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Short Communication

Crystal structure of potassium tetrafluoroargentate (III)

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It is confirmed, from X-ray powder crystallographic measurements, that $KAgF_4$(III) is isostructural with $KAuF_4$(III) and $KBrF_4$(III).

The preparation of potassium tetrafluoroargentate(III) by the direct fluorination of an equimolar mixture of potassium chloride and silver nitrate at 200°–400°C has been described[1]. The only property reported for the compound was the violent reaction with water. During a study of the fluorinating behaviour of transition metal fluorocomplexes towards organic compounds, the tetrafluoroargentate(III) has been reinvestigated and unit cell parameters determined.

When this work was almost complete the preparations and crystal structures of the alkali metal tetrafluoroargentates(III) and tetrafluoroaurates(III) were reported[2]. The results for potassium tetrafluoroargentate(III) are in reasonable agreement with our crystallographic measurements.

Experimental

Fluorination of a 2:1 mixture of potassium chloride and silver oxide at 300°C in a nickel reactor produced a homogeneous yellow product (Found K, 16.2; Ag, 49.2; F, 33.6. Calc. for $KAgF_4$: K, 17.5; Ag, 48.4; F, 34.1%). X-ray powder photographs (Cu$K\alpha$ radiation, $\lambda = 1.5418$ Å) were obtained of samples sealed under vacuum in thin-walled silica capillary tubes, since attempts to use Pyrex capillaries resulted in attack on the glass and sample decomposition.

Results and discussion

The powder diffraction results were indexed on the basis of a tetragonal unit cell, with dimensions very close to those for[3] potassium tetrafluorobromate(III) and[4] potassium tetrafluoroaurate(III), as shown in Table 1. The indices of the reflections are consistent with a body-centred unit cell ($h + k + l = 2n$) in line with the space-group $I4/mcm$ (D^{18}_{4h}, No. 140) established for the bromine and gold compounds[5]. Calculated $\sin^2\theta$ values are compared with those observed in Table 2.

TABLE 1

UNIT CELL DIMENSIONS

	a_0	c_0 (Å)	U (Å^3)	Reference
$KBrF_4$	6.17	11.10	423	3
$KAuF_4$	5.99	11.38	408	4
$KAgF_4$	5.84	11.52	393	present work
[$KAgF_4$	5.90	11.15	388	2]

TABLE 2

X-RAY POWDER DIFFRACTION RESULTS FOR POTASSIUM TETRAFLUOROARGENTATE(III)

h k l		$\sin^2\theta$ (calc.)	$\sin^2\theta$ (obs.)	I (obs.)
1, 1, 0		0.0349	0.0352	w
1, 1, 2		0.0527	0.0532	s
2, 0, 0		0.0698	0.0699	w
2, 0, 2		0.0877	0.0882	vw
2, 1, 1		0.0918	0.0923	vw
1, 1, 4		0.1066	0.1067	vw
2, 2, 0		0.1395	0.1401	w
2, 0, 4		0.1415	0.1420	m
3, 1, 2		0.1923	0.1929	m
1, 1, 6		0.1962	0.1969	w
3, 0, 3		0.1973		
2, 2, 4		0.2112	0.2118	w
2, 0, 6		0.2311	0.2321	vw
3, 2, 1		0.2312		
3, 1, 4		0.2461	0.2473	w
3, 3, 2		0.3318	0.3320	vw
3, 1, 6		0.3357	0.3364	m
4, 2, 0		0.3488	0.3502	m
4, 0, 4		0.3507		
2, 0, 8		0.3565	0.3569	w
4, 2, 4		0.4205	0.4204	w
2, 2, 8		0.4262	0.4264	w
5, 1, 0		0.4534	0.4534	w
1, 1, 10		0.4829	0.4824	vw
5, 3, 2		0.6109	0.6098	vw
5, 1, 6		0.6147	0.6139	vw
3, 1, 10		0.6224	0.6216	vw
4, 2, 8		0.6355	0.6350	vw
6, 2, 0		0.6976	0.6972	vw
2, 0, 12	α_1	0.7136	0.7125	vw
	α_2	0.7173	0.7165	vw
5, 3, 6	α_1	0.7529	0.7520	w
	α_2	0.7568	0.7560	vw
6, 2, 4	α_1	0.7680	0.7675	vw
	α_2	0.7719	0.7712	vw

The observed reflections correspond only with the more intense reflections reported[3] for potassium tetrafluorobromate(III), due to the high background intensity on the films. The observed $\sin^2\theta$ values are in only fair agreement with those reported by Hoppe and Hohmann, and the discrepancies are not systematic, although their results were obtained using a Guinier camera.

In the structures of potassium tetrafluorobromate(III) and potassium tetrafluoroaurate(III) there are separate K^+ and MF_4^- ions, with a square-planar co-ordination of bromine or gold by fluorine atoms in the anion[5]. The present results confirm that, as expected, silver(III) has the same square-planar co-ordination as gold(III) in a fluoride environment.

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