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Electron-Density Distribution in Crystals of Potassium Hexachloroplatinate(IV), $K_2[PtCl_6]$

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Abstract. $M_r = 486{\cdot}0$, cubic, $Fm3m$, $Z = 4$, $a = 9{\cdot}7431\,(5)$ Å, $V = 924{\cdot}88\,(9)$ Å^3, $D_m = 3{\cdot}50$, $D_x = 3{\cdot}49$ Mg m^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å, $\mu = 17{\cdot}90$ mm^{-1}, $T = 300\,(2)$ K, $F(000) = 872$, final $R = 0{\cdot}009$ for 135 observed unique reflections with $\sin\theta/\lambda \le 0{\cdot}8$ Å^{-1}. The Pt^{IV} atom is surrounded octahedrally by six Cl$^-$ ions with Pt—Cl distance 2·314 (1) Å. X–X synthesis shows a peak of 0·5 (2) e Å^{-3} in the [111] direction at 0·5 Å from the Pt nucleus; this may be due to the non-bonding 5*d* electrons in t_{2g} orbitals.

Introduction. Aspherical *d*-electron distribution in 3*d* or 4*d* transition-metal complexes has been studied by accurate X-ray structure analysis (Coppens & Hall, 1982; Toriumi & Saito, 1983). The 5*d* transition-metal complex has been scarcely examined because of the strong absorption effect and a small valence/total electron ratio (Stevens & Coppens, 1976). The difference synthesis of the square-planar complex $[PtCl_4]^{2-}$ showed a negative peak on the Pt—Cl bond axis which may be explained in terms of electron deficiency in the $d_{x^2-y^2}$ orbital (Ohba, Sato, Saito, Ohshima & Harada, 1983). The reliability of the X–X synthesis in the study of charge asphericity around heavy metals such as Pt has been tested with crystals of the title compound, $K_2[PtCl_6]$, which has a CaF_2-type structure and has only one positional parameter of the Cl atom (Ewing & Pauling, 1928).

Experimental. D_m reported by Archibald (1910). Single crystals obtained from an aqueous solution by slow cooling; orange octahedra surrounded by {111} faces. A sphere 0·22 (1) mm in diameter prepared with a piece of sandpaper. Rigaku AFC-5 automated four-circle diffractometer, Mo $K\alpha$ radiation, graphite monochromator, collimator 0·5 mm ∅, detector aperture 1·55 × 1·55°, θ–2θ scan, scan speed 2° min^{-1} in θ, scan width $(1{\cdot}3 + 0{\cdot}7\tan\theta)°$, max. number of repetitions 4, criterion to terminate repetitions $\sigma(|F|)/|F| \le 0{\cdot}01$, Ni-foil attenuators inserted when the diffracted beam exceeded 15000 counts s^{-1} ($2{\cdot}34 \le$ attenuation factors $\le 12{\cdot}77$), circuit of correction for counting loss according to equation (4) of Fukamachi (1969), pulse-height analyser, background-correction formula by Iwata & Saito (1973). Variation of standards < 1%, 10 619 $\pm h$, $\pm k$, $\pm l$ reflections with $\chi > -30°$ ($\frac{3}{4}$ of reciprocal space with $\sin\theta/\lambda \le 1{\cdot}22$ Å^{-1}) measured; 8117 with $|F_o| > 3\sigma(|F_o|)$; 410 observed unique reflections. Variation of $|F(111)|$ with azimuthal angle around the scattering vector 7%. Variation of $|F_o|$ arising from crystal non-sphericity 3–5% (Ohba, Sato & Saito, 1981). Neglecting slight anisotropy in the secondary-extinction effect or in absorption, equivalent reflections were averaged; $R_{\rm int}$ $(\sum||F_o| - \langle|F_o|\rangle|/\sum|F_o|) = 0{\cdot}039$ for all 8117 observed reflections and 0·016 for 2946 reflections with $\sin\theta/\lambda \le 0{\cdot}8$ Å^{-1}. Lattice constant determined based on 24 2θ values ($60 < 2\theta < 64°$). Lorentz–polarization and absorption corrections, $\mu r = 1{\cdot}98$ [$2{\cdot}6 < (A^*)^{1/2} < 3{\cdot}6$]. Transmission factors from *International Tables for X-ray Crystallography* (1959) on the basis of which the mean path length of each reflection was calculated (Ohba, Saito & Noda, 1982). Atomic parameters refined with a scale factor by the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). $\sum w(|F_o| - |F_c|)^2$ minimized; $w^{-1} = [\sigma_F(\text{count.})]^2 + (0{\cdot}015|F_o|)^2$. By introducing an isotropic secondary-extinction correction parameter (Zachariasen, 1967), R slightly reduced from 0·044 to 0·043 for the 410 unique reflections. At this stage of the refinement $|F_o|$ of high-angle reflections was found to be generally greater than $|F_c|$. Because this seemed to be due to X-ray diffuse scattering as in the case of $K_2[PtCl_4]$, high-order reflections ($\sin\theta/\lambda > 0{\cdot}8$ Å^{-1}) were excluded from the refinement. $B_{\rm eq}$ then increased by 0·16–0·19 Å^2. R became 0·011 and $wR = 0{\cdot}018$ for the 135 unique reflections. The valence-orbital populations of the Pt and Cl atoms were then refined. Charge of the K$^+$ ion was fixed as +1 and total charge in the unit cell was kept neutral. The orbital scattering factors of Pt were calculated from the Hartree–Fock wavefunctions (Mann, 1967) using the program *FORM* provided by Professor S. Wakoh; those of Cl$^-$ and K$^+$ were from Fukamachi (1971). Valence orbitals of the Pt and Cl atoms were assumed to be $(5s)^2(5p)^6(5d)^6$ and $(3p)^6$,

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Table 1. *Positional and thermal* (Å^2) *parameters*

The thermal parameters are expressed as follows:
$\exp[-2\pi^2a^{*2}(h^2U_{11}+k^2U_{22}+l^2U_{33})]$.

	x	y	z	U_{11} or $U_{\rm iso}$	U_{22}	U_{33}
Pt	0	0	0	0·01658 (8)		
Cl	0·23750 (7)	0	0	0·01913 (24)	0·04703 (21)	$(=U_{22})$
K	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·04102 (25)		

respectively, and radial parameters were not introduced. Effective charge of the Pt and Cl atoms was determined to be +2·3 (3) and −0·7 (3), respectively. Final $R = 0{\cdot}009$ and $wR = 0{\cdot}017$, $S = 0{\cdot}61$.* $\Delta/\sigma < 0{\cdot}06$. Reflection:parameter ratio 135:8. Smallest extinction factor (F_o^2/F_c^2) 0·71 for 400. Anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic parameters are given in Table 1.

The Pt—Cl bond distance of 2·314 (1) Å is almost the same as that in $K_2[PtCl_4]$ [2·310 (1) Å; Ohba *et al.*, 1983]. Anisotropy in the Cl thermal vibration was found. The ratio of the largest (⊥Pt—Cl bond) and the smallest (∥Pt—Cl bond) mean displacements is 1·6 (1) while that in $K_2[PtCl_4]$ is 1·4 (1). The thermal parameters of the Pt and Cl atoms could not be explained completely by the rigid-body motion of $[PtCl_6]^{2-}$. The r.m.s. amplitudes of the isotropic translational and vibrational motion of the $(Cl^-)_6$ moiety are 0·14 (2) Å and 4·2 (5)°, respectively, whereas the r.m.s. amplitude of the central Pt atom is 0·13 (1) Å (Cruickshank, 1956). Difference electron densities were calculated based on the 135 unique reflections with $\sin\theta/\lambda \leq 0{\cdot}8$ Å^{-1}, where the densities of spherical atoms with refined charge, $Pt^{2\cdot3+}$, $Cl^{0\cdot7-}$ and K^+, were subtracted in order to show the charge asphericity clearly. The scale factor for $|F_o|$ in the last cycle of the charge refinement was used. The section of the (110) plane through the Pt nucleus is shown in Fig. 1. A positive peak of 0·5 (2) e Å^{-3} is located on the threefold axis 0·5 Å from the Pt nucleus, whereas a negative trough is observed on the Pt—Cl bond axis. The standard deviation assigned to the deformation density was estimated from the errors in $|F_o|$ and an error in the scale factor (Toriumi & Saito, 1978). The charge asphericity is the same as was found around the transition-metal atoms in $K_2Na[Co(NO_2)_6]$ (Ohba, Toriumi, Sato & Saito, 1978) and in FeS_2 (Stevens, De Lucia & Coppens, 1980). This asphericity may be due to the non-bonding 5*d* electrons. In fact, the electron configuration of Pt^{IV} is $(5d)^6$. The electrons occupy t_{2g} orbitals in an octahedral ligand field and the electron density in the [111] direction increases relative to that in the [100] direction. The distance of the *d*-electron peak from the Pt nucleus, 0·5 Å, is reasonable since those of the 3*d* transition-metal complexes range from 0·3 to 0·5 Å. The present study confirmed that the charge asphericity around the 5*d* transition-metal atoms can be detected on the deformation density maps even when the *d*/total electron ratio is 6/78. The number of electrons with a sphere centred at the Pt nucleus was calculated by the direct integration of charge density (Kobayashi, Marumo & Saito, 1972). It was estimated to be 77·8 (8), since the number of electrons in the Pt sphere did not increase significantly when the radius of the sphere was varied from 1·3 to 1·5 Å. The Pt atom is largely neutralized in accordance with Pauling's (1960) electroneutrality rule. The negative deformation densities around the Cl atom in Fig. 1 suggest the polarization of the electron density. The bonding electron was not found on the Pt—Cl bond axis, although it was observed for $K_2[PtCl_4]$. This discrepancy cannot be rationalized at present. The effect of the diffuse scattering which may be caused mainly by the lattice defects was observed for crystals of both $K_2[PtCl_4]$ and $K_2[PtCl_6]$, while the disturbance has not been reported in the study of charge density around the 3*d* transition-metal atoms. Further study should be carried out to confirm whether diffuse scattering is always observed for crystals for heavy-metal complexes.

Note on $K_2[PtCl_4]$

Our previous paper reported that the neutron diffraction data of $K_2[PtCl_4]$ produced thermal parameters which were 10–30% higher than those obtained by the X-ray study (Ohba *et al.*, 1983). Recently Harada (1983) pointed out that the high-angle reflections could not be covered by the ω-scan technique with a detector aperture of 3·01 × 3·01° when the incident-beam divergence was more than 1°

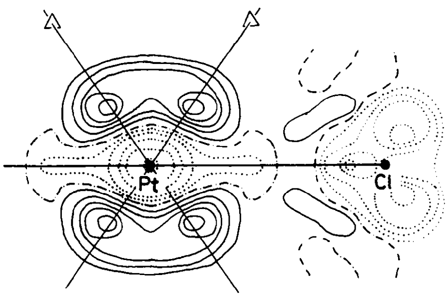

Fig. 1. A section of the *X–X* synthesis through the Pt nucleus and two threefold axes. Contours are drawn at intervals of 0·1 e Å^{-3}. Negative contours are dotted, zero contours chain-dotted.

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* A list of structure factors for $K_2[PtCl_6]$, and a recalculated list of structure factors and atomic parameters for $K_2[PtCl_4]$ based on neutron data with $\sin\theta/\lambda \leq 0{\cdot}6$ Å^{-1} have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39539 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and monochromatization was not sufficient. Recalculation based on only the low-order reflections with $\sin\theta/\lambda \le 0{\cdot}6$ Å^{-1} gave $R(F)$ 0·028 for 110 unique reflections and $wR(F) = 0{\cdot}035$.* Equivalent isotropic thermal parameters, $B_{\rm eq}$, for Pt, Cl and K decreased from 2·22 (10), 2·89 (6) and 3·33 (24) Å^2 to 1·83 (10), 2·49 (6) and 2·92 (21) Å^2, respectively and approached the X-ray values, 1·69 (1), 2·47 (2) and 2·85 (3) Å^2.

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* See deposition footnote.

References

Archibald, E. H. (1910). *Z. Anorg. Chem.* **66**, 191.

Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.

Coppens, P. & Hall, M. B. (1982). Editors. *Electron Distributions and the Chemical Bond.* New York: Plenum.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.

Ewing, F. J. & Pauling, L. (1928). *Z. Kristallogr.* **68**, 223–230.

Fukamachi, T. (1969). *Jpn. J. Appl. Phys.* **8**, 851–854.

Fukamachi, T. (1971). Tech. Rep. B12. Institute for Solid State Physics, Univ. of Tokyo.

Harada, J. (1983). Private communications.

International Tables for X-ray Crystallography (1959). Vol. II, 2nd ed., p. 300. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Iwata, M. & Saito, Y. (1973). *Acta Cryst.* B**29**, 822–832.

Kobayashi, A., Marumo, F. & Saito, Y. (1972). *Acta Cryst.* B**28**, 2709–2715.

Mann, J. B. (1967). *Atomic Structure Calculations* I. Report LA-3690. Los Alamos Scientific Laboratory, Univ. of California.

Ohba, S., Saito, Y. & Noda, Y. (1982). *Acta Cryst.* A**38**, 725–729.

Ohba, S., Sato, S. & Saito, Y. (1981). *Acta Cryst.* A**37**, 697–701.

Ohba, S., Sato, S., Saito, Y., Ohshima, K. & Harada, J. (1983). *Acta Cryst.* B**39**, 49–53.

Ohba, S., Toriumi, K., Sato, S. & Saito, Y. (1978). *Acta Cryst.* B**34**, 3535–3542.

Pauling, L. (1960). *The Nature of the Chemical Bond,* 3rd ed. Ithaca: Cornell Univ. Press.

Stevens, E. D. & Coppens, P. (1976). *Acta Cryst.* A**32**, 915–917.

Stevens, E. D., De Lucia, M. L. & Coppens, P. (1980). *Inorg. Chem.* **19**, 813–820.

Toriumi, K. & Saito, Y. (1978). *Acta Cryst.* B**34**, 3149–3156.

Toriumi, K. & Saito, Y. (1983). *Advances in Inorganic Chemistry and Radiochemistry*, pp. 27–81. New York: Academic Press.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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Preparation and Structure of the Aluminium Ammonium Phosphate Dihydrate $Al_2[NH_4](OH)(PO_4)_2.2H_2O$:* A Tunnel Structure with Ammonium Ions in the Channels

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Abstract. $M_r = 315{\cdot}0$, monoclinic, $P2_1/n$, $a = 9{\cdot}553$ (1), $b = 9{\cdot}577$ (1), $c = 9{\cdot}614$ (1) Å, $\beta = 103{\cdot}56$ (1)°, $V = 855{\cdot}1$ Å^3, $Z = 4$, $D_x = 2{\cdot}45$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 6{\cdot}4$ cm^{-1}, $F(000) = 640$, $T = 293$ K. Final $R = 0{\cdot}025$ for 2449 observed data. The structure is isomorphous with $GaPO_4.2H_2O$ with columns of Al-centred corner- and edge-shared octahedra linked *via* PO_4 tetrahedra to outline channels approximately parallel to the b axis. Ammonium groups occupy these channels and are hydrogen-bonded to framework O atoms and water molecules.

Introduction. Aluminium phosphate hydrates with Al/P = 1·0 have been reported as the minerals variscite (Kniep, Mootz & Vegas, 1977) and metavariscite (Kniep & Mootz, 1973). In these structures P and Al are in tetrahedral and octahedral coordination respectively. Recently a new class of molecular sieves constructed by a network of corner-shared AlO_4 and PO_4 tetrahedra has been described and one of these phases has had its structure determined from single-crystal X-ray data (Wilson, Lok & Flanigen, 1982; Wilson, Lok, Messina, Cannan & Flanigen, 1982). It was during the attempted synthesis of the aluminium phosphate molecular sieve, $AlPO_4$-14 (Wilson, Lok & Flanigen, 1982), that a new structure type for $AlPO_4$ was synthesized. In this structure Al is in an octahedrally coordinated site thereby relating it to variscite and metavariscite.

Subsequent to the determination of the structure of the compound reported here it was found to be isomorphous with $GaPO_4.2H_2O$ (Mooney-Slater,

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* Dialuminium ammonium hydroxide bis(orthophosphate).