

Neutron and X-ray Diffraction Study of the Thermal Motion in K_2PtCl_6 as a Function of Temperature

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Abstract

The crystal structure and thermal displacement parameters of potassium hexachloroplatinate, K_2PtCl_6 , have been studied as functions of temperature between 8 and 380 K, using four single crystal neutron diffraction, five single crystal X-ray diffraction and two neutron powder diffraction data sets. Third-order anharmonic Gram-Charlier terms have been determined in all the neutron single crystal and two of the X-ray refinements. Results are consistent with a predominantly ionic compound $K_2^+(PtCl_6)^{2-}$. The dimensions of the octahedral $(PtCl_6)^{2-}$ ion hardly vary with temperature. During thermal expansion, these rigid ions move farther apart. The temperature dependence of the atomic mean-square displacements agrees well with that of ensemble-averaged quantized harmonic oscillators. The thermal motion of $(PtCl_6)^{2-}$ is dominated by rigid-body libration and translation, but contributions from internal vibrations are also identified. The anharmonic coefficients of Cl at high temperature agree with curvilinear motion due to the rigid-body libration. The motion of K^+ is also anharmonic.

1. Introduction

Combined X-ray and neutron diffraction investigations of crystal structures as functions of temperature provide, at least in principle, information on harmonic and anharmonic motions and electron density distributions. They may also serve to assess the precision attainable with and the systematic errors typical for these methods (e.g. see Coppens *et al.*, 1984). The experimental determination of electron distributions by X-ray diffraction in compounds containing heavy transition metals presents a number of unsolved problems. One such problem is due to the anharmonic motion of heavy atoms whose effect on the X-ray Bragg inten-

sities may be much more important than that of the anharmonic motion of light atoms. The very large electron density of the atomic core of a heavy element scatters X-rays strongly, even at large momentum transfers, as evidenced by the relatively small fall-off of the scattering factor curve at large $\sin \theta/\lambda$. X-ray scattering from such atoms is therefore very sensitive to thermal motion, both harmonic and anharmonic, whose effects may in fact dominate those of chemical bonding. It is well known that atomic vibrations and chemical bonding are not always easily distinguished by X-ray diffraction (Hirshfeld, 1991). In contrast, neutron diffraction gives direct information on thermal motion. Examples of neutron (and also X-ray) studies of the temperature dependence of thermal motion in simple compounds can be found in Willis & Pryor (1975). Out of the abundant more recent work we mention deuterobenzene (Jeffrey *et al.*, 1987), metallic Mg (Iversen *et al.*, 1995) and a silver perchlorate–benzene π complex (McMullan *et al.*, 1997). A combination of X-ray and neutron data may yield an unambiguous separation of vibrational effects and chemical bonding (Coppens, 1967). However, differences in the importance of, and corrections for, systematic errors may result in systematic differences between neutron and X-ray results (Blessing, 1995). Disagreement may also arise from differing resolutions of the respective data sets. The temperature dependence of harmonic atomic mean-square displacements is given by a sum of harmonic quantum oscillator curves, which in simple structures may be dominated by a single or very few terms, e.g. by the librational and translational movements of a rigid group. Results obtained with different experiments may therefore be judged not only by their internal consistency, but also by a comparison with an expected functional dependence on temperature.

K_2PtCl_6 forms a very simple cubic structure suitable for the study of the role of thermal motion in a heavy-

Table 1. Neutron (ILL, BNL) and X-ray single crystal data sets, harmonic (h) and anharmonic (a) refinements

The anharmonic displacement factor expression is $\exp[-2\pi^2 a^{-2} \sum U^i h_i h_i][1 - i(4/3)\pi^3 a^{-3} \sum c^{ijk} h_i h_j h_k]$, the sums including all permutations of the indices ijk and the nonzero terms $U^{11} = U^{22} = U^{33}$ for K and Pt, $U^{11}, U^{22} = U^{33}$ for Cl, c^{123} for K, $c^{111}, c^{122} = c^{133}$ for Cl, and all other terms zero. For harmonic refinements $c^{ijk} = 0$. Weights are $[\sigma_{\text{counting}}^2(|F|^2) + (0.05|F|^2)^2]^{-1}$.

Temperature (K)	380	295	98	20	8
Instrument	D9/ILL	D9/ILL	H4M/BNL	H4M/BNL	X-ray
Wavelength, λ (Å)	0.7023 (1)	0.7023 (1)	1.0462 (1)	1.0462 (1)	0.5608
Measured reflections	840	532	516	473	6141
Independent reflections	171	223	119	119	545
Max. $\sin \theta/\lambda$ (Å ⁻¹)	1.00	1.00	0.77	0.76	1.37
Internal R value	0.010	0.011	0.017	0.011	0.038
μ (mm ⁻¹)	0.0375	0.0375	0.0557	0.0557	9.83
a (Å)	9.7799 (10)	9.7525 (13)	9.6781 (9)	9.6555 (3)	9.649 (4)
K:					
U (Å ² , h)	0.0475 (4)	0.0353 (4)	0.0156 (6)	0.0092 (6)	0.00649 (4)
U (Å ² , a)	0.0474 (4)	0.0352 (4)	0.0158 (6)	0.0092 (6)	
c^{123} (10 ⁵ Å ³)	52 (13)	8 (13)	23 (18)	-10 (17)	
Pt:					
U (Å ² , h)	0.02095 (12)	0.01353 (13)	0.0083 (3)	0.0048 (4)	0.00192 (1)
U (Å ² , a)	0.02091 (11)	0.01347 (13)	0.0086 (3)	0.0047 (4)	
Cl:					
x (h)	0.23654 (4)	0.23723 (4)	0.23918 (8)	0.23973 (8)	0.23997 (2)
x (a)	0.23633 (7)	0.23682 (8)	0.2390 (2)	0.2397 (2)	
U^{11} (Å ² , h)	0.02237 (15)	0.01519 (15)	0.0105 (4)	0.0079 (4)	0.00330 (5)
U^{11} (Å ² , a)	0.02213 (14)	0.01508 (15)	0.0101 (4)	0.0080 (4)	
U^{22} (Å ² , h)	0.05305 (16)	0.04041 (17)	0.0210 (3)	0.0122 (3)	0.00673 (4)
U^{22} (Å ² , a)	0.053145 (15)	0.04042 (16)	0.0209 (3)	0.0122 (3)	
c^{111} (10 ⁵ Å ³)	5 (3)	-9 (3)	-5 (10)	-7 (11)	
c^{122} (10 ⁵ Å ³)	-18 (2)	-15 (3)	-1 (4)	3 (5)	
$R(F)$; $wR(F ^2)$ (h)	0.032:0.030	0.036:0.028	0.056:0.051	0.048:0.045	0.016:0.020
$R(F)$; $wR(F ^2)$ (a)	0.029:0.028	0.034:0.027	0.055:0.051	0.048:0.045	

atom compound (Williams *et al.*, 1973). The space group is $Fm\bar{3}m$. All atoms occupy sites with high symmetries: $m\bar{3}m$ for Pt at 4(a) (000), $\bar{4}3m$ for K at 8(c) ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$) and $4mm$ for Cl at 24(e) ($x00$). The structure is described later in §3. The charge density determined from X-ray diffraction has been reported to show features near Pt typical for a d^8 ion in an octahedral ligand field (Takazawa *et al.*, 1990). In contrast, accurate X-ray studies at room temperature (Restori & Schwarzenbach, 1993) and 100 K (Restori & Schwarzenbach, 1996) indicated that nonspherical features near K and Cl can be attributed exclusively to anharmonic thermal motion rather than to bonding. Results for Pt also indicate the presence of anharmonic motion, but are more uncertain since the relevant features are very close to the atom center and may be influenced by the uncertainty of the dispersion corrections and the limited resolution of the data.

The present paper presents the structural parameters of K_2PtCl_6 derived from 11 data sets. Six neutron diffraction data sets have been collected at different sources and instruments, at several temperatures between 20 and 380 K, and using single crystals as well as powder samples. We also report results obtained with X-ray diffraction data measured at 8 K. These new data permit verifying the X-ray results published previously and also studying the precision attainable in a determination of the thermal parameters with neutrons.

2. Experimental and data analysis

2.1. Single crystal neutron diffraction

Single crystal neutron diffraction experiments (Table 1) were carried out both at Brookhaven National Laboratory (BNL) and at the Institut Laue Langevin (ILL). At BNL, data were collected at 20 and 98 K on instrument H4M of the HFBR reactor, using a neutron wavelength of $\lambda = 1.0462$ (1) Å and in-pile collimation of $20'$. The monochromator was Be(002) with take-off angle $2\theta_M = 34^\circ$. Data collection was carried out using ω scans with a scan width of $10'$. The collimation defining the range of the scattering angle $\Delta(2\theta)$ covered by the single-tube BF_3 detector was adjusted experimentally; significantly increased $\Delta(2\theta)$ ranges were used for $2\theta > 62'$. The crystal, with linear dimensions 5 mm, was mounted with high-vacuum silicon grease on an aluminium pin inside an aluminium can of 20 mm diameter. A closed-cycle helium refrigerator was used for cooling; an additional heat shield was used at temperatures above liquid nitrogen temperature. The total measuring time for both data sets was 7 days.

At ILL, data were collected at 295 and 380 K on diffractometer D9 at the hot source with neutron wavelength $\lambda = 0.7023$ (1) Å. The instrument is equipped with a small area detector yielding a much improved separation of signal and background (Wilkinson & Khamis, 1988). The crystal with linear dimen-

sions of approximately 5 mm was mounted on a ceramic material and kept at the required temperature inside a small furnace. The total measuring time for both data sets was 4 d.

The values of the merging factors given in Table 1 range from 0.010 to 0.017 and indicate the internal consistency of the data sets to be acceptable. The absorption corrections were calculated analytically. Structure refinements against $|F|^2$ were carried out with the *UPALS* package (Lundgren, 1978), with weights equal to the inverse variances of $|F|^2$. Neutron scattering lengths were taken from Sears (1992). A type I extinction correction parameter (Becker & Coppens, 1974) was included as a variable parameter. Anharmonic displacements were represented by the Gram-Charlier series expansion (Coppens, 1993).

2.2. Neutron powder diffraction

The sample was prepared from commercially available K_2PtCl_6 powder (Fluka puris, p.a.), and enclosed under He gas atmosphere into a cylindrical vanadium container of approximately 9 mm inner diameter and 50 mm height. The sample was cooled with a closed-cycle helium refrigerator. Diffraction experiments (Table 2) at 22 and 295 K were carried out in high-resolution mode on the multi-detector powder diffractometer DMC (Schefer *et al.*, 1990) situated at the Saphir reactor of the Paul Scherrer Institute. The neutron wavelength of $\lambda = 1.0863$ (2) Å was obtained from a vertically focusing Ge (511) monochromator. The data used for structure refinement extended to $(\sin \theta/\lambda)_{\max} = 0.84$ Å⁻¹.

The observed profile intensities were corrected for absorption; the linear absorption coefficient μ was measured with a neutron transmission experiment which resulted in $\mu r = 0.220$, where $r = 4.5$ mm is the sample radius. The structural parameters were refined with the Rietveld profile analysis program of Boysen (1992), which also offers the refinement of third-order anharmonic displacement parameters. Neutron scattering lengths were taken from Sears (1992). The background was interpolated linearly from points chosen in the intervals between Bragg reflections. Thermal diffuse scattering was not corrected for. Third-order anharmonic displacements represented by the Gram-Charlier series expansion (Coppens, 1993) refined to insignificant values, as judged by the large standard uncertainties (s.u.'s). Final refinements were therefore carried out with the program *FullProf* (Rodríguez-Carvajal, 1993) in the anisotropic harmonic approximation, assuming a general peak shape (Thompson-Cox-Hastings pseudo-Voigt); only the harmonic model is reported here. The powder patterns are shown in Fig. 1. They contain 152 inequivalent reflections. The fit with the calculated profile obtained in the structure refinement is satisfactory, except at

Table 2. Neutron powder diffraction data sets and harmonic refinements

Wavelength $\lambda = 1.0863$ (2) Å, linear absorption coefficient measured with transmission experiment $\mu = 0.0489$ mm⁻¹, number of reflections 152, $(\sin \theta/\lambda)_{\max} = 0.84$ Å⁻¹. R_{wp} is the weighted agreement factor for the complete profile, R_{exp} is the corresponding expected value from counting statistics, the goodness-of-fit $S = R_{wp}/R_{exp}$, R_{Bragg} is the usual agreement factor for integrated Bragg intensities.

Temperature (K)	295	22
Lattice parameter a (Å)	9.7537 (5)	9.6654 (3)
K: U (Å ²)	0.0306 (8)	0.0064 (3)
Pt: U (Å ²)	0.0127 (3)	0.0026 (2)
Cl: x	0.2368 (1)	0.2396 (1)
U^{11} (Å ²)	0.0160 (4)	0.0034 (2)
U^{22} (Å ²)	0.0400 (4)	0.0090 (2)
R_{wp} ; R_{exp}	0.034; 0.024	0.041; 0.029
S ; R_{Bragg}	1.42; 0.061	1.41; 0.035

$2\theta \simeq 33^\circ$ where an unexplained residual peak remains near the 333/511 reflection.

2.3. X-ray single crystal data sets

The results of the refinements on the neutron data sets will be compared with those obtained for five X-ray data sets whose resolutions are considerably larger than those of the neutron data sets. Three extensive and precise X-ray data sets were measured at 293, 100 (Restori & Schwarzenbach, 1993, 1996) and 8 K, using Ag $K\alpha$ radiation ($\lambda = 0.5608$ Å) and the same crystal. The resolutions at 293 and 100 K are $(\sin \theta/\lambda)_{\max} = 1.30$ and 1.54 Å⁻¹; the redundancies defined by the ratios of the numbers of observed and symmetry-independent

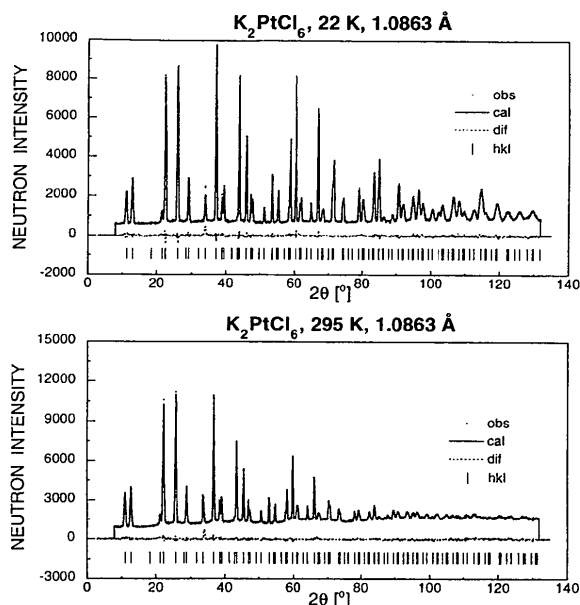


Fig. 1. Observed (background subtracted), calculated and difference neutron powder diffraction patterns of K_2PtCl_6 at 22 and 295 K. Vertical bars show the positions of the Bragg maxima.

Table 3. Selected interatomic distances (\AA) from harmonic refinements

The standard uncertainties given in parentheses refer to the last digits; the uncertainty of the neutron wavelength is not included. The letters n , p and x refer to the neutron single crystal, powder and X-ray single crystal data sets, respectively. Interionic contacts in the cubic closest sphere packing are denoted by c.c.p.

Data set temperature	Pt—Cl ($PtCl_6$) ²⁻	Cl—Cl ($PtCl_6$) ²⁻	Cl—Cl c.c.p.	Cl—K c.c.p.	K—Pt
n , 380	2.3133 (4)	3.2716 (6)	3.6439 (6)	3.4602 (4)	4.2348 (4)
n , 295	2.3136 (5)	3.2719 (7)	3.6242 (7)	3.4503 (5)	4.2230 (6)
p , 295	2.3097 (10)	3.2664 (14)	3.6305 (14)	3.4509 (2)	4.2235 (2)
x , 293	2.3133 (8)	3.2715 (11)	3.6179 (11)	3.4468 (11)	4.2188 (13)
x Ag $K\alpha$, 120	2.3164 (8)	3.2758 (11)	3.5768 (11)	3.4280 (1)	4.1964 (1)
x Mo $K\alpha$, 120	2.3152 (4)	3.2742 (6)	3.5750 (6)	3.4262 (1)	4.1942 (1)
x , 100	2.3144 (5)	3.2730 (7)	3.5668 (7)	3.4215 (7)	4.1885 (9)
n , 98	2.3148 (8)	3.2736 (11)	3.5698 (11)	3.4233 (3)	4.1907 (4)
p , 22	2.3158 (10)	3.2751 (14)	3.5594 (14)	3.4187 (1)	4.1852 (1)
n , 20	2.3147 (8)	3.2735 (12)	3.5540 (12)	3.4152 (1)	4.1810 (1)
x , 8	2.3155 (7)	3.2746 (11)	3.5483 (11)	3.4128 (11)	4.1781 (13)

reflections are 18.4 and 14.4. Measuring times were approximately a month for each. Two data sets measured at 120 K with Ag $K\alpha$ and Mo $K\alpha$ radiations have been reported by Takazawa *et al.* (1990). Respective resolutions are $(\sin \theta/\lambda)_{\max} = 1.15$ and 1.22 \AA^{-1} , with redundancies of 8.4 and 12.7. Results from published work are not reproduced explicitly here. We only note that anharmonic terms of K and Cl at 293 and 100 K assume significant values. The 8 K data shown in Table 1 have not been reported previously. They were collected at Aarhus (Denmark) on a Huber four-circle diffractometer equipped with a displax helium cooling device. A precise absorption correction was carried out as in Restori & Schwarzenbach (1993, 1996). Structure refinements including a correction for secondary extinction (Becker & Coppens, 1974) were performed with the program *LSYEXP* (Restori & Schwarzenbach, 1992). For the 8 K data, the anharmonic terms were not significant and only the harmonic model is reported here.†

3. Results and discussion

Resulting structural parameters and reliability factors from the hitherto unpublished data sets are given in Tables 1 and 2. The crystal structure of K_2PtCl_6 is related to the fluorite CaF_2 -type structure: octahedral $(PtCl_6)^{2-}$ ions occupy the corners and face centers of the unit cell, and K^+ occupies interstices formed by four such ions. In an alternative description, K and Cl are arranged together in a slightly distorted cubic closest packing (c.c.p.), where K is coordinated cuboctahedrally by 12 Cl atoms and Pt occupies half the octahedral

voids formed by Cl. Important interatomic distances, as shown in Table 3, are therefore Pt—Cl and Cl—Cl in the $(PtCl_6)^{2-}$ ion, interionic Cl—Cl and Cl—K contacts in the closest sphere packing, and Pt—K.

3.1. Thermal expansion

The observed lattice constants a are given in Table 1 and in the literature (Takazawa *et al.*, 1990; Restori & Schwarzenbach, 1993, 1996). They may also be calculated from the distances $d(Pt—K) = a(3)^{1/2}/4$ in Table 3. A linear regression line fitted to a as a function of temperature yields an average temperature-independent linear expansion coefficient. However, the spread of the individual values about this line shows the standard uncertainties (s.u.'s) to be considerably underestimated, on average by a factor of ~ 4 . This factor may be attributed to actual systematic errors to each experiment (Parrish, 1960). The coefficient of linear expansion α derived from the slope of the unweighted regression line through all data points $a(T) = a_0(1 + \alpha T)$ is $\alpha = 3.7(2) \times 10^{-5} \text{ K}^{-1}$, the lattice constant at zero temperature being $a_0 = 9.645(3) \text{ \AA}$. The X-ray data alone yield a similar fit with $\alpha = 3.4(2) \times 10^{-5} \text{ K}^{-1}$ and $a_0 = 9.646(4) \text{ \AA}$.

The first two columns of Table 3 show the dimensions of the $(PtCl_6)^{2-}$ ion to be almost independent of temperature, with an unweighted average Pt—Cl distance of $2.3142(2) \text{ \AA}$. The s.u. of an individual distance calculated from the spread about this average is 0.0017 \AA . The individual s.u.'s in Table 3 thus appear to be underestimated by a factor of about three. The apparent very slight contraction of the ion with increasing temperature is probably due to rigid-body libration, as discussed later. The thermal expansion of the Cl—Cl c.c.p. distance is particularly pronounced with $\alpha = 7.2(3) \times 10^{-5} \text{ K}^{-1}$ and a distance at 0 K of $d_0 = 3.547(2) \text{ \AA}$. The thermal expansion of Pt—K is exactly equal to, and that of K—Cl very close to, that of the lattice constant a . These expansions of the interatomic

† The numbered intensity of each measured point on the profile, $|F|^2$ values derived from the four neutron single crystal and the 8 K X-ray single crystal data sets, and the two neutron powder diagrams have been deposited with the IUCr (Reference: AB0382). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances simply describe rigid $(\text{PtCl}_6)^{2-}$ ions moving farther apart with increasing temperature.

3.2. Thermal harmonic displacement parameters

The temperature dependence of the four displacement parameters U^{ij} resulting from the harmonic refinements is illustrated in Fig. 2. Although the spread of the individual U^{ij} values attributable to various systematic errors is much larger than the s.u.'s given in Tables 1 and 2, the general trends are consistent. $U^{11}(\text{Cl})$ representing the m.s. displacement along the Pt–Cl bond is of the same order of magnitude, but consistently slightly larger than $U(\text{Pt})$. The Pt–Cl bond thus appears to be close to, but not quite, rigid (Hirshfeld, 1976). The difference $U^{11}(\text{Cl}) - U(\text{Pt})$ attributable to internal vibrations of the $(\text{PtCl}_6)^{2-}$ ion, to bond stretching, in particular, fluctuates somewhat, but does not increase from the lowest to the highest temperatures, as would be expected for a relatively stiff Pt–Cl bond exhibiting mainly zero-point vibration. The m.s. displacements $U^{22}(\text{Cl})$ perpendicular to the Pt–Cl bond and $U(\text{K})$ are between two and three times larger than $U(\text{Pt})$ and $U^{11}(\text{Cl})$. They represent the vibrations of the joint cubic closest packing of Cl and K. If it is assumed that the $(\text{PtCl}_6)^{2-}$ ion vibrates as a rigid body, the m.s. libration amplitude L (Fig. 3) is obtained from

$$L = [U^{22}(\text{Cl}) - U^{11}(\text{Cl})]/[a^2 x_{\text{Cl}}^2].$$

The r.m.s. amplitudes $L^{1/2}$ vary between $4.3 (2)^\circ$ at 380 K and $1.5 (5)^\circ$ at 8 K. These values represent upper limits since internal angle bending modes of the $(\text{PtCl}_6)^{2-}$ ion are also expected to contribute to $U^{22}(\text{Cl})$. The m.s. displacement as a function of temperature of an atom vibrating in an effective harmonic mean-field potential is represented by the quantized harmonic oscillator curve (Dunitz *et al.*, 1988)

$$U = (h/8\pi^2 \mu \nu) \coth(h\nu/2kT)$$

or by a sum over several such expressions; μ is the reduced mass, ν the frequency, h Planck's constant and k Boltzmann's constant. The curves for $U(\text{K})$ and $U^{22}(\text{Cl})$ in Fig. 2 represent single oscillators where the respective masses are assumed to be equal to the atomic masses $m(\text{K})$ and $m(\text{Cl})$. The respective frequencies obtained by a weighted fit to all data points are $\nu(\text{K}) = 70$, $\nu_{22}(\text{Cl}) = 68 \text{ cm}^{-1}$. The curves for $U(\text{Pt})$ and $U^{11}(\text{Cl})$ represent sums of two oscillator contributions, *viz.* $U_{\text{trans}} + U_{\text{int}}(\text{Pt})$ and $U_{\text{trans}} + U_{\text{int}}(\text{Cl})$, with a total of three adjusted frequencies. U_{trans} is the same for Pt and Cl; it represents the effect of the translational movement of a rigid $(\text{PtCl}_6)^{2-}$ ion with an effective mass of $m(\text{Pt}) + 6m(\text{Cl})$. U_{int} is an overall representation of internal vibrations of $(\text{PtCl}_6)^{2-}$; the effective masses are assumed to be $m(\text{Pt})$ and $m(\text{Cl})$ for $U_{\text{int}}(\text{Pt})$ and $U_{\text{int}}(\text{Cl})$, respectively. The corresponding frequencies are $\nu(\text{Pt, int}) = 106$, $\nu_{11}(\text{Cl, int}) = 256$, $\nu(\text{trans}) = 38 \text{ cm}^{-1}$. With U_{trans} alone, no satisfactory fit with the

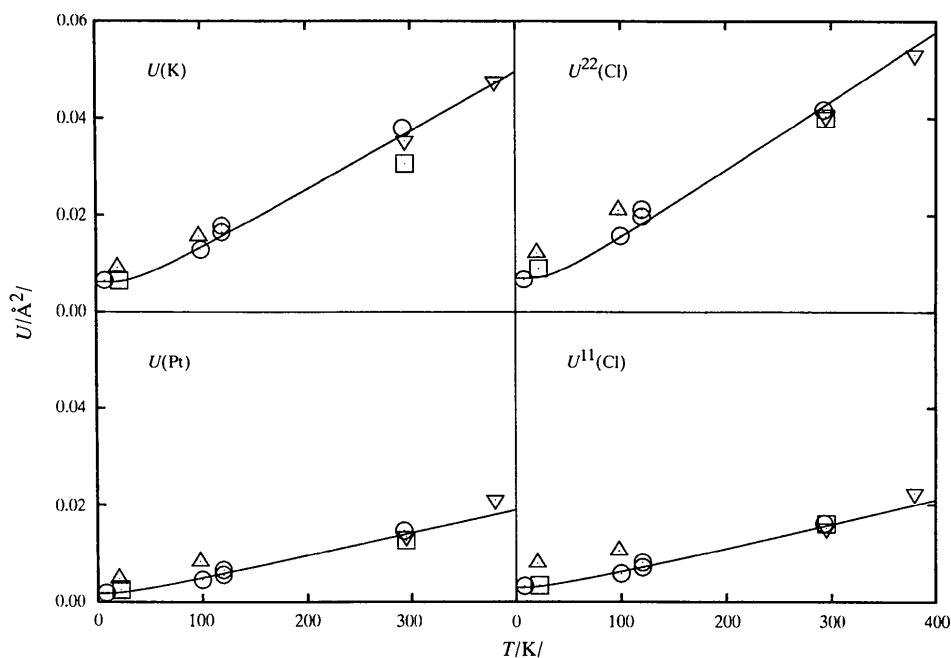


Fig. 2. Displacement parameters U^{ij} as a function of temperature. Symbols: circles for X-ray data, triangles for neutron single crystal data (pointing downward ILL, pointing upward BNL) and squares for neutron powder data. S.u.'s from least squares are in all cases smaller than the symbols. The curves represent quantized harmonic oscillators. Single crystal X-ray data at 120 K are taken from Takazawa *et al.* (1990), and at 100 and 293 K from Restori & Schwarzenbach (1993, 1996).

observations is obtained, which indicates that the effects of the internal contributions are substantial. Fig. 3 shows the oscillator curve for the librational movement of $(PtCl_6)^{2-}$, assuming the moment of inertia $4m(Cl)d^2$, d being the Pt–Cl distance extrapolated to 0 K; $\nu(\text{libr}) = 44 \text{ cm}^{-1}$. All these frequencies represent averages over several normal modes, but they are of the expected order of magnitude (Labonville *et al.*, 1972). Their s.u.'s calculated from the fit with the data are less than 1 cm^{-1} ; considering the approximate nature of the model, they are certainly far too small.

3.3. Anharmonic motions

One of the motivations of the present study was to corroborate the anharmonic vibration parameters published by Restori & Schwarzenbach (1993, 1996) on the basis of extensive and precise X-ray diffraction data measured at 293 and 100 K. In these studies statistically significant values were obtainable for the third-order coefficients $c^{123}(K)$ and $c^{122}(Cl)$ [in units of 10^{-5} \AA^3 : 42 (4) and -27 (5) at 293 K, 4.6 (8) and -3.3 (7) at 100 K, respectively], which agreed well with the expected temperature dependence $c^{ikl} \simeq T^2$. Moreover, $c^{111}(Cl)$ turned out to be zero. The corresponding values obtained from the single crystal neutron diffraction data (Table 1) are less precise, as evidenced by the much larger s.u.'s. This is attributed to the fact that the neutron data sets are less extensive than the X-ray data sets, since experimental time available at a

neutron source cannot match the time available at a laboratory X-ray source. Nevertheless, the neutron data tend to corroborate the above findings. At 380 K, $c^{123}(K)$ and $c^{122}(Cl)$ are statistically significant and have magnitudes and signs consistent with the X-ray results, whereas $c^{111}(Cl)$ is again close to zero. At the other temperatures, the s.u.'s of the third-order coefficients are so large that they neither contradict nor validate the X-ray results. More definite results may be expected from neutron experiments performed at higher temperatures.

The interpretation of these coefficients is straightforward. K has a somewhat distorted cuboctahedral coordination with four small and four large triangular faces. The small triangles are faces of the $(PtCl_6)^{2-}$ octahedron and the large triangles are faces of the unoccupied octahedral voids bordered by Cl only. The positive $c^{123}(K)$ term indicates that the m.s. amplitude of K is larger in the direction of the large triangles and the largest structural voids, and smaller towards the small triangles and Pt, in agreement with intuition. The negative $c^{122}(Cl)$ term is explained by the rigid-body libration of the $(PtCl_6)^{2-}$ ion. A librating Cl atom moves on the surface of a sphere with radius Pt–Cl, whereas the conventional **U** tensor represents rectilinear motion. The difference between rectilinear and curvilinear motions can be described by anharmonic terms. The leading term for the $(PtCl_6)^{2-}$ ion calculated using the theory of Willis & Pawley (1970) is

$$c^{122} = -[U^{22}(Cl) - U^{11}(Cl)]^2 / [ax_{Cl}].$$

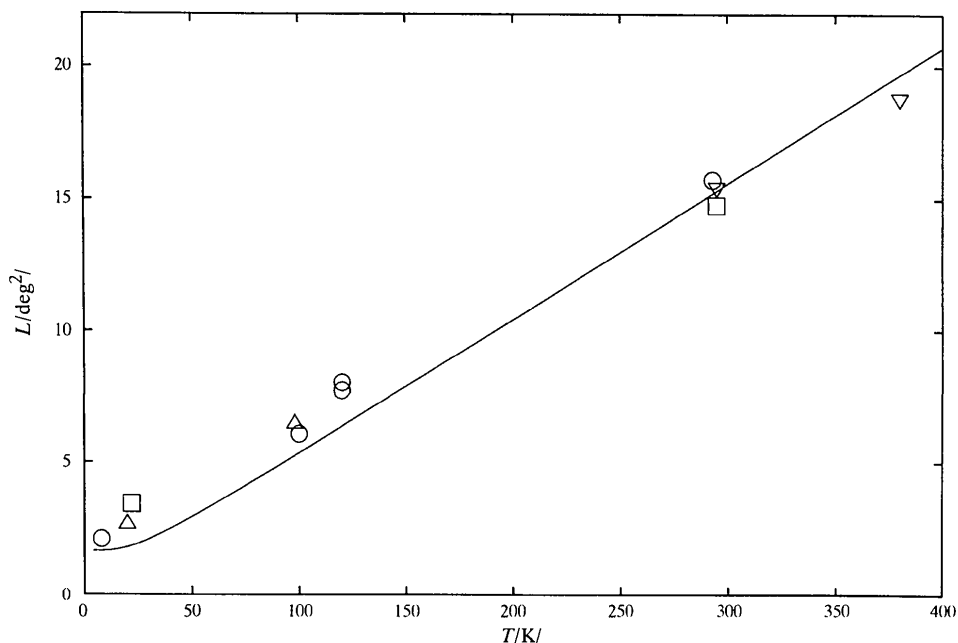


Fig. 3. Mean-square libration amplitude L of the $(PtCl_6)^{2-}$ ion as a function of temperature. The curve represents a single harmonic quantum oscillator. The symbols are defined in Fig. 2.

Calculated values are $c^{122} = -31.5 (5)$, $-4.44 (7)$ and $-42.1 (6) \times 10^{-5} \times \text{\AA}^3$ for the 293 and 100 K X-ray data, and the 380 K neutron data, respectively. The agreement with experiment for the X-ray data is excellent, whereas the refined value for the neutron data is different by a factor of two. This shows that the precision of the neutron data may be just barely sufficient for an assessment of anharmonicity at the highest temperatures.

It has been mentioned earlier that X-ray diffraction is very sensitive to the anharmonic motions of heavy atoms. For example, the values of the fourth-order anharmonic terms of Pt determined with the 293 K and 100 K X-ray data are statistically significant (Restori & Schwarzenbach, 1996). The nonspherical part $c^{111} - 3c^{122}$ is negative and shows the expected T^3 temperature dependence. This anharmonicity may tentatively be attributed to the low-frequency translational motion of $(\text{PtCl}_6)^{2-}$ described above, the amplitudes along the $\langle 111 \rangle$ directions towards the voids containing K^+ being somewhat larger than those along $\langle 100 \rangle$.

4. Conclusions

The extensive data on K_2PtCl_6 reveal a consistent picture of the thermal vibrations. The structure contains almost rigid $(\text{PtCl}_6)^{2-}$ ions whose dimensions are virtually independent of temperature. During thermal expansion these ions move farther apart, as evidenced by increasing Cl—Cl van der Waals contacts. Rigid-body translation and libration of the complex ion give the main contributions to the displacement parameters of Pt and Cl. However, the temperature dependences of $U(\text{Pt})$ and $U^{11}(\text{Cl})$ parallel to the Pt—Cl bond indicate the presence of substantial internal motions. The m.s. libration amplitude as a function of temperature follows closely a harmonic oscillator curve. The libration is corroborated by the c^{122} anharmonic coefficient of Cl at high temperature, which is consistent with curvilinear motion. At room temperature, the r.m.s. libration amplitude is $\sim 4^\circ$ and thus as large as for many organic molecular structures. Diffuse broad intensity maxima observed in the neutron powder diffraction diagram taken at 295 K confirm the presence of important thermal vibration amplitudes at room temperature. However, large libration amplitudes call for a libration correction of bond lengths. The required expression for the Pt—Cl bond, $d_{\text{corr}} = d(1 + L)$, results in an increase in the bond length of 0.01 Å at 380 K and only 0.001 Å at 8 K. It thus appears that the dimension of the ion is not exactly constant with temperature. This agrees with the bond-valence model of Brown (1992). The valence of the Pt—Cl bond according to this model is ~ 0.7 . According to Brown *et al.* (1997), the correlation of the thermal motions of Pt and Cl along the bond is then

0.75 (the correlation would be 1.0 for a rigid bond) and the corresponding thermal expansion of the bond at room temperature is indeed expected to be of the order 0.01 Å.

One of the most prominent features of the difference electron density described in Restori & Schwarzenbach (1993, 1996) is an octopolar deformation of the K^+ ion. The agreement of the high-temperature X-ray and neutron values of the third-order anharmonic coefficient $c^{123}(\text{K})$ indicates the origin of this feature to be anharmonicity rather than chemical bonding. This corroborates the conclusion that the compound is essentially ionic, $\text{K}_2^+(\text{PtCl}_6)^{2-}$.

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