METAL (II) HEXAFLUOROARSENATES: PREPARATION AND VIBRATIONAL SPECTROSCOPY OF $MF_2 \cdot 2AsF_5$ (M = Mg, Ca, Sr, Ba, Mn, Co, Ni, Cd, Hg, Pb) ADDUCTS [1]

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SUMMARY

Adducts of the type $MF_2 \cdot 2AsF_5$ (M = Mg, Ca, Sr, Ba, Mn, Co, Ni, Cd, Hg, Pb) have been prepared by reaction of the metal difluorides with AsF_5 in anhydrous HF at room temperature. Vibrational spectroscopic studies and X-ray powder diffraction patterns of the solids indicate that adducts of three distinct structural types occur. The differences in structure have been rationalized in terms of the fluoride ion donor abilities of the metal difluorides.

INTRODUCTION

Many novel cationic species have been produced in reactions involving strong Lewis acids. The reagents which have found most widespread application are the pentafluorides, SbF_5 and AsF_5. Although not such a powerful Lewis acid as SbF_5, AsF_5 is a particularly useful reagent because its high volatility facilitates easy manipulation and purification.

Although a large number of hexafluoroarsenates containing non-metallic cations have been isolated, relatively little investigation of metal hexafluoroarsenates has occurred. Recent advances in understanding of the nature of noble-gas difluoride adducts [2-5], however, prompted us to initiate a study of metal difluoride adducts.

The earliest work in this area was carried out in the fifties by Clifford et al. who found that hydrogen fluoride solutions of AsF_5 dissolved a wide range of electropositive metals. They claimed that AsF_5 did not bring CoF_2 and CuF_2 into solution in anhydrous HF [6], but succeeded in preparing and isolating $BaF_2.2AsF_5$ [7] by evaporation of anhydrous HF solutions of BaF_2 containing excess of AsF_5. This compound had already been identified by Woolf and Eméleus a few years earlier in the reaction of barium halides and excess of arsenic trioxide with bromine trifluoride [8].

In 1971 Birchall et al. [9] prepared $SnF_2.AsF_5$ and interpreted vibrational and ^{119}Sn Mössbauer spectroscopic data for the adduct in terms of a species containing a fluorine-bridged $(Sn-F)_n^{n+}$ cation. More recently we prepared fresh samples of $SnF_2.AsF_5$ by reaction of SnF_2 with AsF_5 in anhydrous HF. Direct analytical evidence for the presence of AsF_6^- [10] and an X-ray crystal-structure investigation on these samples showed that the structure consists of discrete, cyclic $(Sn-F)_3^{3+}$ cations and octahedral anions [11] and so confirmed the overall correctness of Birchall's model.

While our work has continued it has been demonstrated that, contrary to the earlier observation [6], CoF_2 and CuF_2 do form HF-soluble fluoroarsenates and the $CoF_2.AsF_5$ adduct has been isolated [12]. The adducts $FeF_2.AsF_5$, $NiF_2.AsF_5$, $MnF_2.2AsF_5$ [13] and $NiF_2.2AsF_5.2SO_2$ [14] have also been obtained by the reactions of the metals with AsF_5 in SO_2, and ^{57}Fe Mössbauer spectra of the $FeF_2.AsF_5$ adduct have shown that the compound contains six-coordinate iron (II) [13].

In the meantime we have found that a wide range of metal difluorides, which are practically insoluble in anhydrous hydrogen fluoride, can be readily taken into solution in the presence of arsenic pentafluoride. The adducts formed can be isolated as crystalline solids by the removal of excess of AsF_5 and HF solvent under vacuum. In many cases the products have the stoicheiometries $MF_2.2AsF_5$ and details of the preparations and the vibrational spectroscopy of these adducts are the subject of this paper.

RESULTS AND DISCUSSION

Gravimetry, chemical analysis, X-ray crystallography, vibrational spectroscopy and magnetic susceptibility measurements have shown that reactions of metal difluorides with AsF_5 in anhydrous HF give rise to adducts of four different stoicheiometries, $MF_2.2AsF_5$, $2MF_2.3AsF_5$, $MF_2.AsF_5$ and $2MF_2.AsF_5$ [1, 10, 11, 15]. When the difluorides of the metals magnesium, calcium, strontium, barium, manganese, cobalt, nickel, cadmium, mercury or lead are used, adducts of composition $MF_2.2AsF_5$ are formed. These are white solids except for the manganese, cobalt and nickel compounds which are pink, purple and yellow respectively.

When considering the structural possibilities for these adducts it is possible to imagine formulations in terms of simple or polyatomic cationic species or in terms of covalent fluorine-bridged structures. It is also probable that both ionic and fluorine-bridged contributions to the bonding of particular adducts occur, which are dependent on the fluoride ion donor ability of the difluoride involved.

Vibrational spectroscopic and X-ray powder diffraction data clearly show that adducts of the $MF_2.2AsF_5$ type exist in three distinct structural forms:

$MF_2.2AsF_5$ (M = Sr, Ba, Pb)

The adduct, $BaF_2.2AsF_5$, is highly crystalline and gives excellent X-ray powder diffraction patterns but the quality of photographs for the strontium and lead adducts is poorer. Comparison of the $\underline{d}$ spacings and intensities of the lines in the diffraction patterns for the three compounds (Table 1) shows that, although the adducts are not iso-structural, the diffraction patterns are related. The rather simple nature of the patterns is suggestive of an ionic lattice.

The observed Raman and infrared frequncies for the series of adducts are listed in Table 2. An unassociated AsF_6^- ion has O_h symmetry and, accordingly, six normal modes of vibration are expected. Two of these are infrared active and three are Raman active. Assignments of bands for the lead compound are quite straight-forward. The frequency for $\nu_1(a_g)$ is coincident with that for the AsF_6^- ion in $Cs^+AsF_6^-$ [16] and other absorptions correlate well with those of other alkali metal [16] and nitrosyl salts [17,18] and with those of $Hg_2^{2+}(AsF_6^-)_2$ [19] where the extent of $Hg\cdots\cdots F$-As bridge formation is minimal.

TABLE 1

X-ray powder diffraction patterns of $MF_2 \cdot 2AsF_5$ (M = Sr, Ba, Pb)

$SrF_2 \cdot 2AsF_5$		$BaF_2 \cdot 2AsF_5$		$PbF_2 \cdot 2AsF_5$	
$d(\text{Å})$	I^f	$d(\text{Å})$	I^f	$d(\text{Å})$	I^f
5.25	s	5.25	s	5.31	s
4.64	m	4.78	m	4.54	m
4.13	w	4.27	m	4.19	w
				4.01	m
				3.75	s
3.28	vs	3.39	vs	3.34	vs
3.20	w	3.20	w	3.23	w
3.11	w			3.08	w
2.89	m	2.90	m	2.89	m
2.74	vw			2.75	vw
		2.66	vw	2.67	vw
		2.57	vw	2.52	w
2.45	m/w	2.41	m/w	2.43	vw
2.25	m	2.21	s		
		2.16	m		
2.13	vw	2.10	m	2.10	w
2.06	m	2.06	vw	2.06	vw
1.96	m	1.97	s/m	1.95	m

s = strong; m = medium; w = weak; v = very

f = intensities were estimated visually

For the strontium and barium adducts ν_1 is at slightly higher frequency than in the lead adduct. Most significantly, for the strontium adduct, ν_1 appears in both the infrared and Raman spectra with different frequencies [690 (i.r.) and 698 (Ra)]: this splitting can only originate in coupling of two or more AsF_6^- groups in the primitive unit cell. The barium adduct may have a different structure from the strontium analogue in that ν_1 does not appear in its infrared spectrum. The splittings shown in the ν_2 and ν_5 regions of both compounds imply low site symmetry as two and three components respectively are found.

TABLE 2

Observed infrared and Raman frequencies and tentative assignments for $MF_2.2AsF_5$ (M = Sr, Ba, Pb)

$SrF_2.2AsF_5$		$BaF_2.2AsF_5$		$PbF_2.2AsF_5$		Assignment
R(cm^{-1})	IR(cm^{-1})	R(cm^{-1})	IR(cm^{-1})	R(cm^{-1})	IR(cm^{-1})	O_h
	730 vs		720 vs		715 vs	$\nu_3(AsF_6^-)$
698(100)	690 s	696(100)		685(100)		$\nu_1(AsF_6^-)$
598(4)	597 w	594(8)	592 m		570 m	$\nu_2(AsF_6^-)$
575(26)		576(25)		549(21)		
395(19)		389(12)				
377(16)		376(23)				$\nu_5(AsF_6^-)$
374(28)		373(20)		370(38)		

s = strong; m = medium; w = weak; v = very

If there were significant $M^{2+}\cdots FAsF_5^-$ interactions one or more bands would be expected at significantly lower frequencies than is usual for AsF_6^-. It is also clear that none of the compounds contain $As_2F_{11}^-$ ion. Absorptions due to As-F-As bridging normally occur in the 480-510 cm^{-1} region (c.f. $Et_4N^+As_2F_{11}^-$ and $Bu_4N^+As_2F_{11}^-$ [20]) and evidence of bands in this region have not been found in either the infrared or the Raman spectra.

For the strontium, barium and lead adducts, therefore, salt-like structures, $M^{2+}(AsF_6^-)_2$, are implied with minimal contribution to the bonding from fluorine-bridged structures such as $F_5As-F-M-F-AsF_5$.

2. $\underline{MF_2.2AsF_5}$ (M = Ca, Mn, Cd, Hg)

Although only of moderate quality the X-ray powder diffraction patterns of the cadmium and mercury adducts indicate that they are essentially isostructural (Table 3). The calcium and manganese species, though closely related in the sense that the lines which appear occur in the same position, display significant intensity differences (Table 4).

490

TABLE 3

X-ray powder diffraction patterns of $MF_2 \cdot 2AsF_5$ (M = Cd, Hg)

CdF$_2 \cdot$2AsF$_5$ d(Å)	I^f	HgF$_2 \cdot$2AsF$_5$ d(Å)	I^f
6.87	s	6.89	s
4.83	w		
4.41	w	4.32	w
3.82	s	3.87	s
3.61	w		
3.32	s	3.37	s
3.08	w		
2.86	m	2.89	m
2.71	s	2.74	s
	vvw		vvw
2.41	vw	2.42	vw
2.29	m	2.31	m
2.21	m	2.23	m
2.14	w		
1.96	m	1.98	m
1.91	m	1.93	m
1.84	m	1.86	m
1.80	w		
1.75	w	1.76	w
1.71	m	1.73	w
1.68	w	1.69	w

TABLE 4

X-ray powder diffraction patterns of $MF_2 \cdot 2AsF_5$ (M = Ca, Mn)

CaF$_2 \cdot$2AsF$_5$ d(Å)	I^f	MnF$_2 \cdot$2AsF$_5$ d(Å)	I^f
6.87	vs	6.36	m
4.72	vs		
4.25	w	4.22	s
3.89	s	3.69	s
		3.22	w
3.05	w		
2.87	w	2.80	w
2.73	w		
		2.63	m
2.38	vw	2.35	vw
2.23	w	2.26	w
2.13	w	2.17	w
		2.09	w
1.94	m	1.92	w
1.87	w	1.86	w
		1.79	w
1.73	w	1.72	w
1.68	w	1.66	m

s = strong; m = medium; w = weak; v = very. ^{f} intensities were estimated visually

The vibrational spectra also suggest an overall close structural relationship for this group of compounds. More absorptions are found than in the strontium, barium and lead adducts, however, and it is evident that the spectra cannot be interpreted in terms of $M^{2+}(AsF_6^-)_2$ species in which only minor distortions of the O_h symmetry about the AsF_6^- ions occur. Clearly, a significant lowering of site symmetry has occurred.

The observed Raman and infrared frequencies are listed in Table 5 where they are correlated with those of alkali-metal and noble-gas hexafluoroarsenate species. For an assignment on the basis of C_{4v} symmetry about the $(F-AsF_5)^-$ parts of the molecules eleven normal modes of vibration are expected which are related to the six vibrational modes of the AsF_6^- anion of O_h symmetry. In particular, the frequencies of the normal modes for the C_{4v} molecule, $\nu_1(a_1)$, $\nu_2(a_1)$, $\nu_8(e)$, $\nu_3(a_1)$, and $\nu_7(b_2)$ should correspond closely to those of the respective normal modes of the O_h molecule, $\nu_1(a_g)$, $\nu_2(e_g)$, $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, and $\nu_5(t_{2g})$. In the case of the metal difluoride adducts the correlation on the basis of the C_{4v} assignment is good and frequencies of the absorptions and shifts are close to those for $\alpha-KrF_2 \cdot AsF_5$ and $XeF_2 \cdot AsF_5$, especially at the lower frequency end. The splittings of ν_8, ν_2, ν_5 and ν_7 in several of the spectra, result from site symmetry effects.

The band observed at 562 cm^{-1} in the infrared spectrum of $PbF_2 \cdot SnF_2$ has been assigned to the PbF^+ cation [22] and is about 30 cm^{-1} higher in frequency than the symmetric stretching vibration (ν_1) in PbF_2 [23]. Noble gas cationic species, KrF^+ [4,5] and XeF^+ [2,3], similarly have absorptions at frequencies more than 100 cm^{-1} higher than those found in the neutral molecules. Since no bands can be found in the difluoride adduct spectra which correlate in the same way with the symmetric stretching frequencies of the neutral metal difluorides, it seems unlikely that the adducts can be formulated as $MF^+ (As_2F_{11})^-$ species. The fact that, there are no absorptions in the 480-510 cm^{-1} region, which are characteristic of the $As_2F_{11}^-$ ion, bears this out further.

TABLE 5

Observed infrared and Raman frequencies and tentative assignments for $MF_2 \cdot 2AsF_5$ (M = Ca,Mn,Cd,Hg) and related spectra

$CaF_2 \cdot 2AsF_5$		$MnF_2 \cdot 2AsF_5$		$CdF_2 \cdot 2AsF_5$		$HgF_2 \cdot 2AsF_5$		$\alpha KrF_2 \cdot AsF_5$[4]	$XeF_2 \cdot AsF_5$[4]	Assignment		$CsAsF_6$[16]		$KAsF_6$[21]	
$R(cm^{-1})$	$IR(cm^{-1})$	$R(cm^{-1})$	$IR(cm^{-1})$	$R(cm^{-1})$	$IR(cm^{-1})$	$R(cm^{-1})$	$IR(cm^{-1})$	$R(cm^{-1})$	$R(cm^{-1})$	C_{4v}	O_h	$R(cm^{-1})$	$IR(cm^{-1})$	$R(cm^{-1})$	$IR(cm^{-1})$
769(34)	770 m	774(35)	775 s	770(39)	770 m	766(40)	770 s		731 (5)	ν_8	ν_3		699		698 vs
	745 m		730 m		721 s		720 m	713 (8)	724 (5)						
687(100)	670 m/s	696(100)	685 m	688(100)	680 m	682(100)	680 m	679 (7)	678(20)	ν_1	ν_1	685		692 s	
			630 m		640 m	657(15)	645 w		667(4)	ν_2					
					600 vw		630 w								
569(17)	585 w	570(23)	575 m	560(20)	560 w	564(23)	550 w		586(10)	ν_5	ν_2	576		580 m	
	565 w	544(25)	545 m	547(20)		539(14)	510 w								
416(12)				413(17)		408(10)		453 (1)	443 (3)	ν_4	ν_4				
381(11)				382(10)				417 (9)	417 (5)	ν_3					
366(22)		364(25)		364(23)		365(23)		383 (5)	387 (6)	ν_9					
356(20)		354(25)		335				371 (1)		ν_7	ν_5	372	392	375 m	382(sh)
								276 (1)		ν_{11}					

$\underline{MF_2 \cdot 2AsF_5 \ (M = Mg, \ Co, \ Ni)}$

All three adducts produce X-ray powder diffraction patterns
of similar and moderately good quality (Table 6). It is clear from
these data that the compounds are close to being isostructural.
Although some lines which appear in the patterns from the nickel
adduct are not observed in the magnesium and cobalt compounds, this
may simply be due to their being very weak. Also, since the films
were not calibrated, the minor differences in d-spacings are probably
not significant.

The vibrational spectra of the adducts are shown in Table 7.
They have a marked similarity to those of the calcium, manganese,
cadmium and mercury series and, in common with them, display a
larger number of bands than can be reasonably accounted for by
molecules containing simple AsF_6^- octahedra. A striking feature
is the relationship of the spectra to that of AsF_5 itself and, in
particular, the observation of bands in each of the spectra in the
810 cm^{-1} region. The occurrence of ν_4 in the cobalt and nickel
spectra is also novel.

The appearance of additional bands in the high-frequency
regions of the spectra of pentafluoride-containing adducts of TaF_5
and NbF_5 when compared with the analogous SbF_5 adducts has been
attributed to the anionic components of these adducts being less
ionic and more pentafluoride-like [3]. The implication is that the
fluorine-bridged contribution to the bonding becomes more significant
and so absorptions due to fluorine-bridge bonding should be evident.
These are expected at 450-510 cm^{-1} [20, 3]. The observation of the
bands at about 810 cm^{-1} in the Raman and infrared spectra and those
at 458 and 490 cm^{-1} in the Raman spectra of the cobalt and nickel
adducts respectively, suggest, therefore, that the adducts may be
formulated in terms of the fluorine-bridged structure AsF_5-F-M-F-AsF_5
and that, compared with the previous two classes, the ionic contri-
butions to the bonding are minimized.

General Observations

Although the X-ray powder photographs are of variable quality
and have not been calibrated it has been found [26] that they can be
indexed on the basis of tetragonal cells which have similar cell
parameters (Table 8). The experimental and calculated densities are
in acceptable agreement and indicate 8 formula units per cell.

TABLE 6

X-ray powder diffraction patterns of $MF_2 \cdot 2AsF_5$ (M = Mg, Co, Ni)

$MgF_2 \cdot 2AsF_5$		$CoF_2 \cdot 2AsF_5$		$NiF_2 \cdot 2AsF_5$	
d(Å)	I^f	d(Å)	I^f	d(Å)	I^f
4.15	s	4.02	m	3.97	m
3.64	s	3.57	s	3.54	s
3.16	w	3.01	w	broad-diffuse	
2.63	m	2.61	m	2.59	m
2.45	vw			2.45	w
2.18	s	2.16	s	2.14	s
				2.02	w
1.82	m	1.80	m	1.79	m
				1.72	vw
1.65	s	1.65	s/m	1.63	s
1.59	w	1.58	w	1.56	w
1.53	vw			1.53	vw
1.44	w	1.44	w	1.45	w
		1.43	w	1.42	w
1.38	w			1.38	vw
				1.36	vw
1.31	w	1.31	w	1.30	w
1.26	w	1.27	w	1.26	w

s = strong; m = medium; w = weak; v = very

f intensities were estimated visually.

It has been noted that for pentafluorides [27] and many carbonyls and carbonyl fluorides [28], unit cell volumes calculated assuming close-packed arrays for the non-metallic atoms and an atomic volume for fluorine of 17 Å^3, correlate closely with experimentally obtained values. On this basis, the calculated cell volume for the adducts is 1632 Å^3 and comparison with the observed values (Table 8) shows only one adduct, $SrF_2 \cdot 2AsF_5$, which has a smaller (1584 Å^3) volume than this.

The fact that the powder patterns can be indexed on the basis of the same cell suggests that the heavy atoms within the cells are in essentially the same atomic positions in each of the adducts. The minor differences in the patterns are almost certainly due to

TABLE 7

Observed infrared and Raman frequencies and tentative assignments for $MF_2 \cdot 2AsF_5$ (M = Mg, Co, Ni) and related spectra

AsF_5 R(cm^{-1})[25]	IR(cm^{-1})[24]	Assignment D_{3h}	$MgF_2 \cdot 2AsF_5$ R(cm^{-1})	IR(cm^{-1})	$CoF_2 \cdot 2AsF_5$ R(cm^{-1})	IR(cm^{-1})	$NiF_2 \cdot 2AsF_5$ R(cm^{-1})	IR(cm^{-1})	Assignment C_{4v}	$XeF_2 \cdot AsF_5$[4] R(cm^{-1})
813m	811	ν_5	808(25)	812m	805(28)	810m	785(12)	812m		731(5)
	784	ν_3		775vs		765vs		775svs	ν_8	724(5)
774w		$2\nu_8$	771(58)		765(34)		771(21)			
734.3vs		ν_1	713(100)	720s	707(100)	715m	710(100)	712m	ν_1	678(20)
644m		ν_2		635s		640m		605s	ν_2	667(4)
			573(14)	585w	560(13)	570m	565(14)	580w(sh)	ν_5	586(10)
				540w		510w		535w		
					458(19)		490(12)		ν_4	443(3)
	400								ν_3	417(5)
386m		ν_8	389(25)		384(32)		384(38)		ν_9	387(6)
	372	ν_6							ν_7	
259vw		$2\nu_7$			276(13)				ν_{11}	
					225(18)					
					207(14)					
							158(21)			
130m	132	ν_7	105(27)		107(33)				ν_6	180(2)

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TABLE 8

Unit cell parameters, densities and volumes of the tetragonal compounds $MF_2 \cdot 2AsF_5$ (26)

Compound	$a(\text{Å})$	$c(\text{Å})$	$V(\text{Å}^3)$	δ calc.(g/cm^3)	δ exp.(g/cm^3)
$SrF_2 \cdot 2AsF_5$	13.0_7	9.2_7	1584	3.90	3.7
$BaF_2 \cdot 2AsF_5$	13.4_9	9.5_9	1745	3.91	
$PbF_2 \cdot 2AsF_5$	13.4_4	9.5_0	1716	4.53	3.8
$CaF_2 \cdot 2AsF_5$	13.7_1	9.7_1	1825	3.04	
$MnF_2 \cdot 2AsF_5$	13.6_3	9.6_4	1791	3.21	3.4
$CdF_2 \cdot 2AsF_5$	13.7_1	9.6_6	1816	3.59	3.5
$HgF_2 \cdot 2AsF_5$	13.4_3	9.4_8	1710	4.49	
$MgF_2 \cdot 2AsF_5$	13.6_4	9.6_3	1792	2.98	
$CoF_2 \cdot 2AsF_5$	13.6_0	9.6_2	1779	3.26	
$NiF_2 \cdot 2AsF_5$	13.6_2	9.6_3	1786	3.25	3.02

differences in the atomic parameters of the surrounding fluorine atoms and these differences are evident in the vibrational spectroscopic results.

It appears that compounds of the $MF_2 \cdot 2AsF_5$ stoicheiometry can be discussed in terms of ionic formulations, $M^{2+}(AsF_6)_2^-$, or covalent fluorine-bridged structures, $F_5As-F-M-F-AsF_5$, and the bonding can range between these two limiting cases depending on the fluorine ion donor ability of the particular difluoride. An estimation of these abilities can be made on the basis of effective ionic radii. Metal difluoride donor abilities should increase down each group along the transition series of the periodic table with increasing ionic radius of the metal.

The strong Lewis basicity of the metal difluorides in the barium, strontium and lead compounds is evidenced by their forming normal ionic hexafluoroarsenates. Both fluoride ions are donated and octahedrally symmetrical AsF_6^- species formed. The effective ionic radii [29] of these three metal ions are around 1.3 Å and are much bigger and more polarizable than the other metals and consequently, their fluoride ion donor ability is higher.

The Ca^{2+}, Cd^{2+}, Hg^{2+} and Mn^{2+} ions are less polarisable than those of Ba^{2+}, Sr^{2+} and Pb^{2+} and their radii, which are of the order of 1.0Å, are distinctly smaller. The difluorides of these metals will, therefore, act as somewhat weaker donors of fluoride and, consequently, some reduction in ionic character and increase in fluorine bridging in the structures is envisaged.

The effective ionic radii of Co^{2+} and Mg^{2+} are even smaller (~0.7Å) than those of the Ca^{2+}, Cd^{2+}, Hg^{2+} and Mn^{2+}, and the structures of the adducts are the same. The spectroscopic data for the two compounds suggest that distortion of the AsF_6^- octahedra due to the covalent contribution to the bonding is significant and fluorine-bridged structures are the most probable formulations.

EXPERIMENTAL

Materials. Magnesium, calcium, strontium, barium, manganese, cadmium and lead difluorides were prepared by dissolution of the metal carbonates in 40% hydrofluoric acid followed by evaporation and drying of the residual solids at elevated temperature. Cobalt difluoride was prepared by hydrofluorination of cobalt dichloride at $300^{\circ}C$. Nickel difluoride was obtained by decomposition of hydrazinium (I) trifluoronickelate (II) at $150^{\circ}C$, followed by fluorination with elemental fluorine at $400^{\circ}C$. Mercury difluoride was prepared by fluorination of mercury dichloride with elemental fluorine under pressure in a nickel can at $300^{\circ}C$. The excess of fluorine and the chlorine trifluoride formed in the reaction were removed at room temperature by pumping.

Commercial anhydrous hydrogen fluoride was purified using sodium fluoride in a nickel container. The bifluoride formed was heated under vacuum at $100^{\circ}C$ to remove impurities, and then heated to $450^{\circ}C$ to decompose the bifluoride and obtain hydrogen fluoride. This was purified further by trap to trap distillation.

Arsenic pentafluoride was prepared by pressure fluorination of arsenic trioxide with elemental fluorine in a nickel reactor at $300^{\circ}C$ and a total pressure of 40 atmospheres. The excess of fluorine and the residual oxygen formed were removed by pumping at $-183^{\circ}C$.

Preparation of the hexafluoroarsenates. In a typical experiment about 3 millimoles of the difluoride were loaded into an all-KelF reaction vessel in a dry box. About 4 grammes of anhydrous hydrogen

fluoride was distilled onto the difluoride via an all KelF vacuum line. Arsenic pentafluoride was added stepwise and the mixture shaken at room temperature after each addition. The last traces of insoluble fluorides disappeared when the $MF_2:AsF_5$ ratio of 1:2 was reached. After removal of volatiles at room temperature the crystalline hexafluoroarsenates were isolated. Material balances were monitored carefully throughout the experiments.

Chemical analyses. Metals (Mg, Ca, Sr, Ba, Mn, Co, Ni, Cd, Hg, Pb) were determined by direct, indirect or substitution complexometric titration. The analysis for AsF_6^- was achieved by determination as the insoluble tetraphenylarsonium salt [1]. The results are summarized below:

$MgF_2 \cdot 2AsF_5$. Found: Mg, 5.9; AsF_6^-, 93.2; Calc.: Mg, 6.1; AsF_6^-, 94.0%
$CaF_2 \cdot 2AsF_5$. Found: Ca, 9.6; AsF_6^-, 90.1; Calc.: Ca, 9.6; AsF_6^-, 90.4%
$SrF_2 \cdot 2AsF_5$. Found: Sr, 18.2; AsF_6^-, 81.2; Calc.: Sr, 18.8; AsF_6^-, 81.2%
$MnF_2 \cdot 2AsF_5$. Found: Mn, 12.7; AsF_6^-, 87.8; Calc.: Mn, 12.7; AsF_6^-, 87.3%
$CoF_2 \cdot 2AsF_5$. Found: Co, 13.6; AsF_6^-, 86.2; Calc.: Co, 13.5; AsF_6^-, 86.5%
$NiF_2 \cdot 2AsF_5$. Found: Ni, 13.7; AsF_6^-, 86.3; Calc.: Ni, 13.5; AsF_6^-, 86.6%
$CdF_2 \cdot 2AsF_5$. Found: Cd, 22.9; AsF_6^-, – Calc.: Cd, 22.9; AsF_6^-, 77.1%
$HgF_2 \cdot 2AsF_5$. Found: Hg, 35.2; AsF_6^-, – Calc.: Hg, 34.7; AsF_6^-, 65.3%
$PbF_2 \cdot 2AsF_5$. Found: Pb, 33.7; AsF_6^-, 62.2; Calc.: Pb, 35.4; AsF_6^-, 64.6%

Spectroscopy and X-ray diffraction studies. Infrared spectra of powdered solids in Nujol mulls on silver chloride windows were obtained using a Zeiss UR 20 spectrometer. The mulls were prepared in a dry box. Raman spectra of the solids contained in Pyrex tubes were recorded using a modified Coderg PH1 Raman spectrometer with the exciting radiation of the 4880 Å line of a Coherent Radiation Laboratories Model 52 Ar Ion laser. X-ray powder diffraction data were obtained with a Guinier type camera and CuK_α radiation.

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