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THE PREPARATION AND ^{119}Sn MÖSSBAUER SPECTRA OF $[Sn_2F_3][MF_6]$ (M = As, Sb)

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SUMMARY

Tin(II) fluoride reacts with Lewis acids, AsF_5 and SbF_5, in a 2:1 ratio, to give salts of the $[Sn_2F_3^+]$ cation. Reaction of $SnF{\cdot}MF_6$ with SnF_2 in liquid SO_2 also produces the $[Sn_2F_3][MF_6]$ salt. Tin-119 Mössbauer data are presented and compared with those for SnF_2, $SnF{\cdot}MF_6$ and $Sn(SbF_6)_2$.

INTRODUCTION

Some time ago it was reported that the reaction between SnF_2 and the strong Lewis acids BF_3, AsF_5 and SbF_5 gave $SnF_2{\cdot}BF_3$, $SnF_2{\cdot}AsF_5$, $SnF_2{\cdot}SbF_5$ and $SnF_2{\cdot}2SbF_5$ [1]. It was suggested that the 1:1 adducts consisted of fluorine bridged cations $[SnF]_n^{n+}$ with the appropriate anion $[BF_4^-]$ or $[MF_6^-]$, while the 1:2 adduct was regarded as $Sn(SbF_6)_2$. The $[SnF]_n^{n+}$ cations were shown, by ^{119}Sn Mössbauer spectroscopy, to have a stereochemically active non-bonding electron pair. On the other hand the Sn(II) in the $Sn[SbF_6]_2$ compound had no resolvable quadrupole splitting and a very high isomer shift, 4.44 mm s^{-1}, indicating a stereochemically inactive non-bonding electron pair and a symmetric tin environment.

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Since then, an X-ray study of the $[SnF]_n^{n+}[AsF_6]_n$ adduct has shown that n = 3, and the cation consists of a six membered Sn-F ring [2]. Each tin(II) then has two near fluorine atoms and a non-bonding electron pair in its immediate environment with longer fluorine contacts from the $[AsF_6]^-$ anions completing the tin coordination. The SnF_2-BF_3 system has been studied by Bergerhoff and coworkers [3]. They obtained X-ray crystallographic evidence for $[Sn_2F_3][BF_4]$ in which the $[Sn_2F_3]^+$ cation is the base unit of a polymeric chain. A related $[Sn_3F_5][BF_4]$ compound has the cation in Sn_6F_{10} rings. These structures appear to be related to the various crystalline modifications, α, β, γ, of stannous fluoride studied by Pannetier _et al_. [4]. Another $[Sn_2F_3]_n^{n+}$ cation has been characterised in the compound Sn_2ClF_3 where each tin has three near fluorine neighbours [5]. Very recently Edwards _et al_. [6] have reported the synthesis and X-ray crystallographic characterisation of $Sn(SbF_6)_2 \cdot 2AsF_3$.

We now report the preparation of the $[AsF_6]^-$ and $[SbF_6]^-$ salts of the $[Sn_2F_3]^+$ cation by three different procedures and their ^{119}Sn Mössbauer spectra are compared with those for the corresponding $[Sn]^{2+}$, $[SnF]_3^{3+}$ species and SnF_2.

EXPERIMENTAL

Materials

Antimony pentafluoride (Ozark-Mahoning) was purified by double distillation in an all-glass apparatus under a dry N_2 atmosphere. Arsenic pentafluoride was prepared by the direct fluorination of freshly sublimed arsenic in a nickel can at liquid N_2 temperature. Tin(II) fluoride (ultrapure, Ventron, Alfa Products) was dried by heating to 60°C under vacuum for ~ 12 hrs. Sulphur dioxide (Canadian Liquid Air Ltd.) was distilled from and stored over P_4O_{10} before use. $[SnF][SbF_6]$ was prepared according to reference [1], although a slightly modified reaction vessel and technique were used which are described as follows:

1 Direct reaction of SnF_2 and MF_5 in anhydrous HF

A procedure similar to that of Frlec *et al*. [7] was used. About 3 mmoles of SnF_2 were loaded into an all Kel-F reaction vessel in a dry atmosphere box after which the vessel was attached to an all Kel-F vacuum line and 3-4 g anhydrous HF were distilled onto the SnF_2. All of the SnF_2 dissolved: the solubility of SnF_2 in HF is ~ 218 g L^{-1}. Antimony pentafluoride, or arsenic pentafluoride, was then added to give a SnF_2:MF_5 ratio of 2:1. After removal of the HF under vacuum at room temperature white solids of stoichiometry $2SnF_2 \cdot MF_5$ (M = As, Sb) were obtained.

2 Direct reaction of SnF_2 and SbF_5 in anhydrous liquid SO_2

The procedure used was basically that of Birchall *et al*. [1]. The two-bulbed Pyrex vessel used for the preparation of tin(II) fluorosulphate, was slightly modified to accommodate a Rotaflo Teflon-stemmed (TF2/13) valve. This valve was glass-blown between the medium-sintered glass frit and the round bottomed flask. In this way the added SbF_5 in the flask could be contained between a Teflon union closing the 1/4 in. tubing of the flask and the Rotaflo valve. The second flask contained a 1 × 5/16" Teflon covered magnetic stirrer bar. In so doing the amount of antimony pentafluoride taken can be accurately weighed.

In a typical experiment a solution of SbF_5 (4.04 m mol) in sulphur dioxide (ca. 35 cm^3) was added to a suspension of SnF_2 (8.09 m mol) in SO_2 (30 cm^3) at room temperature. The reactants were stirred for a week after which time a white homogeneous solid was obtained. The solution was filtered to the other side of the ampoule and the precipitate was washed several times with SO_2 before it was pumped to dryness and isolated.

3 Direct reaction of $SnF \cdot SbF_6$ with SnF_2 in liquid SO_2

In a typical experiment $SnF \cdot SbF_6$ (5.94 m mol) and SnF_2 (5.95 m mol) were placed in one arm of a double ampoule vessel inside a dry-box. The ampoule was brought to a vacuum line and approximately 50 cm^3 of sulphur dioxide was condensed onto the fluorides, and the apparatus was sealed. On warming to room temperature the contents of the ampoule were stirred for about a week after which time a white homogeneous product was produced. The mother liquid was filtered to the other side of the ampoule and the white material was pumped dry and isolated.

4 Preparation of $Sn(SbF_6)_2$

Using the modified ampoule and the technique described in preparation No. 2 (above), $Sn(SbF_6)_2$ was obtained by the direct reaction of a solution of SbF_5 (4.21 mmol) in sulphur dioxide (ca. 30 cm^3) and a suspension of SnF_2 (2.10 m mol) in SO_2 (34 cm^3) at room temperature. The product was confirmed to be $Sn[SbF_6]_2$ by its characteristic Raman spectrum.

Analysis

$2SnF_2 \cdot AsF_5$ % Found: Sn 48.2; $[AsF_6]^- = 38.7$; $F_f^- = 11.6$
% Calcd: Sn 49.1; $[AsF_6]^- = 39.1$; $F_f^- = 11.8$

$2SnF_2 \cdot SbF_5$ % Found: F_t 32.9; $F_f^- = 14.7$
% Calcd: F_t 32.25; $F_f^- = 14.33$

The percentage AsF_6^- was determinated directly, F_f^- represents the fluoride ion not bound to As or Sb, F_t represents the total percentage fluorine.

Tin-119 Mössbauer Spectroscopy

Tin-119 Mössbauer spectra were recorded on apparatus that has already been described [8]. The apparatus was calibrated periodically using a standard iron foil and a $^{57}Co/Rh$ source. The ^{119}Sn source in the form of $CaSnO_3$ was obtained from Amersham and was maintained at room temperature throughout. Spectra were measured at 298 K and 77 K and some at an intermediate temperature of 185 K. All isomer shifts are quoted with respect to $CaSnO_3$ as zero isomer shift. Spectra were computer fitted using the programme of Stone [9] after modification by Dr. D. Grundy, Dept. of Geology, McMaster University.

RESULTS AND DISCUSSION

The ^{119}Sn Mössbauer data are summarised in the Table and a representative spectrum of $[Sn_2F_3][SbF_6]$ is shown in Figure 1. The spectra of the $[Sn_2F_3]^+$ compounds all consisted of two strong absorptions, characteristic of a tin(II) quadrupole doublet. In all cases a small absorption in the tin(IV) region of the spectrum (~ 0.0 mm s^{-1}) was visible: this Sn(IV) impurity is present in the starting SnF_2. All of the samples had their spectra recorded at 77 K and some were measured at higher temperatures. The Mössbauer parameters showed only minor variation with temperature, the isomer shift changes being due to the expected second order Doppler shift; there is also a small increase in quadrupole splitting as the temperature is lowered. It should be pointed out of course that the spectra obtained at 77 K are of much superior quality to those at higher temperature.

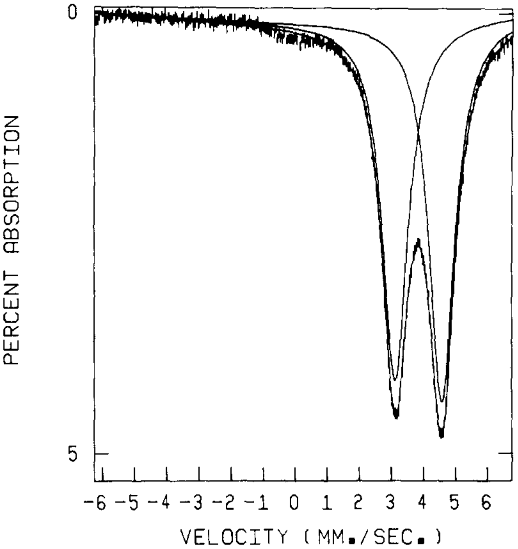

Fig. 1. The ^{119}Sn Mössbauer spectrum of $[Sn_2F_3][SbF_6]$ at 77 K.

TABLE

^{119}Sn Mössbauer Data for $[Sn_2F_3][MF_6]$ and related compounds

	Temp. K	mm s^{-1} (± 0.01)		
		δ	Δ	Γ
SnF_2	298	3.48	1.56	0.94
$Sn_2F_3 \cdot AsF_6$	77	3.73	1.47	0.96
$SnF \cdot AsF_6$	77*	3.97	1.54	1.00
$Sn_2F_3 \cdot SbF_6$	77	3.77	1.46	0.96
$SnF_2 \mid \frac{1}{2}SbF_5 \mid SO_2$	298	3.67	1.40	1.09
	185	3.70	1.44	1.01
	77	3.73	1.47	1.11
$SnF_2 \mid SnF \cdot SbF_6 \mid SO_2$	298	3.66	1.39	1.10
	185	3.70	1.41	1.08
	77	3.73	1.43	1.19
$SnF \cdot SbF_6$	298	3.92	1.37	0.96
	77	3.98	1.48	1.17
$Sn(SbF_6)_2$	77*	4.44*	-	1.21
	298	4.56	-	1.17
	77	4.63	-	1.00

* Ref. 1.

An examination of the data obtained from the three different preparations of $[Sn_2F_3][SbF_6]$ shows that the Mössbauer parameters are the same within experimental error, and indicates that all three methods of preparation lead to the same product. This is gratifying since while the reaction in HF is a homogeneous one, those in liquid SO_2 appear to be heterogeneous, though both SnF_2 and $SnF \cdot SnF_6$ may well have a small solubility in this solvent which allows reaction to take place slowly. The compounds give a significant absorption at room temperature indicating that the Debye temperatures for these materials are relatively high for compounds of tin(II). This is consistent with the structure found for the $[BF_4]^-$ analogue, which is a fluorine bridged polymer [3] with each tin(II) having three near fluorine neighbours in a pyramidal arrangement. This is similar in some respects to the structure of γ-SnF_2 which has chains of SnF_2 units cross-linked to give a polymeric structure and a high Debye temperature [4].

A comparison of the data for the $[Sn_2F_3][MF_6]$ compounds with those of SnF_2 and $[SnF]_n[MF_6]_n$ shows that the $[Sn_2F_3][MF_6]$ materials cannot be mixtures of the starting ingredients, SnF_2 and $[SnF][MF_6]$, since this would lead to significant line broadening particularly of the lower velocity component of the quadrupole doublet and this is not observed. There is a trend towards increasing isomer shift as one goes from the neutral SnF_2, through the $[Sn_2F_3]^+$, to the $[SnF]^+$. This reflects the increased positive charge on the tin(II) which contracts the orbitals, particularly the 5s, increases the s electron density on tin and hence the more positive isomer shift. It is difficult to compare the quadrupole splitting values since the structures of the compounds vary considerably. Stannous fluoride has a tetrameric structure containing two different types of tin [10,11], the $[Sn_2F_3]^+$ cation is a long chain polymer [3], while $[SnF]^+[AsF_6]^-$ has been shown to contain a trimeric cation $[SnF]_3^{3+}$: presumably the $[SbF_6]^-$ analogue has the same structure.

These cations all have quite high isomer shifts but distorted environments indicating that the non-bonding electron pair on tin is stereochemically active. Such is not the case for $Sn[SbF_6]_2$ which shows a single narrow line with a very high isomer shift. We had earlier [1] reported an isomer shift of 4.44 mm s^{-1} for this compound but the recent report by Edwards [6] on $Sn[SbF_6]_2 \cdot 2AsF_3$ (δ = 4.66 mm s^{-1}) has prompted us to remeasure the spectrum of $Sn[SbF_6]$ prepared in liquid SO_2. We find a value of 4.63 mm s^{-1} with a narrower line width than previously reported [1]. The spectrum is shown in Figure 2 and one again notes the small tin(IV) impurities which originate from the starting SnF_2. The differences from the earlier results we attribute to the improvements that have been made in spectrometers since the early seventies, to the superior counting statistics and better fitting procedures that are now available.

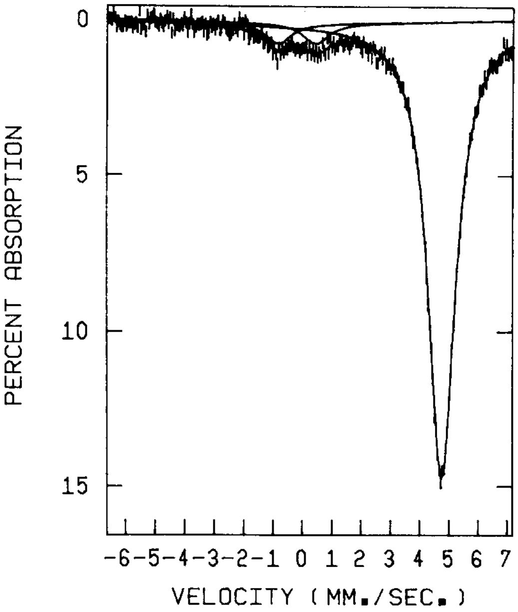

Fig. 2. The ^{119}Sn Mössbauer spectrum of $Sn[SbF_6]_2$ at 77 K.

We have previously suggested that $Sn[SbF_6]_2$ has the Sn(II) atom in a cubic environment with very weak interactions from the fluorines of the$[SbF_6]^-$ anion. The recent X-ray crystal structure determination on $Sn[SbF_6]_2 \cdot 2AsF_3$ [6] confirms that the short interactions to the Sn(II) are from the $[SbF_6]^-$ anions to give an octahedral arrangement of six close bridging fluorines. The virtually identical Mössbauer isomer shifts for $Sn[SbF_6] \cdot 2ASF_3$ and $Sn[SbF_6]_2$ and the very narrow line widths obtained for these compounds indicates that the non-bonding electron pair on the Sn(II) is not stereochemically active. However Edwards and Khallow [6] argue that the non-bonding electron pair on tin is stereochemically active. This conclusion was based on bond length differences from F to Sn but no discussion of the F-Sn-F angles was given. If there is an active non-bonding electron pair on tin we believe that the isomer shift would be much less positive and the linewidth would be larger due to the presence of a small quadrupole interaction. We have no AsF_3 in our molecule and analysis [1], and Raman spectroscopy, indicates that there are no SO_2 molecules incorporated into the system which could provide a source of secondary interactions from O to Sn, yet our Mössbauer parameters are virtually identical to those of Edwards and Khallow [6]. We believe that the secondary fluorine bridges to tin in $Sn[SbF_6]_2 \cdot 2AsF_3$ [6] have no detectable influence on the Mössbauer parameters and that their positions are dictated by crystallographic constraints rather than arising from the influence of a stereochemically active electron pair in tin.

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