

Alkali-metal fluoroarsenates(III) revisited; the $\text{As}_4\text{F}_{13}^-$ anion, the crystal structure of $\text{CsAs}_4\text{F}_{13}$ and Raman spectra of $\text{MAS}_4\text{F}_{13}$ (M = Cs, Rb)

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Alkali-metal tridecafluorotetraarsenates(III), $\text{CsAs}_4\text{F}_{13}$ and $\text{RbAs}_4\text{F}_{13}$ were synthesized by the reaction of CsF and RbF with liquid AsF_3 at 353 K.

In contrast to numerous alkali-metal fluoroantimonates(III), the only alkali-metal fluoroarsenates(III) known were those with the general formulae MASF_4 (M = Cs, Rb, K, Tl) and MAS_2F_7 (M = Cs, Rb, K),^{1,2} synthesized by reaction of the corresponding alkali-metal fluorides and liquid AsF_3 at 353 K and isolated at room temperature or above. Based on the similarity of stoichiometries and structures of fluoroarsenates(III) and fluoroantimonates(III), the existence of fluoroarsenates(III) with the general formula $\text{MAS}_4\text{F}_{13}$ was expected. Alkali-metal fluoroarsenates(III) MASF_4 and MAS_2F_7 are less stable than corresponding fluoroantimonates(III) and decompose to MF and AsF_3 when heated above room temperature.¹ Therefore, $\text{MAS}_4\text{F}_{13}$ was expected to be stable at temperatures below room temperature. Herein we report on the synthesis of the first alkali-metal tridecafluorotetraarsenates(III), $\text{CsAs}_4\text{F}_{13}$ and $\text{RbAs}_4\text{F}_{13}$.[†]

$\text{CsAs}_4\text{F}_{13}$ and $\text{RbAs}_4\text{F}_{13}$ were synthesized by the reaction of the corresponding alkali-metal fluoride and liquid AsF_3 at 353 K and isolated as colourless crystals by removing excess AsF_3 at 273 K on a vacuum line. $\text{CsAs}_4\text{F}_{13}$ and $\text{RbAs}_4\text{F}_{13}$ decompose at room temperature, releasing AsF_3 gas, but are stable under liquid AsF_3 . The mass loss *vs.* time curve (Fig. 1) in the system $\text{CsF}-\text{AsF}_3$ obtained at 273 K indicates a change of the slope at the composition $\text{CsF} : \text{AsF}_3 = 1 : 4$, which is evidence of a new phase, $\text{CsAs}_4\text{F}_{13}$.

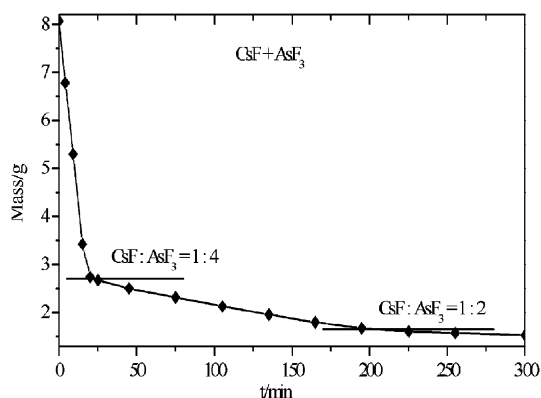


Fig. 1 Dependence of the total mass of the sample during the pumping off of volatiles in the course of $\text{CsAs}_4\text{F}_{13}$ preparation at 273 K.

The structure of $\text{CsAs}_4\text{F}_{13}$ consists of Cs^+ cations and $\text{As}_4\text{F}_{13}^-$ anions. Very distorted pseudo-trigonal bipyramidal AsF_4 units (Fig. 2) are tetrahedrally disposed about a shared common central fluorine atom F1 placed at the $\bar{4}$ symmetry axis. An arsenic atom is coordinated by the three nearest fluorine atoms at distances of 172.6(4), 172.7(4) and 176.2(4)

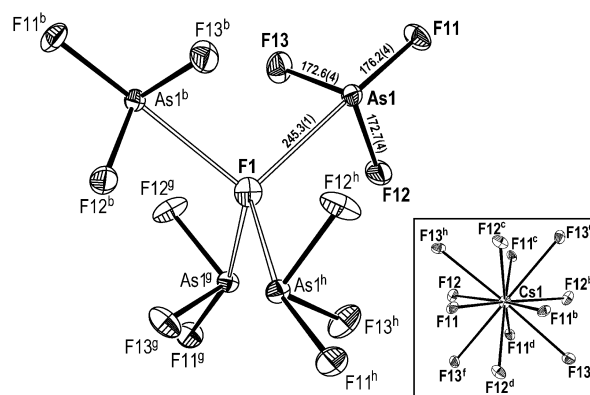


Fig. 2 ORTEP¹⁴ drawing of the $\text{As}_4\text{F}_{13}^-$ anion in $\text{CsAs}_4\text{F}_{13}$ with thermal ellipsoids representing 50% probability, and the fluorine environment of the Cs1 atom (inset).

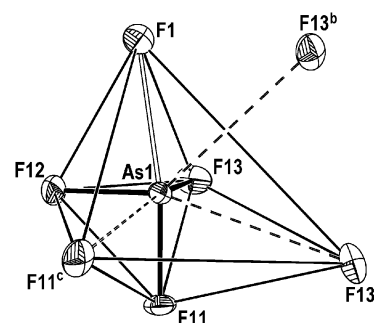


Fig. 3 ORTEP drawing of the As1 atom environment in $\text{CsAs}_4\text{F}_{13}$ with thermal ellipsoids representing 50% probability, showing arsenic(III) electron lone pair steric activity.

pm, giving an average of 173.2 pm (Fig. 3). The average distance from an arsenic atom to the three closest fluorine atoms observed in $\text{N}_2\text{H}_6\text{AsF}_4\text{F}$ (173.8 pm)³ is close to this value, while in a gaseous AsF_3 molecule⁴ the slightly shorter bond distance $\text{As}-\text{F}$ [170.63(6) pm] was determined by electron diffraction. The distance between central fluorine atom F1 and arsenic atoms in the anion is 245.3(1) pm. In the AsF_4 unit angles $\text{F11}-\text{As1}-\text{F12}$ and $\text{F11}-\text{As1}-\text{F13}$ are 89.7(2) and 90.7(2)°, respectively, and the angle $\text{F12}-\text{As1}-\text{F13}$ is 95.0(2)°. Angle $\text{F1}-\text{As1}-\text{F11}$ is 164.3(1)° as a result of the steric activity of the electron lone pair at the As1 atom.

The $\text{As}_4\text{F}_{13}^-$ anions are weakly connected by $\text{As1}-\text{F11}$ bonds at 292.2(1) pm (Fig. 3). The next shortest distances of As1 to fluorine atoms are: 315.5(4) pm to F13^h , and 317.3(4) pm to F13^b , and are not considered as bonding, though they are close to the $\text{As}-\text{F}$ van der Waals distance of 235 pm.⁵ The Cs atoms are placed at the $\bar{4}$ symmetry axis. Each Cs atom is surrounded by twelve F-ligands, in three four-fold planar sets mutually at right angles (Fig. 2). The planar sets are set (1) F11 , F12 , F12^b , F11^b with $\text{Cs1}-\text{F11}$ 301.3(1) pm and $\text{Cs1}-\text{F12}$ is 320.7(4) pm,

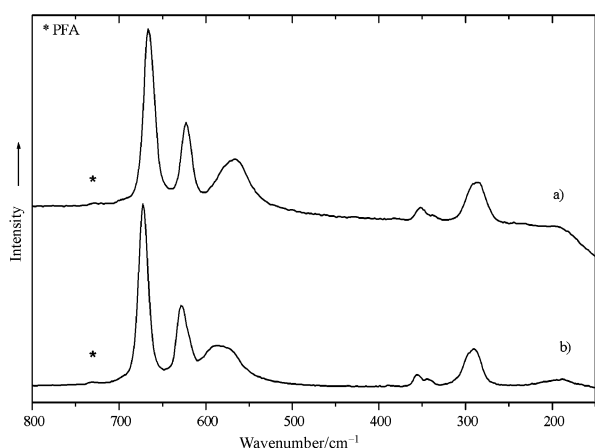


Fig. 4 Raman spectra of RbAs₄F₁₃ a) and CsAs₄F₁₃ b); bands denoted by the asterisks are due to PFA (copolymer of tetrafluoroethylene with perfluoroalkyl vinyl ether) from the tube reactor wall.

set (2) F11^c, F12^c, F11^d, F12^d which is identical to set (1) and set (3) F13^e, F13^f, F13^g, F13^h with a more distinct contact, Cs1–F13, of 351.5(4) pm. The structure of CsAs₄F₁₃ contains a similar anion to that found in the structures of the members in the isomorphous series of antimony compounds MSb₄F₁₃ (M = Cs, Rb, K, Tl, NH₄).^{6,7} It is worth noting that As₄X₁₃⁻ anions are unknown for the heavier halogens.⁸

The Raman spectra of RbAs₄F₁₃ and CsAs₄F₁₃, shown in Fig. 4, are similar, and suggest that the two compounds are isostructural. The small differences in frequencies in the Raman spectra of RbAs₄F₁₃ and CsAs₄F₁₃ may be explained by the stronger interaction of the smaller Rb⁺ cation and fluorine atoms F11, F12 and F13 in the former in comparison to the interaction of the Cs⁺ cation and the same set of fluorine atoms in the latter.

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Notes and references

† X-Ray structure determination: crystals of CsAs₄F₁₃ were transferred from liquid AsF₃ in a PFA tube onto a watch glass and immersed in perfluorinated oil (ABCR, FO 5960). A suitable crystal was selected

under the microscope and transferred into the cold nitrogen stream of the diffractometer by a capillary mounted at the goniometer head.

Crystallographic data for CsAs₄F₁₃: MW = 679.59, crystal dimensions 0.30 × 0.15 × 0.10 mm, tetragonal, space group *I*4̄, *a* = *b* = 956.8(4), *c* = 672.6(3) pm, *V* = 0.6158(4) nm³, *Z* = 2, *D*_c = 3.665 g cm⁻³, μ(Mo-Kα) = 13.814 mm⁻¹, *F*(000) = 608, *T* = 200(1) K, λ = 0.71070 Å, ω and φ scans. From 760 independent reflections, 695 were considered with *I* > 2σ(*I*). Final *R* indices *R*1 = 0.0378 (all), *R*1 = 0.0363 [for *I* > 2σ(*I*)], *wR* = 0.0686 (all), *wR* = 0.0683 [for *I* > 2σ(*I*)]. Maximum and minimum residual electron densities, 1297 and -1333 e nm⁻³. Rigaku AFC7 diffractometer coupled with Mercury CCD area detector; programs used: Rigaku CrystalClear,⁹ SHELXL-97.¹⁰ CCDC reference number 196171. See <http://www.rsc.org/suppdata/dt/b210507a/> for crystallographic data in CIF or other electronic format.

Raman spectra (cm⁻¹): CsAs₄F₁₃, 672 (10.0), 628 (4.4), 589 (2.2) 571 (2.1), 355 (0.8), 343 (0.5), 192 (2.0), 188 (0.4); RbAs₄F₁₃, 666 (10.0), 623 (4.9), 566 (3.0), 352 (0.8), 336 (0.4), 288 (2.3).

Chemical analysis: the total fluoride content was determined after complete decomposition of the sample using a fluoride ion selective electrode¹¹ and the content of As(III) was determined by titration with KBrO₃.¹² The contents of Rb and Cs were determined by flame atomic emission spectroscopy.¹³ Calc. for CsAs₄F₁₃: Cs, 19.56; As, 44.10; F, 36.35. Found: Cs, 17.8; As, 44.3; F, 36.2%. Calc. for RbAs₄F₁₃: Rb, 13.52; As, 47.41; F, 39.07. Found: Rb, 14.4; As, 47.5; F, 39.1%.

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