Alkali-metal Heptafluorodiarsenates(III): their Preparation and the Crystal Structure of the Potassium Salt

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Heptafluorodiarsenates(III), MAs_2F_7 (M = K, Rb, or Cs), have been prepared by the dissolution of the alkali-metal fluoride in arsenic trifluoride and crystallisation from the solvent at room temperature. Loss of arsenic trifluoride and formation of the tetrafluoroarsenate(III) occurs on heating to 100 °C under vacuum. The structure of the potassium salt has been determined by the heavy-atom method from 799 reflections, and refined by full-matrix least-squares methods to *R* 0.070. Crystals are monoclinic, space group $P2_1/c$, with a = 10.99(1), b = 7.39(1), c = 8.75(1) Å, and β = 110.8(2)°. The structure consists of potassium ions, tetrafluoroarsenate(III) ions, and arsenic trifluoride molecules, with some interaction between anions and molecules to form a complex chain arrangement.

ALTHOUGH anionic complexes formed by antimony trifluoride have been much investigated, and a wide variety of such complexes structurally characterised,[1] there have been very few reports on corresponding compounds of arsenic. Alkali-metal tetrafluoroarsenates(III) were reported to result [2,3] from the interaction of the corresponding fluorides with arsenic trifluoride, but no structural investigations of these compounds were made. We have now reinvestigated the arsenic trifluoride–alkali-metal fluoride system and characterised the previously unreported heptafluorodiarsenates(III).

EXPERIMENTAL

Arsenic trifluoride was prepared by the action of sulphuric acid on a mixture of calcium fluoride and arsenic(III) oxide, purified by distillation, and stored over dry sodium fluoride prior to use. Alkali-metal fluorides were prepared by reaction of 40% aqueous hydrogen fluoride on the appropriate carbonate in platinum apparatus, immediately prior to use. Excess of hydrogen fluoride was removed by fusion of the salt, and the fluoride dried by heating under high vacuum in the Pyrex glass apparatus.

Heptafluorodiarsenates(III).—Fused Pyrex glass apparatus, equipped with Teflon O-ring taps, was used for the reactions. An excess of arsenic trifluoride was distilled from sodium fluoride into a bulb containing the dried alkali-metal fluoride. On heating, the alkali-metal fluoride dissolved, and crystals of the heptafluorodiarsenates(III) were obtained by cooling to room temperature. Excess of arsenic trifluoride was removed by pumping under vacuum at room temperature. The products, which were white powders, were dissolved in aqueous sodium hydroxide solution and analysed for arsenic and fluorine (Found: As, 46.2; F, 40.8. KAs_2F_7 requires As, 46.5; F, 41.3. Found: As, 41.2; F, 35.3. $RbAs_2F_7$ requires As, 40.7; F, 36.3. Found: As, 36.6; F, 33.6. $CsAs_2F_7$ requires As, 36.0; F, 32.0%).

Tetrafluoroarsenates(III).—Samples of the heptafluorodiarsenates(III) were heated to 100 °C for *ca.* 1 h, while under evacuation. Arsenic trifluoride was evolved and collected in a trap cooled in liquid air, and samples of the corresponding tetrafluoroarsenate(III) remained. These products were again dissolved in aqueous sodium hydroxide solution and analysed for arsenic and fluorine (Found: As, 39.0; F, 40.1. Calc. for $KAsF_4$: As, 39.4; F, 40.0. Found: As, 31.6; F, 31.0. Calc. for $RbAsF_4$: As, 31.7; F, 31.2. Found: As, 25.7; F, 27.2. Calc. for $CsAsF_4$: As, 26.1; F, 26.8%).

Analysis.—After dissolution of the sample in sodium hydroxide solution, arsenic was determined volumetrically with standard potassium iodate solution, and fluorine both volumetrically by the Volhard method after precipitation as lead chloride fluoride, and using a fluoride ion selective electrode (Activion).

Preparation of Single Crystals.—Crystals of the potassium salt were obtained from arsenic trifluoride solution. A hot saturated solution of the salt was transferred by adroit manipulation from the reaction bulb to thin-walled Pyrex-glass capillary tubes, previously fused to the reaction apparatus. On standing and cooling to room temperature crystals formed in the tubes. The arsenic trifluoride was removed by careful evacuation of the apparatus, and single crystals sealed in small sections of capillary tube using a microflame. This operation required great care, as too little evacuation, leaving crystals coated with a film of arsenic trifluoride, led to attack on the tube and decomposition; too much evacuation caused the transparent crystals to develop a white, powdery appearance.

Crystallography.—Unit cell and space group data were obtained photographically and intensity data with a diffractometer.

Crystal data. As_2F_7K, $M = 322$, Monoclinic, $a = 10.99(1)$, $b = 7.39(1)$, $c = 8.75(1)$ Å, $\beta = 110.8(2)°$, $Z = 4$, $D_c = 3.22$ g cm^{-3}, $U = 664$ Å^3, $F(000) = 592$, space group $P2_1/c$ (C_{2h}^5, no. 14) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$, Mo-K_α radiation, λ 0.710 7 Å, μ 47 cm^{-1}. The density of the crystals was not measured, but $Z = 4$ was assumed, as the volume per fluorine and potassium atom was then 20.7 Å^3, comparable with that of 21.0 in the corresponding antimony compound.[4]

Structure determination. Intensity data were collected about the b axis (layers $h0$—$8l$) with a Stoe two-circle computer-controlled diffractometer, as described previously.[5] Within the range $0.1 < (\sin\theta)/\lambda < 0.65$, 799 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarisation factors but not for absorption.

The structure was solved by conventional Patterson–Fourier techniques. The positions of three heavy atoms (2As + K) were initially deduced, and the indentity of two of these (As and K) interchanged after the first cycles of least-squares refinement, when temperature parameters showed their incorrect assignment. Scattering factors used were those for neutral atoms,[6] with corrections for the effects of anomalous dispersion.[7] Initial refinement by full-matrix least-squares methods was with layer scale-factors refined separately, all atoms vibrating isotropically, and with unit weights. Refinement was continued with layer scale-factors held constant and with the introduction of anisotropic thermal parameters for the heavy atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. In the final stages of refinement the weighting scheme $w = [\sigma^2|F_o| + (0.001|F_o|^2)]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. Final parameter shifts were $<0.1\sigma$, the final R was 0.070, and $R'\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ also 0.070. The calculations were carried out on the ICL 1906A computer at Birmingham University Computer Centre using the program[8] SHELX-76. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22787 (7 pp.);* final positional parameters, with their estimated standard deviations, are in Table 1, and interatomic distances and angles in Table 2.

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
As(1)	0.402 9(2)	0.167 5(3)	0.124 0(2)
As(2)	0.223 8(2)	0.678 6(2)	0.163 4(2)
K	0.080 2(5)	0.153 2(5)	0.223 4(5)
F(1)	0.393 8(12)	−0.060 3(16)	0.067 4(14)
F(2)	0.373 0(12)	0.119 9(16)	0.299 2(14)
F(3)	0.240 5(12)	0.197 8(15)	0.014 9(14)
F(4)	0.066 2(10)	0.816 2(13)	0.100 8(12)
F(5)	0.132 4(11)	0.509 7(15)	0.206 3(13)
F(6)	0.174 8(11)	0.627 6(14)	−0.044 9(12)
F(7)	0.356 4(12)	0.502 2(16)	0.195 3(14)

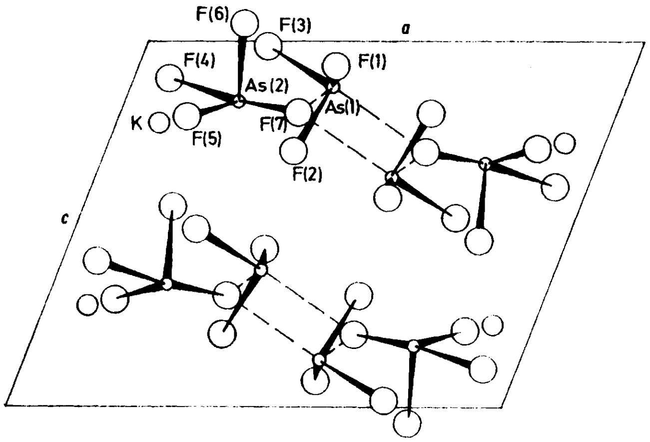

FIGURE 1 Projection of the structure of KAs_2F_7 down [010], showing the atom numbering and the anion linking

DISCUSSION

Although the earlier work on the interaction of arsenic trifluoride with alkali-metal fluorides reported that tetrafluoroarsenates(III) were produced, the species which crystallise from arsenic trifluoride solution at room temperature are heptafluorodiarsenates(III). Arsenic trifluoride is readily lost on heating these compounds to 100 °C under vacuum, leading to the formation of the tetrafluoroarsenate(III). Since the previous workers[2,3] heated or pumped their products, to remove excess of arsenic trifluoride, the results are consistent.

The structure determination of the potassium salt has established the formulation of the products as heptafluorodiarsenates(III). The structure consists of separate potassium cations, tetrafluoroarsenate anions, and arsenic trifluoride molecules, with the anions and molecules weakly linked together to form endless ribbons parallel to [010].

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses *

(*a*) Distances

As(1)–F(1)	1.75(1)	As(2)–F(4)	1.91(1)
As(1)–F(2)	1.71(1)	As(2)–F(5)	1.73(1)
As(1)–F(3)	1.71(1)	As(2)–F(6)	1.75(1)
As(1) · · · F(7)	2.65(1)	As(2)–F(7)	1.90(1)
As(1) · · · F(7^{I})	2.83(1)	F(4) · · · F(5)	2.46(1)
F(1) · · · F(2)	2.50(2)	F(4) · · · F(6)	2.47(1)
F(1) · · · F(3)	2.48(2)	F(5) · · · F(6)	2.56(1)
F(2) · · · F(3)	2.46(2)	F(5) · · · F(7)	2.50(2)
F(2) · · · F(7)	2.95(2)	F(6) · · · F(7)	2.51(2)
F(3) · · · F(7)	2.78(2)	K · · · F(2)	3.06(1)
F(1) · · · F(7^{I})	2.83(2)	K · · · F(3)	2.97(1)
F(2) · · · F(7^{I})	3.08(2)	K · · · F(4)	2.70(1)
K · · · F(5)	2.71(1)	K · · · F(4^{II})	2.73(1)
K · · · F(6^{II})	3.13(1)	K · · · F(3^{III})	2.76(1)
K · · · F(6^{III})	2.83(1)	K · · · F(4^{IV})	2.86(1)
K · · · F(5^{IV})	2.83(1)		

(*b*) Angles

F(1)–As(1)–F(2)	92.7(5)	F(1)–As(1)–F(3)	91.4(6)
F(2)–As(1)–F(3)	91.9(6)	F(7)–As(1)–F(2)	82.3(4)
F(7)–As(1)–F(3)	76.0(5)	F(7)–As(1)–F(7^{I})	119.5(6)
F(1)–As(1)–F(7^{I})	72.0(5)	F(2)–As(1)–F(7^{I})	81.3(4)
F(4)–As(2)–F(5)	84.8(5)	F(4)–As(2)–F(6)	84.5(4)
F(5)–As(2)–F(6)	94.8(5)	F(7)–As(2)–F(5)	87.0(5)
F(7)–As(2)–F(6)	86.7(5)	F(4)–As(2)–F(7)	167.3(5)
As(1)–F(7)–As(2)	144.0(6)	As(2)–F(7)–As(1^{VI})	107.4(6)
As(1)–F(7)–As(1^{VI})	108.2(5)		

(*c*) Contacts <3.5 Å

F(1) · · · As(1^{V})	3.33(1)	F(2) · · · As(1^{III})	3.16(1)
As(1) · · · F(1^{VI})	3.47(1)	As(2) · · · F(1^{VII})	3.01(1)
As(2) · · · F(1^{III})	3.47(1)	As(2) · · · F(6^{VIII})	3.14(1)
F(6) · · · F(1^{VII})	3.23(1)	F(7) · · · F(1^{VII})	3.49(2)
F(1) · · · F(1^{V})	3.10(2)	F(5) · · · F(1^{III})	3.45(1)
F(7) · · · F(1^{III})	3.16(2)	F(2) · · · F(1^{VI})	3.38(2)
F(7) · · · F(1^{VI})	2.83(2)	F(7) · · · F(2)	2.95(2)
F(3) · · · F(2^{III})	3.07(2)	F(2) · · · F(6^{III})	3.47(1)
F(7) · · · F(2^{IV})	3.08(2)	F(5) · · · F(3)	3.31(2)
F(6) · · · F(3)	3.26(2)	F(7) · · · F(3)	2.78(2)
F(4) · · · F(3^{II})	3.16(2)	F(5) · · · F(3^{III})	2.96(2)
F(4) · · · F(4^{IX})	3.28(1)	F(6) · · · F(5^{II})	3.32(1)
F(6) · · · F(5^{VIII})	3.38(1)	F(4) · · · F(6^{VIII})	2.93(1)

* Roman numerals as superscripts refer to atoms in the positions: I $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; II, $-x, 1 - y, -z$; III $x, \frac{1}{2} - y, \frac{1}{2} + z$; IV, $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; V $1 - x, -y, -z$; VI, $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; VII $x, 1 + y, z$; VIII, $x, \frac{3}{2} - y, \frac{1}{2} + z$; IX $-x, 2 - y, -z$.

The atomic arrangement is shown in Figure 1. As(2) has four nearest fluorine-atom neighbours, which define the tetrafluoroarsenate anion. The arrangement can be considered by valence-shell electron-pair repulsion (VSEPR) theory to be derived from a trigonal-bipyramidal geometry with four bond pairs and one lone pair of electrons directed to the apices. The lone pair is in an

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

equatorial position, and the As–F(equatorial) bonds, averaging 1.73 Å, are shorter than the As–F(axial) bonds, averaging 1.91 Å (Table 2). The $F_{eq.}$–As–$F_{eq.}$ angle of 95° and the $F_{ax.}$–As–$F_{ax.}$ angle of 167° can be considered distorted from the values of 120 and 180° for a regular trigonal bipyramid, by the repulsion of the lone pair.

This arrangement is very similar to that in the isoelectronic selenium tetrafluoride,[9] in the vapour phase, in which it has been shown by microwave spectroscopy Se–$F_{eq.}$ 1.682, Se–$F_{ax.}$ 1.771 Å, $F_{eq.}$–Se–$F_{eq.}$ 100.55, and $F_{ax.}$–Se–$F_{ax.}$ 169.37°. The longer distances in the arsenic species may be due to the overall negative charge, and the smaller angles are a consequence of these longer distances, with fluorine to fluorine contacts similar in the two cases.

The reverse effect can be seen in a comparison with the tetrafluoroantimonate(III) anion[4] in KSb_2F_7. Here the bond distances are longer, Sb–$F_{eq.}$ 1.92, Sb–$F_{ax.}$ 2.07 Å, and the angles smaller, $F_{eq.}$–Sb–$F_{eq.}$ 90.4, $F_{ax.}$–Sb–$F_{ax.}$ 155.2°. Again the fluorine to fluorine contacts are similar.

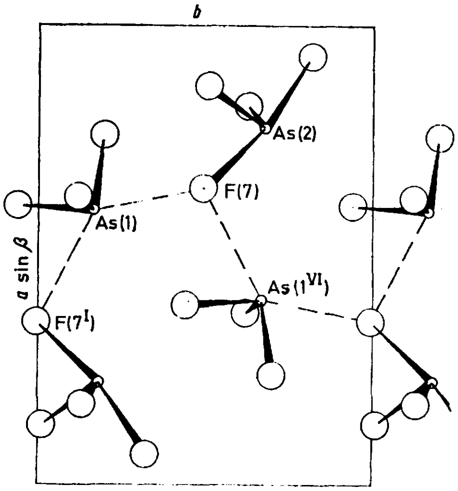

FIGURE 2 Projection down [001] of one of the anionic chains, showing the anion linking *via* an axial fluorine atom of the AsF_3 molecules

As (1) has three nearest fluorine atom neighbours, with an average As–F distance of 1.72 Å, and F–As–F angle of 92°, defining the arsenic trifluoride molecule. On application of VSEPR theory a lone pair of electrons on arsenic completes a distorted tetrahedral arrangement and lone-pair–bond-pair repulsions lead to the diminution of the angle from 109.5°. The parameters for the AsF_3 molecule are similar to those of the free molecule in the vapour phase,[10] determined by electron diffraction (As–F 1.709 Å, F–As–F 95.9°), and also in the solvate[11] $[Te_6][AsF_6]_4 \cdot 2AsF_3$ (As–F 1.69 Å, F–As–F 92°). The smaller angles in the solid-state determinations are probably due to further fluoride interactions with the arsenic atom, as discussed below. In antimony trifluoride itself,[12] and in KSb_2F_7, the Sb–F distance of 1.93 Å is larger and the F–Sb–F angle of 85° smaller than in the arsenic compound.

In addition to the three nearest neighbours, As(1) has two contacts to F(7) atoms in separate anions with As–F distances of 2.64 and 2.83 Å. Although these distances are quite long, the two fluorine atoms complete a greatly distorted square pyramidal arrangement around the arsenic atom, which, with the lone pair of electrons, can be regarded as derived from an octahedral arrangement of five bond pairs and one lone pair. These extra contacts must represent extremely weak bonding. There is no lengthening of the As(2)–F(7) bond compared with As(2)–F(4), and the ratio of As(1)–F(bridge) to As(1)–F(terminal) gives values of 1.53 and 1.64 : 1. These values are very high compared with the ratio of about 1 : 1 for symmetrically bridged pentafluorides. The three arsenic atoms linked to F(7) form an almost planar array with As–F–As angles of 144.2, 107.4, and 108.2°.

In KSb_2F_7 the SbF_3 molecule also has two additional contacts giving a very similar geometry, but with a stronger bonding interaction, with ratios of Sb–F(bridge) to Sb–F(terminal) of 1.24 and 1.32 : 1. In the antimony compound both the axial fluorine atoms of the anion are linked to separate SbF_3 molecules to give a simple chain arrangement. The linking in the arsenic compound, involving only one of the axial fluorine atoms, leads to a much more complex chain, shown in Figure 2.

The potassium ion does not have a regular co-ordination geometry. It has ten fluorine atom neighbours at distances ranging from 2.70 to 3.13 Å.

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