been reinvestigated at -150° using three-dimensional single-crystal X-ray data. The molecules, linked by hydrogen bonds, form infinite chains within the crystal. All hydrogen atoms were located. Systematic deformations of the benzene ring, similar to those of analogous compounds, have been observed.

Introduction

La détermination de la structure du diméthyl (DM)-2,6 phénol se rattache à l'étude structurale des dérivés du

phénol poursuivie au laboratoire (Bois 1970, 1972; Neuman & Gillier-Pandraud, 1973). Nous avons en premier lieu utilisé comme base les données de diffraction enregistrées à température ambiante. Il est