Metal(II) Hexafluoroantimonates: Preparation and Characterization of $MF_2 \cdot 2SbF_5$ (M = Mg, Ni, Zn, Fe, Co, Cu, Cr, Ag, Cd, or Pb) and the *X*-Ray Structure Determination of $AgF_2 \cdot 2SbF_5$†

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Reactions of MF_2 (M = Mg, Ni, Zn, Fe, Co, Cu, Cr, Ag, Cd, or Pb) with excess of SbF_5 in anhydrous HF or SO_2 at room temperature give adducts of composition $MF_2 \cdot 2SbF_5$. Efforts to prepare similar adducts of the difluorides of Ca, Sr, and Ba led only to non-stoicheiometric compounds. Vibrational spectra and *X*-ray powder diffraction studies indicate that the Mg, Ni, and Zn compounds and the Fe, Co, and Cu compounds form two distinct isostructural triads. The remaining adducts have structures which differ from each other and from those of the two triads. A single-crystal *X*-ray study on $AgF_2 \cdot 2SbF_5$ has shown that the crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 5.224(1), b = 5.467(2), c = 8.779(2) Å, α = 75.78(2), β = 89.02(2), γ = 65.29(2)°, and Z = 1. The Ag^{2+} ion has square-planar co-ordination with two Ag–F distances, 2.095(5) and 2.132(4) Å. Two further F atoms at 2.431 (3) Å complete a distorted octahedron. Distorted $[SbF_6]^-$ octahedra in the structure have four Sb–F distances between 1.830(4) and 1.875(3) Å while two others are 1.942(4) and 1.965(4) Å.

Early vibrational spectroscopic work and ^{119}Sn Mössbauer studies suggested the presence of $[(SnF)_n]^{n+}$ cations in the structures of the 1:1 adducts, $SnF_2 \cdot BF_3$, $SnF_2 \cdot AsF_5$, and $SnF_2 \cdot SbF_5$.[1] The overall accuracy of this interpretation has since been confirmed by a single-crystal *X*-ray determination on the arsenic compound which showed that it contains the cyclic cation $[(SnF)_3]^{3+}$.[2] Another metal(II) fluoro-cationic species is $[Sn_2F_3]^+$, found in the SnF_2–BF_3 system,[3] in $2SnF_2 \cdot AsF_5$ and $2SnF_2 \cdot SbF_5$,[4] and in Sn_2ClF_3.[5] The possibility that a wide range of cationic and pseudo-cationic species occur in metal difluoride systems is further evidenced by our own vibrational spectroscopic work which has suggested the presence of $[MF]^+$, $[M_2F_3]^+$,[6,7] or $[(MF)_n]^{n+}$ [6] and our crystallographic work which has confirmed the presence of $[(AgF)_n]^{n+}$ in the $AgF_2 \cdot AsF_5$ compound.[8]

In the present paper we report the results of part of a programme designed to probe to what extent such cations appear in the MF_2–SbF_5 system.

Results and Discussion

The adducts $MF_2 \cdot 2SbF_5$ (M = Mg, Ni, Zn, Fe, Co, Cu, Cr, Ag, Cd, or Pb) were prepared by the reaction of the appropriate metal difluoride with excess of SbF_5 at room temperature in anhydrous HF as solvent. All were soluble in HF but were obtained as crystalline solids after removal of volatiles under dynamic vacuum to constant weight (Scheme).

$$MF_2 + nSbF_5 \xrightarrow{(i)} MF_2 \cdot 2SbF_5(\text{solv.}) + (n-2)SbF_5(\text{solv.}) \xrightarrow{(ii)} MF_2 \cdot 2SbF_5(\text{cryst.})$$

Scheme. (*i*) Anhydrous HF solvent at room temperature. (*ii*) Pump at room temperature

The cobalt compound was also prepared in liquid SO_2 as solvent. In all cases material balances were monitored throughout the experiments. All of the adducts are white except the Ni (yellow), Co (violet), and Ag (blue) compounds. Efforts to prepare the Ca, Sr, and Ba analogues resulted in the formation of only non-stoicheiometric compounds.

Raman and i.r. spectra (Table 1) and *X*-ray powder diffraction data (Table 2) suggest that the Mg, Ni, and Zn compounds and the Fe, Co, and Cu compounds form two distinct structural triads while the rest have structures which differ from each other and from those of the two triads. The adduct $SnF_2 \cdot 2SbF_5$, which has been prepared previously by Gillespie and co-workers,[1] has an *X*-ray powder diffraction pattern which indicates that it also has the same structure as the Fe, Co, Cu triad. This is further supported by the similarity of the vibrational spectra.[1]

Compared with $CsSbF_6$ [1] all of the compounds exhibit more bands in the Raman and i.r. spectra than expected for an isolated $[SbF_6]^-$ anion (O_h point group) and are closer to that of $XeF_2 \cdot SbF_5$ in which the $[SbF_6]^-$ anion was found to have C_{4v} symmetry.[9] It is clear that none of the compounds contains an $[Sb_2F_{11}]^-$ anion which is characterized by a large number of bands in the 590—750 cm^{-1} region.[1,9,10]

The triad of Mg, Ni, and Zn adducts are notable in that they have the same structure as the related $MgF_2 \cdot 2AsF_5$ compound [7] but with a bigger unit cell. For all of these adducts more bands are observed than expected for an octahedral hexafluorometalate(V) anion, and most are in the high-frequency region. With other pentafluoride-containing adducts such observations have been interpreted in terms of a reduction in the ionic contribution to the bonding and a more significant contribution from fluorine-bridged structures.[7,9]

The Fe, Co, Cu triad, together with $SnF_2 \cdot 2SbF_5$,[1] appear to be isostructural. Because of the complexity and variations in the vibrational spectra it is not possible to make meaningful assignments by use of the known ionic hexafluoroantimonate. However, it is clear that the adducts have structures that can be considered in terms of an $M[SbF_6]_2$ formulation rather than the alternative $[(MF)_n]^{n+} \cdot n[Sb_2F_{11}]^-$. The i.r. spectra in

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† Silver bis(hexafluoroantimonate).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Raman (R)* and i.r. spectra (cm^{-1}) of $MF_2 \cdot 2SbF_5$ adducts

SbF_5		$MgF_2 \cdot 2SbF_5$		$NiF_2 \cdot 2SbF_5$		$ZnF_2 \cdot 2SbF_5$		$FeF_2 \cdot 2SbF_5$		$CoF_2 \cdot 2SbF_5$	
$R_{liq.}$	i.r.	R	i.r.	R	i.r.	R	i.r.	R	i.r.	R	i.r.
	742		742vs		740 (sh)		738s				
717			718w (sh)				712w (sh)				
	705	705(30)	708vs	712(37)	710vs	704.5(29)	707vs	704(33)	702vs		692vs
									685m (sh)		
670	669	670(100)	676s	674(100)	675ms	668(100)	670s	667(100)	670m	664(100)	670vw (sh)
											650w (sh)
			602vs	612(20)					618m		
						598(18)	590vs				592s
			572w (sh)	576(25)			564w (sh)	562(19)		558(9.2)	557w (sh)
			532m			538(9.5)			540m		
					527m						
						516(19)	518w			480(8.2)	
	450					458(13)	458vw				460w (sh)
			387mw								
			360mw								
	310			300(25)		294(37)		292(80)		286(22)	
						273(23)		268(28)		274(22)	
				238(38)							

$CuF_2 \cdot 2SbF_5$		$CrF_2 \cdot 2SbF_5$		$AgF_2 \cdot 2SbF_5$		$CdF_2 \cdot 2SbF_5$		$PbF_2 \cdot 2SbF_5$		$CsSbF_6$	
		726(36)							718w (sh)		
	703vs	704(22)				703(37)	707vs	702(18)	701s		
		692(20)	694vs		692vs		690m (sh)				
665(100)	676s			668(100)	668ms				668w (sh)		674 (sh)
	636m (sh)	648(100)	630m	658(75)	640m	654(100)	642w (sh)	647(100)	638vs	650(100)	658s
	612m (sh)		600w	600(37)			615vs	607(19)	612vs		
594(15)				580(31)	583w				582w		
	560m (sh)	564(7)	555m	552(20)	554w		553.5mw		562m (sh)	572(19)	
544(10)						546(15)		545(24)	546s		
		524(8)	520m					523(26)	525s (sh)		
					496w						
	450 (sh)										
						344(9)					
287(30)		298(11)		290(37)				285(21)		285(27)	287s
274(20)		274(22)				272(27.5)		273.5(17)		279(18)	
		248(5)									
		202(8)									

* Relative intensity in parentheses.

particular are very similar to that of $AgF_2 \cdot 2SbF_5$ and this implies similarity of structure.

The crystal structure of $AgF_2 \cdot 2SbF_5$ is of the $CdCl_2$ type in which $[SbF_6]^-$ octahedra form a cubic close-packed array and the Ag^{2+} ions occupy one half of the octahedral holes. The chosen space group requires the Ag^{2+} cation to have a centrosymmetric environment, surrounded by six fluorine atoms in a distorted octahedral arrangement. The octahedron is elongated in one direction so that the co-ordination around silver is probably best regarded as square planar. The Ag–F bond lengths (Table 3) may be compared with a similar arrangement found in the structure of AgF_2.[11] Those which constitute the square plane of fluorine about silver [Ag–F(6), Ag–F(6^{IV}) at 2.132(4); Ag–F(3^{I}), Ag–F(3^{V}) at 2.095(5) Å; mean 2.114(5) Å] are, on average, a little longer than their equivalents (Ag–F 2.07 Å) in the AgF_2 structure, the remaining two elongated bonds [Ag–F(2^{II}), Ag–F(2^{III}) at 2.431(3) Å] are 0.15 Å shorter. This may be a consequence of a small covalent interaction through fluorine bridging between anion and cation.

The shape of the $[SbF_6]^-$ anion is that of a distorted octahedron as implied by the vibrational spectroscopic data. The Sb–F bond lengths range from 1.830(4) to 1.965(4) Å and the F–Sb–F angles vary between 83.9(2) and 97.3(2)°. The

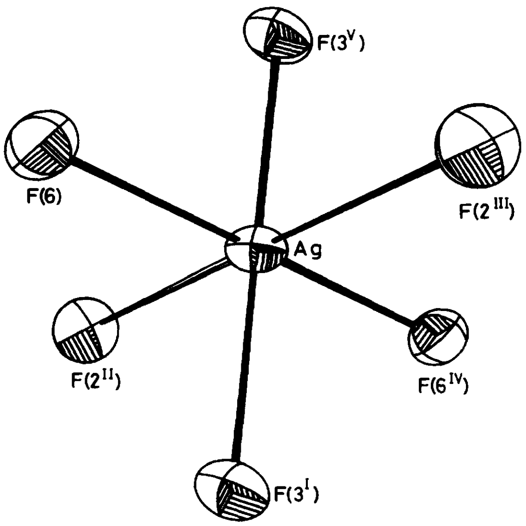

Figure 1. An ORTEP view of the Ag^{2+} environment. The atoms are represented by thermal ellipsoids drawn at the 50% probability level

Table 2. X-Ray powder diffraction patterns of the $MF_2{\cdot}2SbF_5$ adducts

$MgF_2{\cdot}2SbF_5$	$NiF_2{\cdot}2SbF_5$	$ZnF_2{\cdot}2SbF_5$	$FeF_2{\cdot}2SbF_5$	$CoF_2{\cdot}2SbF_5$	$CuF_2{\cdot}2SbF_5$	$CrF_2{\cdot}2SbF_5$	$CdF_2{\cdot}2SbF_5$	$PbF_2{\cdot}2SbF_5$
			4.98m	4.98m	4.96s			
							4.82s	
						4.64m		
4.56m	4.56m	4.56m						
	4.26m					4.22s	4.24s	
								4.07w
								3.88w
						3.85m		
4.17m	4.17m	4.18m						
3.68s	3.68s	3.69s	3.70m	3.70m	3.68m	3.68m		
						3.63m		
	3.58m		3.55s	3.54s	3.54s			
								3.38w
							3.19s	
			2.90w	2.88w	2.89w		2.93w	
2.70m	2.70m	2.69m				2.78m		
2.51w	2.51w	2.50w					2.55w	
2.32w	2.33w							
2.22w	2.22m	2.22w	2.26w	2.25w	2.25w	2.24w		
						2.12m	2.14m	
2.10w	2.10w	2.10w	2.06m	2.05m	2.06m		2.10m	
						1.93w	1.95m	
1.86m	1.86m	1.86m					1.91m	
			1.78w	1.78w	1.79w	1.76w		
						1.73w	1.73w	
1.70m	1.70m	1.69m	1.68w	1.68m	1.68w	1.70w		
						1.66w	1.64w	
1.60m	1.61m	1.61m	1.60m	1.60m	1.60m	1.61w	1.62m	
1.50w	1.50w	1.50w	1.52w	1.52w	1.52w	1.54w	1.50w	
1.47w	1.47w	1.47w	1.46w	1.46w	1.46w			
1.43w	1.44w	1.43w	1.40w	1.40w	1.40w			
			1.36w	1.35w	1.35w			

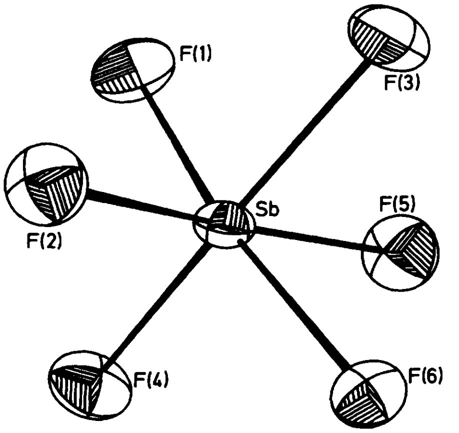

Figure 2. An ORTEP view of the $[SbF_6]^-$ anion

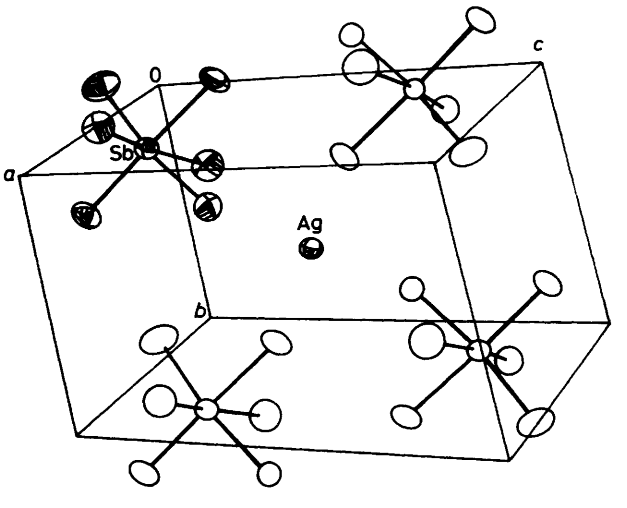

Figure 3. A view of the unit cell of $Ag[SbF_6]_2$

distortions are probably also due to partial fluorine bridging as a result of the strong polarizing effect of the Ag^{2+} cation. An ORTEP[12] view of the environment of the silver(II) cation is shown in Figure 1 and that of the $[SbF_6]^-$ anion in Figure 2. The inter-relationship between the two is clearly shown in the view of the unit cell in Figure 3.

The remaining adducts, those of Cr, Cd, and Pb, have X-ray powder diffraction patterns which differ from each other, from that of $AgF_2{\cdot}2SbF_5$ and from those of the two triads. The vibrational spectra, however, are clearly related to those of the other $MF_2{\cdot}2SbF_5$ compounds and it seems certain that they should be thought of in terms of essentially an $M[SbF_6]_2$ type formulation.

Experimental

Starting Materials.—The metal difluorides were prepared as described previously[6,7] except those of chromium (Koch-Light Laboratories Ltd.) and copper (Alfa Inorganics, Ventron GmbH), which were used as supplied. Antimony pentafluoride (Ozark-Mahoning Co.), anhydrous hydrogen fluoride (J. T. Baker Chemical Co.), and sulphur dioxide (Merck) were purified by standard procedures. The purity of the metal difluorides was checked by chemical analysis and of SbF_5 by vibrational spectroscopy.

Table 3. Interatomic distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

Ag^{2+} environment					
Ag–F(6), F(6^{IV})	2.132(4)	F(6)–Ag–F(3^{I})	91.1(2)		
Ag–F(3^{I}), F(3^{V})	2.095(5)	F(6)–Ag–F(2^{II})	98.1(1)		
Ag–F(2^{II}), F(2^{III})	2.431(3)	F(3^{I})–Ag–F(2^{III})	90.2(1)		
$[SbF_6]^-$ ion					
Sb–F(1)	1.831(5)	F(1)–Sb–F(2)	93.7(2)	F(2)–Sb–F(6)	84.7(2)
Sb–F(2)	1.875(3)	F(1)–Sb–F(3)	86.8(2)	F(3)–Sb–F(4)	174.8(2)
Sb–F(3)	1.965(4)	F(1)–Sb–F(4)	97.3(2)	F(3)–Sb–F(5)	86.6(2)
Sb–F(4)	1.830(4)	F(1)–Sb–F(5)	94.2(2)	F(3)–Sb–F(6)	83.9(2)
Sb–F(5)	1.846(4)	F(1)–Sb–F(6)	170.6(2)	F(4)–Sb–F(5)	96.3(2)
Sb–F(6)	1.942(4)	F(2)–Sb–F(3)	84.0(2)	F(4)–Sb–F(6)	92.0(2)
		F(2)–Sb–F(4)	92.6(2)	F(5)–Sb–F(6)	85.8(2)
		F(2)–Sb–F(5)	167.3(2)		

Symmetry code: I $x, 1 + y, z$; II $-1 + x, 1 + y, z$; III $2 - x, -y, 1 - z$; IV $1 - x, 1 - y, 1 - z$; V $1 - x, -y, 1 - z$.

Table 4. Chemical analyses of $MF_2 \cdot 2SbF_5$ adducts (%)

	M^{2+}		Total fluorine		Free fluoride	
Adduct	Found	Calc.	Found	Calc.	Found	Calc.
$MgF_2 \cdot 2SbF_5$	5.0	4.90	45.9	46.00	7.6	7.65
$NiF_2 \cdot 2SbF_5$	10.5	11.05	42.6	43.00	6.9	7.15
$ZnF_2 \cdot 2SbF_5$	11.8	12.20	42.2	42.45	6.7	7.10
$FeF_2 \cdot 2SbF_5$	10.3	10.60	42.8	43.25	7.0	7.20
$CoF_2 \cdot 2SbF_5$	11.0	11.10	42.9	43.00	7.2	7.15
$CuF_2 \cdot 2SbF_5$	11.6	11.90	42.5	42.60	7.3	7.10
$CrF_2 \cdot 2SbF_5$	9.6	9.95	43.1	43.55	7.3	7.25
$CdF_2 \cdot 2SbF_5$	18.9	19.25	38.9	39.05	5.9	6.50
$PbF_2 \cdot 2SbF_5$	30.5	30.55	33.6	33.60	5.4	5.60

Apparatus.—Kel-F or FEP reaction tubes, fitted with Kel-F valves were used. The reaction vessels were pre-treated with anhydrous HF or fluorine and pumped to high vacuum before use. The non-volatile materials were handled in an argon filled dry-box and the volatiles, SbF_5 and HF, were distilled using a prefluorinated metal vacuum line.

Characterizations.—Reaction stoicheiometries were monitored by weighing the reaction vessels and their contents on a Mettler analytical balance. The adducts isolated were characterized by chemical analysis in which the metal,[13] free fluoride, and total fluorine[14] were determined (Table 4).

I.r. spectra of the powdered solids pressed between KBr or AgCl windows were obtained using Zeiss UR20 and Perkin-Elmer 580 spectrophotometers. The Raman spectra of the adducts contained in Pyrex tubes were recorded using Coderg model T800 or Spex 14 01 instruments with the exciting radiation of the 514.5 nm line of an Ar laser (Coherent Radiation). *X*-Ray powder diffraction patterns were recorded on a Debye–Scherrer type camera using Cu-K_α radiation.

Preparation of $MF_2 \cdot 2SbF_5$.—In a typical experiment the difluoride (*ca.* 3 mmol) was loaded into a reaction vessel in a dry-box. Antimony pentafluoride, in a large excess, or in a stoicheiometric amount as appropriate, was distilled onto the difluoride and anhydrous HF (3—11 g) was added. The cobalt compound, $CoF_2 \cdot 2SbF_5$, was also prepared in liquid SO_2 solvent. When the mixtures were warmed to room temperature colourless solutions were obtained except for $NiF_2 \cdot 2SbF_5$ (yellow), $CoF_2 \cdot 2SbF_5$ (violet), and $AgF_2 \cdot 2SbF_5$ (blue). The solvent and excess of SbF_5 were removed at room temperature and, after prolonged pumping, solids of composition $MF_2 \cdot 2SbF_5$ were isolated. Material balances were monitored carefully throughout the experiments.

X-Ray Structure Determination of $AgF_2 \cdot 2SbF_5$.—Suitable crystals were prepared by the slow concentration of solutions (in HF) of $AgF_2 \cdot 2SbF_5$ in vertical 6-mm (outside diameter) Kel-F tubes. Once crystals began to appear the concentrate was held at 40 °C until good crystals were obtained. Excess of solvent was removed under vacuum and the crystals were transferred into prefluorinated glass capillaries in a nitrogen-filled dry-box.

Crystal data. $AgF_{12}Sb_2$, $M = 579.3$, triclinic, $a = 5.224(1)$, $b = 5.467(2)$, $c = 8.779(2)$ Å, $\alpha = 75.78(2)$, $\beta = 89.02(2)$, $\gamma = 65.29(2)$°, $U = 219.7$ Å^3 (by least-squares refinement of the 2θ values of 35 reflections with $10 < \theta < 20°$, λ(Mo-K_α) = 0.710 69 Å, space group $P\bar{1}$ (no. 2) assumed, $Z = 1$, $D_c = 4.377$ g cm^{-3}, $F(000) = 257$. Crystal dimensions 0.09 {010} × 0.12 {001} × 0.27 {211} mm, μ(Mo-K_α) = 84.89 cm^{-1}.

Data collection. CAD4 diffractometer, ω–2θ mode, scan width = 0.9 + 0.3 tanθ, max. scan time 30 s, $T = 293(1)$ K; 1 632 reflections measured ($0 < \theta < 30°$, $+h \pm k \pm l$), 1 212 unique after an exact absorption correction (max., min. transmission factors = 0.277, 0.134) with $I > 3\sigma(I)$, corrected for variations in reference reflections.

Structure analysis and refinement. Conventional heavy-atom methods following a trial solution with Ag at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Full-matrix least-squares refinement with all atoms anisotropic and an isotropic extinction parameter x [= 0.0170(7)]. The source of the scattering factors for neutral atoms is given in ref. 15. The weighting scheme $w = 36.9/[\sigma^2(F_o) + 0.000\,04\,F_o^{\,2}]$ with $\sigma^2(F_o)$ from counting statistics gave a uniform distribution of $\Sigma w(\Delta F)^2$ over $\sin\theta/\lambda$ and $|F_o|$. A final difference Fourier map was featureless apart from peaks <7.5 e Å^{-3} close to the Ag and Sb atoms. The largest shift/error in the final cycle was <0.03. Final R and R' values were 0.032 and 0.033 respectively. Fractional atomic co-ordinates are given in Table 5. The SHELX 76[16] computer program running on the DEC 10

Table 5. Fractional atomic co-ordinates ($\times 10^5$ for Ag, Sb; $\times 10^4$ for F)

Atom	*x*	*y*	*z*
Ag	50 000	50 000	50 000
Sb	73 221(7)	1 298(6)	23 400(4)
F(1)	6 906(9)	−2 270(8)	1 338(5)
F(2)	11 209(7)	−2 080(7)	2 899(4)
F(3)	6 922(8)	−2 272(7)	4 310(4)
F(4)	7 935(9)	2 401(8)	606(4)
F(5)	3 479(8)	2 279(9)	2 258(5)
F(6)	7 739(8)	2 253(7)	3 719(4)

computer at the University Computer Centre, Ljubljana was used for all calculations except the determination of bond lengths for which *X*-RAY 72[17] was used.

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