

## Ammonium Hexafluoroplatinate(IV)

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**Abstract.**  $(\text{NH}_4)_2\text{PtF}_6$ ,  $M_r = 345.1$ , cubic,  $Fm\bar{3}m$ ,  $a = 8.451$  (8) Å,  $U = 603.6$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 616$ ,  $D_c = 3.792$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 22.40$  mm<sup>-1</sup>. The crystals are of the  $\text{K}_2\text{PtCl}_6$  (antifluorite) structure type, with Pt–F = 1.942 (8) Å. The final  $R = 0.029$  for 71 reflections.

**Introduction.** Potassium hexafluoroplatinate(IV) was prepared by direct fluorination of potassium hexachloroplatinate(IV) at 573 K (Peacock, 1960). This was converted to the ammonium salt by treatment of an aqueous solution with a cation exchange resin (Zeocarb 225 SRC 10) previously charged by ammonium chloride solution. Pale-yellow crystals were obtained from the treated solution predominantly as hexagonal plates. A crystal  $0.125 \times 0.28 \times 0.30$  mm was mounted about  $c$  of the triple hexagonal cell of a primitive rhombohedral cell, which in turn is related to a face-centred cubic unit cell. The cell dimensions of the hexagonal cell were obtained from  $2\theta$  values measured on a Stoe Weissenberg diffractometer (graphite-monochromated Mo  $K\alpha$  X-rays) and found to be  $a = 5.976$  (5),  $c = 14.65$  (1) Å. The intensities of all accessible reflections with  $5 \leq 2\theta \leq 60^\circ$  from layers  $hk0$ –15 were collected by an  $\omega$ -scan technique (Clark

& Russell, 1978) and corrected for Lorentz, polarization and absorption effects. Full-matrix least-squares refinement, minimizing  $\sum w(|F_o| - |F_c|)^2$ , was performed in space groups  $R\bar{3}$  [data averaged to 274 independent intensities with  $I > 3\sigma(I)$ ],  $R\bar{3}m$  (171 reflections) and  $Fm\bar{3}m$  (71 reflections). Although lower  $R$  factors were obtained in the lower-symmetry space groups [which are significantly lower according to Hamilton (1965)], this was due entirely to relaxation of constraints on the Pt atomic thermal parameters and was assumed to result from the reduction of residual systematic errors in the absorption correction. Accordingly, the results from the  $Fm\bar{3}m$  and  $R\bar{3}$  refinements are given in Table 1. Final cycles employed a weighting parameter  $\omega = 1/[\sigma^2(F) + gF^2]$  and gave  $R = 0.029$ ,  $R_w = 0.025$  ( $g = 0.0034$ ) for the 71 reflections ( $Fm\bar{3}m$ ) and  $R = 0.027$ ,  $R_w = 0.026$  ( $g = 0.0019$ ) for the 274 reflections ( $R\bar{3}$ )\*.

Computer programs used were *SHELX* (Sheldrick, 1976) and a local version of *ABSCOR* (Alcock, 1969).

\* A list of structure factors for the  $R\bar{3}$  refinement has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35237 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic positions and thermal parameters with *e.s.d.*'s derived from the  $Fm\bar{3}m$  and  $R\bar{3}$  refinements

The temperature factors are in the form  $\exp[-2\pi^2(h^2 U_{11} a^{*2} + \dots + 2hkU_{12} a^* b^*)]$  and are given  $\times 10^4$ .

(a)  $R\bar{3}$  refinement

For each atom the second line gives the  $Fm\bar{3}m$  refined parameters transformed to the  $R\bar{3}$  unit cell.

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pt	0.0	0.0	0.0	168 (2)	168 (2)	113 (4)	0.0	0.0	84 (1)
	0.0	0.0	0.0	156	156	156	0.0	0.0	78
N	0.0	0.0	0.2488 (7)	257 (24)	257 (24)	170 (58)	0.0	0.0	128 (12)
	0.0	0.0	0.25	287	287	287	0.0	0.0	144
F	0.1531 (9)	0.3056 (8)	0.0763 (3)	339 (19)	230 (17)	214 (24)	-97 (14)	-51 (16)	122 (15)
	0.1532	0.3064	0.0766	322	219	287	-97	-49	109

(b)  $Fm\bar{3}m$  refinement

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pt	0.0	0.0	0.0	156 (4)	156	156	0	0	0
N	0.25	0.25	0.25	287 (41)	287	287	0	0	0
F	0.0	0.0	0.2298 (10)	356 (26)	356	150 (32)	0	0	0

**Discussion.** Salts of the  $A_2PtF_6$  type have been made only with Group I elements; all have the  $K_2GeF_6$  structure (Wyckoff, 1965). We have found that  $(NH_4)_2PtF_6$  has the  $K_2PtCl_6$  (antifluorite) structure, in which the  $K^+$  and  $PtCl_6^{2-}$  ions occupy the  $F^-$  and  $Ca^{2+}$  sites of the fluorite structure respectively.

There is no distortion from full  $m\bar{3}m$  symmetry allowed for the  $PtF_6^{2-}$  ion in space group  $Fm\bar{3}m$ , and refinement in lower-symmetry space groups did not lead to any significant departure from this geometry. Other  $MF_6^{n-}$  anions commonly show a departure from  $m\bar{3}m$  symmetry by a compression along a threefold axis (Clark & Russell, 1978). The Pt–F distance is 1.942 (8) Å [1.936 (4) Å in  $R\bar{3}$ ]. The H atoms were not located.

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## Structure of Bismuth Indium Sulphide $Bi_3In_5S_{12}$ \*

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**Abstract.**  $Bi_3In_5S_{12}$ , monoclinic,  $C2/m$ ,  $a = 33.13$  (1),  $b = 3.873$  (1),  $c = 14.413$  (2) Å,  $\beta = 91.21$  (2)°,  $V = 1849.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 5.73$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 345.8$  mm<sup>-1</sup>,  $F(000) = 2744$ ; reflection condition  $hkl: h + k = 2n$ ; final  $R = 0.067$ . The structure is built up by irregular In–S octahedra and distorted mono- and bicapped trigonal prisms of Bi–S, forming chains along  $y$ .

**Introduction.** In the system  $In_2S_3$ – $Bi_2S_3$ , three intermediate compounds were found (Krämer, 1976). Two of these have the compositions  $In_2Bi_4S_9$  and  $Bi_2In_4S_9$  (Krämer, 1971; Chapuis, Gnehm & Krämer, 1972); the composition of the third compound could not be determined chemically with sufficient accuracy. Therefore a structure analysis was performed which shows the correct formula to be  $Bi_3In_5S_{12}$  ( $3Bi_2S_3 \cdot 5In_2S_3$ ).

Crystals could be prepared with chlorine as transport agent in a temperature gradient of 953–873 K. By annealing stoichiometric amounts of  $Bi_2S_3$  and  $In_2S_3$  for several weeks at 873 K only  $Bi_2In_4S_9$  and  $In_2Bi_4S_9$  were formed in the corresponding ratio. Therefore chlorine is thought to stabilize the  $Bi_3In_5S_{12}$  structure and small proportions thereof may be incorporated which cannot be detected by X-ray diffraction.

As-grown crystals are black and elongated along  $y$ , showing the pinacoids  $\{100\}$ ,  $\{010\}$  and  $\{001\}$ . Intensities from a single crystal ( $25 \times 900 \times 63$  µm) were collected on an automatic four-circle diffractometer (Enraf–Nonius CAD-4) with graphite-monochromatized Mo  $K\alpha$  radiation and an  $\omega$ – $2\theta$  scan mode. Calculations were performed with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). 7370 reflections were measured which reduced to 3092 independent reflections, 2788 of which had  $I > 3\sigma(I)$ . Intensities were corrected for Lorentz–polarization and absorption effects. The structure was solved from a Patterson map and successive Fourier syntheses. Refinement of positional and anisotropic

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and their e.s.d.'s ( $< 1$  in last digit for In and Bi)

	x	y = 0	z		x	y = 0	z
Bi(1)	1353		–124	S(1)	–60 (2)		1789 (4)
Bi(2)	3203		2623	S(2)	623 (2)		4009 (4)
Bi(3)	5516		2083	S(3)	1160 (2)		1817 (4)
				S(4)	2224 (2)		2404 (4)
In(1)	0	0	0	S(5)	3939 (2)		1853 (4)
In(2)	0		5000	S(6)	4665 (2)		3936 (4)
In(3)	2150		4167	S(7)	5538 (2)		266 (4)
In(4)	4032		5044	S(8)	6616 (2)		3988 (4)
In(5)	6729		2184	S(9)	8029 (2)		1459 (4)
In(6)	9277		2794	S(10)	8731 (2)		3972 (4)
				S(11)	7718 (2)		4111 (4)
				S(12)	6839 (2)		404 (4)

\* Dedicated to Professor Dr Werner Borchert on the occasion of his 70th birthday.