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METAL (II) HEXAFLUOROARSENATES: PREPARATIONS AND SOME PROPERTIES
OF $2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn), $MF_2 \cdot AsF_5$ (M = Cr, Fe, Cu, Zn, Ag, Sn)
and $2MF_2 \cdot AsF_5$ (M = Ag, Sn)

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SUMMARY

Reactions of iron, copper and zinc difluorides with AsF_5 in anhydrous HF at room temperature have been shown to result in the formation of adducts of the type $2MF_2 \cdot 3AsF_5$. The intermediate thermal decomposition products of these compounds have the composition $MF_2 \cdot AsF_5$.

The products of the reactions of chromium, silver and tin difluorides with AsF_5 in anhydrous HF can be formulated as adducts of the type $MF_2 \cdot AsF_5$. The thermal decompositions of the silver and tin compounds have been shown to proceed via intermediates of the type, $2MF_2 \cdot AsF_5$.

The compositions of the adducts have been established by gravimetry, chemical analysis and X-ray powder diffraction methods and indications of the chemical nature of some of the species have been obtained from vibrational spectroscopic and magnetic susceptibility measurements.

INTRODUCTION

Adducts of the type $MF_2 \cdot 2AsF_5$ (M = Mg, Ca, Sr, Ba, Mn, Co, Ni, Cd, Hg, Pb) can readily be synthesized by the reaction of the metal difluorides with AsF_5 in anhydrous HF at room temperature, and their preparations and some of their properties have already been described [1].

This paper describes the related reactions of iron, copper and zinc difluorides, which yield adducts of the type $2MF_2 \cdot 3AsF_5$, and the intermediate products of the thermal decompositions of the 2:3 adducts, which have 1:1 stoichiometries. The preparations of other adducts of the type $MF_2 \cdot AsF_5$ by the reactions of the difluorides of chromium, silver and tin with AsF_5 in anhydrous HF are also described and the thermal decompositions of the silver and tin compounds have been shown to proceed via intermediates of the type $2MF_2 \cdot AsF_5$.

RESULTS AND DISCUSSION

$2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn) Adducts

Gravimetry, chemical analysis, X-ray crystallography, vibrational spectroscopy and magnetic susceptibility measurements have shown that reactions of iron, copper and zinc difluorides with excess of AsF_5 in anhydrous HF at room temperature yield adducts with the composition $2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn) as white solids. Discrepancies between the observed and theoretical analytical results are greater and the X-ray powder diffraction photographs less distinct than in the case of the $MF_2 \cdot 2AsF_5$ (M = Mg, Ca, Sr, Ba, Mn, Co, Ni, Cd, Hg, Pb) adducts [1], and this points to a possibility that the compounds may not have perfect 2:3 stoichiometries or may contain traces of impurity. This is further borne out by the fact that continuous pumping on the adducts results in small but significant weight losses.

The X-ray powder diffraction patterns of the iron and copper compounds exhibit patterns similar to that of $2ZnF_2 \cdot 3AsF_5$. The zinc adduct, in turn, has d spacings which closely resemble those of $NiF_2 \cdot 2AsF_5$ [1]. The intensities, however, differ and it is clear that the structures are distinct.

Magnetic susceptibility measurements on $2FeF_2 \cdot 3AsF_5$ yielded an effective magnetic moment of 5.09 ± 0.1 B.M. at room temperature. This is close to the spin-only value for iron(II) in an octahedral environment (5.5 B.M.) and confirms that the iron is retained as Fe^{2+} in the adduct. Presumably the Cu and Zn compounds are similar.

Adducts of general formula $2MF_2 \cdot 3AsF_5$ containing the metal in the 2+ oxidation state are most likely accounted for by formulations such as $2(MF)^+(AsF_6)^-(As_2F_{11})^-$ or $(M_2F_3)^+(As_3F_{16})^-$. Adducts of noble-gas difluorides with pentafluorides, however, have contributions to the bonding from fluorine-bridged structures [2-5] and the metal difluoride adducts are likely to be similar. Since the effective ionic radii of Fe^{2+} (0.91Å), Cu^{2+} (0.87Å) and Zn^{2+} (0.88Å) are close to those of Mg^{2+} (0.86Å), Co^{2+} (0.87Å), Ni^{2+} (0.84Å) and Ag^{2+} (0.89Å) [6] the vibrational spectra of the $2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn) species might be expected to resemble those of $MF_2 \cdot 2AsF_5$ (M = Mg, Co, Ni) [1]. Comparison of the spectra (see Table 1 and ref. [1]) reveals close similarities but, in keeping with the occurrence of $(As_3F_{16})^-$ or a mixture of AsF_6^- and $(As_2F_{11})^-$ ions in the 2:3 adducts, the anionic parts of the spectra are more complex. The observation of bands between 795 and 808 cm^{-1} in the infrared and around 495 cm^{-1} in the Raman suggest some fluorine-bridged character [3], and metal-fluorine vibrations associated with $(M-F)^+$ and $(F-M \cdots F)$ in the 600 cm^{-1} and 160-140 cm^{-1} regions respectively are clearly analogous to the $(NgF)^+$ or $(Ng_2F_3)^+$ and $(F-Ng \cdots F)$ (Ng = Xe or Kr) vibrations observed in the noble-gas hexafluoroarsenates.

$MF_2 \cdot AsF_5$ (M = Cr, Fe, Cu, Zn, Ag, Sn) Adducts

The adducts $SnF_2 \cdot AsF_5$ [7,8] $FeF_2 \cdot AsF_5$ and $NiF_2 \cdot AsF_5$ [9] have been reported previously and a structural investigation on the tin compound has been carried out [8]. In the present work the analogous chromium, silver and tin compounds have been prepared by the reaction of the appropriate metal difluoride with excess of AsF_5 in anhydrous HF, and the iron, copper and zinc adducts were obtained by the thermal decompositions of the $2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn) adducts at temperatures between 40 and 60°C. The adduct, $FeF_2 \cdot AsF_5$, was also prepared by reaction of metallic iron with AsF_5 in SO_2 [9] and by direct combination of FeF_2 with AsF_5 in anhydrous HF at 55°C. X-ray powder diffraction photographs showed that the products of thermal decomposition of $2FeF_2 \cdot 3AsF_5$ and from direct combination of FeF_2 with AsF_5 are identical. The product of the reaction of Fe and AsF_5 in SO_2 is amorphous. The adducts are white solids except for the chromium and silver compounds which are green and blue respectively.

TABLE 1

Observed infrared and Raman frequencies and tentative assignments for $2MF_2 \cdot 3AsF_5$ (M = Fe, Cu, Zn).

| $2FeF_2 \cdot 3AsF_5$ | | $2CuF_2 \cdot 3AsF_5$ | | $2ZnF_2 \cdot 3AsF_5$ | | Assignment |
|-----------------------|-----------------|-----------------------|-----------------|-----------------------|-----------------|--|
| R(cm^{-1}) | IR(cm^{-1}) | R(cm^{-1}) | IR(cm^{-1}) | R(cm^{-1}) | IR(cm^{-1}) | |
| | 805m | | 795m | | 808m | } $\nu[F-(AsF_5)_n]^-$ |
| 762(14) | 770w(sh) | 768(3) | 750m | 764(23) | 780m | |
| 705(100) | 705vs | 700(100) | 725m | 704(100) | 720s | |
| | 670s | | 665s | | 675mbr | } $\nu(M-F)$ M = Fe, Cu, Zn |
| 605(19) | 615m | 610(6) | 625m | 606(4) | 595m | |
| 591(12) | | 586(6) | | 598(6) | | } $\nu[F \cdots (AsF_5)_n]^-$ |
| | 565m | | | 563(5) | | |
| 494(17) | | 492(11) | | 496(8) | | |
| 386(16) | | 384(23) | | 384(27) | | |
| 373(16) | | 360(14) | | 363(12) | | |
| | | 292(3) | | | | } $\delta(F-M \cdots F)$ M = Fe, Cu, Zn |
| | | 266(5) | | 240(3) | | |
| | | 164(2) | | 140(3) | | |
| | | 116(7) | | | | lattice modes |

Intensities of Raman shifts are given in parentheses

s = strong; m = medium; w = weak; v = very; (sh) = shoulder

X-ray powder photographs for the series of adducts (Table 2) show that none of them is isostructural. A single crystal structure of the $SnF_2 \cdot AsF_5$ adduct has shown that this contains cyclic $[(Sn-F)_3]^{3+}$ cations of D_{3h} symmetry with an (Sn-F) bond distance of 2.097\AA , which is close to that expected for a pure covalent (Sn-F) bond. The extent of interaction

TABLE 2

X-ray powder diffraction patterns of $MF_2 \cdot AsF_5$ (M = Cr, Fe, Cu, Zn, Ag, Sn)

| $CrF_2 \cdot AsF_5$ | | $FeF_2 \cdot AsF_5$ | | $CuF_2 \cdot AsF_5$ | | $ZnF_2 \cdot AsF_5$ | | $AgF_2 \cdot AsF_5$ | | $SnF_2 \cdot AsF_5$ | |
|---------------------|----------------|---------------------|----------------|---------------------|----------------|---------------------|----------------|---------------------|----------------|---------------------|----------------|
| d(Å) | I ^f | d(Å) | I ^f | d(Å) | I ^f | d(Å) | I ^f | d(Å) | I ^f | d(Å) | I ^f |
| | | | | | | 6.92 | s | | | | |
| 5.68 | s | 5.52 | s | 5.73 | s | 5.71 | s | | | | |
| 4.93 | s | 4.75 | s | 4.88 | s | 4.85 | s | | | | |
| | | | | | | | | 4.52 | m | 4.42 | w |
| 4.05 | s | | | | | 4.12 | s | | | 4.21 | m |
| | | | | | | | | 3.87 | s | 3.81 | w |
| 3.62 | s | 3.63 | s | 3.61 | s | 3.62 | s | 3.51 | s | 3.68 | s |
| | | | | | | 3.33 | s | | | | |
| | | | | 3.16 | m | 3.15 | m | | | | |
| 3.02 | s | 3.00 | s | 2.95 | s | 2.95 | m | 2.97 | m | 2.92 | s |
| 2.87 | m | 2.84 | w | 2.87 | s | | | | | | |
| 2.70 | m | 2.70 | w | 2.68 | m | 2.61 | s | 2.75 | s | 2.63 | m |
| | | | | 2.34 | w | 2.36 | w | 2.48 | w | 2.37 | w |
| | | | | | | 2.27 | w | 2.26 | w | | |
| | | 2.16 | m | 2.15 | m | 2.18 | m | | | 2.13 | w |
| 2.14 | m | 2.10 | m | 2.05 | m | 2.06 | w | | | 2.07 | m |
| 1.83 | m | 1.82 | m | 1.81 | s | 2.18 | m | 1.90 | w | 1.94 | m |
| | | | | | | | | 1.84 | w | 1.90 | m |
| 1.75 | w | 1.75 | m | 1.77 | m | 1.75 | s | 1.74 | m | | |
| 1.69 | w | 1.67 | m | 1.68 | m | 1.66 | m | | | 1.63 | m |

s = strong; m = medium; w = weak; f = intensities were estimated visually

of the cyclic $[(Sn-F)_3]^{3+}$ cations with the nearest $(AsF_6)^-$ anions, however, is small since the bridging bond distance is close to that expected for a purely ionic bond [8]. It may well be that all the 1:1 adducts have structures which are related to that of $SnF_2 \cdot AsF_5$. Vibrational spectroscopic data for $SnF_2 \cdot AsF_5$ and for the chromium, copper and zinc analogues (Table 3) can be assigned on the basis of structures containing

TABLE 3

Observed infrared and Raman frequencies and tentative assignments for M_2AsF_5 (M = Sn, Cr, Cu, Zr, Fe, Ag)

| $SnF_2 \cdot AsF_5^a$ | | Assignment | | $SnF_2 \cdot AsF_5^{b,d}$ | | $CrF_2 \cdot AsF_5^b$ | | $CuF_2 \cdot AsF_5^b$ | | $ZnF_2 \cdot AsF_5^b$ | | $FeF_2 \cdot AsF_5^b$ | | $AgF_2 \cdot AsF_5$ | |
|-----------------------|---------------------------|------------|-------------------------------|---------------------------|---------------------------|-----------------------|---------------------------|-----------------------|---------------------------|-----------------------|---------------------------|-----------------------|---------------------------|---------------------|---------------------------|
| $R(\text{cm}^{-1})$ | i.r. (cm^{-1}) | Q_n^a | C_n^b v_y | $R(\text{cm}^{-1})$ | i.r. (cm^{-1}) | $R(\text{cm}^{-1})$ | i.r. (cm^{-1}) | $R(\text{cm}^{-1})$ | i.r. (cm^{-1}) | $R(\text{cm}^{-1})$ | i.r. (cm^{-1}) | $R(\text{cm}^{-1})$ | i.r. (cm^{-1}) | $R(\text{cm}^{-1})$ | i.r. (cm^{-1}) |
| 704(25) | 710 s | } | v_3 | 739(9) | 765 s | 734(4) | 782 m | 792 m | 805 m | | | | | | |
| | 697 s | | | | | | 710 m | | | | | | | | |
| 678(100) | 672 m | } | v_1 | 702(100) | 678 m | 705(100) | 702 s | 712 s | 670 m | | | | | 692(100) | 700 s |
| | | | | | | 678(24) | | | | | | | | | |
| -565 | 575 m | } | v_2 | 606(15) | | 635(4) | 652 m | 652 m | | | | | | 647(3) ^e | |
| 548 | | | | | | 596(16) | | 609(8) | 607 m | 608(50) | | | | | |
| | | } | v_4 | 572(18) | 565 m | 587(8) | | 575(50) | 570 m | | | | | 573(25) | |
| | | | | | | 572(18) | | | | 549(50) | | | | | |
| | | } | v_5 | 484(19) | | 495(7)br | | 521(60) | | | | | | | |
| | | | | | | | | | | | | | | | |
| | | } | v_6 | 385(23) | | 385(20) | | 362(10) | | | | | | 377(24) | |
| | | | | | | 360(18) | | 362(10) | | 266(8) | | | | | 367(25) |
| 371 | { 21 | } | v_7 | 293(17) | | 266(8) | | 225 | | | | | | | |
| 363 | | | | | | | | | | | | | | | |
| | | } | Other | 204(17) | | 108(7) | | | | | | | | | |
| | | | | | | | | | | | | | | | |
| 202(7) | | } | cation vibrns + lattice | 185(22) | | | | | | | | | | 110(20) | |
| 181(12) | | | | | | | | | | | | | | | 105(17) |
| | | | | | | | | | | | | | | | |

Intensities of Raman shifts are given in parentheses

s = strong; m = medium; w = weak; v = very; (sh) = shoulder

^a = Ref (7) ^b = This work ^c = see Refs. (7) and (10) ^d = see Ref. (11)^e = see Ref. (12)

very strong fluorescence

cationic $[(M-F)_n]^{n+}$ rings and approximately C_{4v} distorted $(AsF_6)^-$ anions. Because of fluorescence no reliable Raman information could be obtained for $FeF_2 \cdot AsF_5$ and, consequently, no evidence for $(Fe-F)^+$ was found. The quality of the Raman spectrum for $AgF_2 \cdot AsF_5$ was also poor because of fluorescence and the assignment of a peak to $(Ag-F)^+$ is ambiguous (Table 3). In both cases, however, peaks associated with $(AsF_6)^-$ indicate that the anions have C_{4v} symmetry or less.

Magnetic susceptibility measurements on the $CrF_2 \cdot AsF_5$ and $AgF_2 \cdot AsF_5$ adducts were obtained. For the chromium compound an effective magnetic moment of 4.68 ± 0.10 B.M. was observed which is close to that expected (4.9 B.M.) for a d^4 high-spin configuration. The value for the silver compound is 0.71 ± 0.1 B.M. which is much lower than the expected value (1.73 B.M.). Although numerous $Ag(II)$ compounds have effective magnetic moments close to or above the spin-only value, these usually have 6 or 4 coordination about the silver. The coordination in $AgF_2 \cdot AsF_5$ is likely to be complicated as in $SnF_2 \cdot AsF_5$, and the effective magnetic moment may differ significantly from the theoretical value. Surprisingly, the analogous $AgF_2 \cdot SbF_5$ adduct, which was prepared for comparison, yielded a magnetic moment of 1.69 B.M.

$2MF_2 \cdot AsF_5$ (M = Ag, Sn) Adducts

Both the silver and the tin adducts are obtained from the thermal decompositions of the related 1:1 adducts, the silver compound as a green, unstable solid, while $2SnF_2 \cdot AsF_5$ is white. The tin compound can also be prepared by direct reaction of the stoichiometric quantities of SnF_2 and AsF_5 in anhydrous HF. Attempts to prepare $2AgF_2 \cdot AsF_5$ by combination of the appropriate amounts of AgF_2 and AsF_5 failed and so reliably pure samples of this compound were not available for a detailed investigation of its physical properties.

X-ray powder diffraction patterns from samples of $2SnF_2 \cdot AsF_5$, obtained by direct reaction of the component fluorides and by thermal decomposition of $SnF_2 \cdot AsF_5$, are identical.

The Raman spectrum of $2SnF_2 \cdot AsF_5$ seems to be related to that of $2XeF_2 \cdot AsF_5$ and tentative assignments have been made which are based on

an ionic formulation $(\text{Sn}_2\text{F}_3)^+(\text{AsF}_6)^-$ (Table 4). The appearance of bands which can be attributed to the Sn-F terminal and Sn.....F bridge stretching modes and F-Sn.....F bending modes is indicative of there being a significant contribution to the bonding from fluorine-bridge structures.

TABLE 4

Comparison of Raman Spectra for $2\text{SnF}_2 \cdot \text{AsF}_5$ and $2\text{XeF}_2 \cdot \text{AsF}_5$ with tentative assignments

| $2\text{SnF}_2 \cdot \text{AsF}_5$ | $2\text{XeF}_2 \cdot \text{AsF}_5^a$ | Assignment |
|------------------------------------|--------------------------------------|---|
| 680 (5) | 678 (20) | } $\nu_1(\text{AsF}_6)^-$ |
| | 667 (4) | |
| 604 (100) | 598 (95) | } $\nu(\text{Sn-F})$ or $\nu(\text{Xe-F})$ |
| 592 (86) | 588 (100) | |
| 570 (sh) | 580 (sh) | $\nu_2(\text{AsF}_6)^-$ |
| 460 (9) | | } $\nu(\text{Sn} \cdots \text{F})$ or $\nu(\text{Xe} \cdots \text{F})$ |
| 444 (8) | 417 (<1) | |
| 432 (4) | 401 (<1) | |
| 372 (9) | 367 (7) | $\nu_5(\text{AsF}_6)^-$ |
| 258 (8) | 255 (5) | } $\delta(\text{F-Sn} \cdots \text{F})$ or $\delta(\text{F-Xe} \cdots \text{F})$ |
| 228 (6) | | |
| 208 (4) | 164 (5) | |

Frequencies are in cm^{-1} ; intensities are given in parentheses

^a = ref. 2

Although the structures of the $(\text{Sn}_2\text{F}_3)^+$ and $(\text{Xe}_2\text{F}_3)^+$ ions are likely to differ significantly in that the xenon, having lone pairs, is likely to have F-Xe-F equal to 180° but the tin, which has only one stereoactive lone pair, may well have F-Sn-F closer to 120° ,

this may not be readily detectable in the Raman. Indeed, this is exemplified by the overall similarity of the Raman spectra of $\text{SnF}_2 \cdot \text{AsF}_5$ (Table 1) and $\text{XeF}_2 \cdot \text{AsF}_5$ [2] in which the tin compound has a $[(\text{Sn-F})_3]^{3+}$ ring structure while the xenon adduct appears to contain monomeric $(\text{XeF})^+$ ions.

EXPERIMENTAL

Materials. Iron difluoride was prepared by the fluorination of iron powder with anhydrous HF in a nickel can at 140°C . The hydrogen produced during the reaction was removed by pumping at -196°C and the excess of HF at room temperature. Zinc difluoride was prepared by repeated dissolution of zinc powder in 40% hydrofluoric acid followed by evaporation. The residual solid was fluorinated with elemental fluorine in a nickel can at 300°C . Tin difluoride was prepared by dissolving tin(II) oxide in 40% hydrofluoric acid under a nitrogen atmosphere. The solvent was evaporated and the residual solid was dried at 80°C . Silver difluoride was prepared by direct fluorination of silver(I) oxide in a nickel can at 250°C and a total pressure of 30 atmospheres. The solid product was powdered in a dry box and the fluorination was repeated. Chromium difluoride (Koch-Light Laboratories Ltd.) and copper difluoride (Alfa Inorganics, Ventron GmbH) were used as supplied.

The difluorides were characterized by chemical analysis.

Preparation of the hexafluoroarsenates. The preparations of $2\text{MF}_2 \cdot 3\text{AsF}_5$ ($\text{M} = \text{Fe}, \text{Cu}, \text{Zn}$) and $\text{MF}_2 \cdot \text{AsF}_5$ ($\text{M} = \text{Cr}, \text{Ag}, \text{Sn}$) adducts were carried out as described previously by reaction of the appropriate molar ratios of metal difluoride and arsenic pentafluoride in anhydrous hydrogen fluoride in all-Kel-F equipment [1]. The remaining adducts were obtained by the thermal decompositions of the appropriate adducts with higher AsF_5 content, except for $2\text{SnF}_2 \cdot \text{AsF}_5$ which was made by direct reaction of SnF_2 and AsF_5 in anhydrous HF as well as by the decomposition of the 1:1 adduct.

Chemical analyses. The metal analyses were obtained by direct, indirect or substitution complexometric titration. The analysis for AsF_6^- was achieved by determination as the insoluble tetraphenylarsonium salt [25].

The results are summarized below:

| | |
|-------------------------------------|--|
| $2\text{FeF}_2 \cdot 3\text{AsF}_5$ | Found: Fe, 15.5; AsF_6^- , 82.6; F_f^- , 2.4; Calc.: Fe, 16.0; AsF_6^- , 81.3; F_f^- , 2.7 |
| $2\text{CuF}_2 \cdot 3\text{AsF}_5$ | Found: Cu, 17.3; AsF_6^- , 78.0; F_f^- , 2.3; Calc.: Cu, 17.8; AsF_6^- , 79.5; F_f^- , 2.7 |
| $2\text{ZnF}_2 \cdot 3\text{AsF}_5$ | Found: Zn, 17.4; AsF_6^- , 80.3; F_f^- , 2.8; Calc.: Zn, 18.3; AsF_6^- , 79.1; F_f^- , 2.7. |
| $\text{CrF}_2 \cdot \text{AsF}_5$ | Found: Cr, 17.5; AsF_6^- , 72.7; F_f^- , 7.9; Calc. Cr, 20.0; AsF_6^- , 72.7; F_f^- , 7.3 |
| $\text{FeF}_2 \cdot \text{AsF}_5$ | Found: Fe, 21.7; AsF_6^- —; F_f^- , 8.4; Calc.: Fe, 21.2, AsF_6^- , 71.6; F_f^- , 7.2 |
| $\text{CuF}_2 \cdot \text{AsF}_5$ | Found: Cu, 23.0; AsF_6^- , 67.0; F_f^- , 6.4; Calc.: Cu, 23.4; AsF_6^- , 69.6; F_f^- , 7.0 |
| $\text{ZnF}_2 \cdot \text{AsF}_5$ | Found: Zn, 22.6; AsF_6^- , 71.1; F_f^- , 6.5; Calc.: Zn, 23.9; AsF_6^- , 69.1; F_f^- , 7.0 |
| $\text{AgF}_2 \cdot \text{AsF}_5$ | Found: Ag, 33.5; AsF_6^- , 59.9; F_f^- , 6.0; Calc.: Ag, 34.2; AsF_6^- , 59.8; F_f^- , 6.0 |
| $\text{SnF}_2 \cdot \text{AsF}_5$ | Found: Sn, 36.0; AsF_6^- , 58.0; F_f^- , 6.2; Calc.: Sn, 36.3; AsF_6^- , 57.8; F_f^- , 5.8 |
| $2\text{AgF}_2 \cdot \text{AsF}_5$ | Not determined |
| $2\text{SnF}_2 \cdot \text{AsF}_5$ | Found: Sn, 48.2; AsF_6^- , 38.7; F_f^- , 11.6; Calc.: Sn, 49.1; AsF_6^- , 39.1; F_f^- , 11.8 |

(F_f^- represents free fluoride which can be determined independently of fluoride bound to arsenic in AsF_6^- [25]).

Spectroscopy, X-ray diffraction, thermal decomposition studies and magnetic susceptibility measurements. Vibrational spectroscopic and X-ray diffraction studies were carried out as described previously [1]. Thermal decomposition studies were carried out using a Mettler TA1 Thermoanalyser in a dynamic argon atmosphere with flow rates of 5 litres per hour. Magnetic susceptibility measurements were performed by the Faraday method on a New Port Instruments magnetic balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the reference substance.

CONCLUSIONS

Very little is known about metal difluoride adducts but recent advances in the understanding of the nature of noble-gas difluoride complexes [2-5] has prompted new interest in the analogous metal compounds, especially metal hexafluoroarsenates. Although a number of adducts are known [1,7-9, 13-17] definitive structural information is available only for $\text{SnF}_2 \cdot \text{AsF}_5$ which contains fluorine-bridged $(\text{Sn-F})_3^{3+}$ cations and $(\text{AsF}_6)^-$ anions [8]. However, studies on a wide range of other tin-fluoride compounds have shown that fluorine-bridged chains and networks [18-21, 23, 24], including cationic networks [22], are commonplace. Other metal difluoride species are likely to be similar.

The adduct $2\text{SnF}_2 \cdot \text{AsF}_5$ almost certainly has a structure related to that of $2\text{XeF}_2 \cdot \text{AsF}_5$ on the basis of the Raman data, and vibrational spectroscopic, magnetic susceptibility and X-ray powder diffraction data suggest that the $\text{MF}_2 \cdot \text{AsF}_5$ ($\text{M} = \text{Cr, Fe, Cu, Zn, Ag}$) adducts may have structures related to that of $\text{SnF}_2 \cdot \text{AsF}_5$. The vibrational spectroscopic and magnetic susceptibility results for the adducts of the type $2\text{MF}_2 \cdot 3\text{AsF}_5$ ($\text{M} = \text{Fe, Cu, Zn}$), although consistent with their having formulations such as $2(\text{MF})^+ (\text{AsF}_6)^- (\text{As}_2\text{F}_{11})^-$ or $(\text{M}_2\text{F}_3)^+ (\text{As}_3\text{F}_{16})^-$ may have more complex arrangements of ions in cationic-anionic pseudo fluorine-bridged arrays.

The data obtained have not evidenced differences between the Cu(II) or Ag(II) adducts and the other difluoride adducts which might be confidently attributed to Jahn-Teller distortions in the structures of the copper or silver compounds.

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