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STUDIES ON ANTIMONY TRIFLUORIDE IN THIOCYANATE SALT MATRICES EVIDENCE FOR THE FORMATION OF FLUORO-THIOCYANATO ANTIMONY(III) SPECIES

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SUMMARY

Antimony trifluoride can be dissolved in fused KNCS or NH_4NCS giving yellow-orange solutions which are stable only for a short time just above their melting point Infrared and Mössbauer results on solidified samples reveal the formation of mixed fluoro-thiocyanato antimony(III) species and indicate a different behaviour in the two matrices

INTRODUCTION

Antimony trifluoride is known to react with neutral donors as well as with anions, including F^-, giving a variety of complex species However, the reaction between SbF_3 and a typical pseudohalide donor such as NCS^- has never been investigated and only fragmentary attention [1,2] has been paid to the formation of antimony(III)-thiocyanato species We have now collected evidence

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that SbF_3 and KNCS can give mixed salts whose stoichiometries, still not precisely identified, depend on the experimental conditions We also observed that antimony trifluoride can be dissolved in melted KNCS or NH_4NCS giving yellow-orange solutions which can be quickly frozen and studied by infrared and 121-antimony Mössbauer spectroscopies in order to obtain some understanding on the coordination at antimony in such thiocyanate media

EXPERIMENTAL

Reagent grade SbF_3 and thiocyanate salts were used KNCS and NH_4NCS were dried at 100°C for several days and kept in dry atmospheres before use All manipulations have been performed under nitrogen

Weighted amounts of SbF_3 and the appropriate thiocyanate were ground together and slowly heated on a oil bath just above the point of complete melting SbF_3 has been found to be soluble in NH_4NCS in the whole range tested, while in the case of KNCS complete solubility has been observed for SbF_3/KNCS ratios slightly larger than 1 2 Melts were rapidly cooled and the spectroscopic measurements performed on ground specimens

The i r spectra have been recorded in the 4000-200 cm^{-1} range as nujol and HCBD mulls between CsI plates using a Perkin-Elmer 1430 instrument

The ^{121}Sb Mössbauer spectra were measured with both source ($Ca^{121m}SnO_3$, 0 5 mCi) and absorber cooled at 40K using the cryostat, the apparatus and procedures described elsewhere [3,4] Each absorber, containing 4-5 mg/cm^2 ^{121}Sb, was prepared by carefully mixing the powdered sample with silicone grease The chemical isomer shift data are quoted with respect to the $Ca^{121m}SnO_3$ source The Mössbauer results are summarized in the Table

DISCUSSION

Fused KNCS is an ionic liquid which has been already used as suitable medium for studying the complex formation between various metal ions and the NCS^- ligand [5 and Refs therein] The use of NH_4NCS, which has a lower melting point than KNCS, could be in principle more convenient but it has been reported to undergo decomposition not far above its melting point A reaction between SbF_3 and ANCS (A = K, NH_4) is clearly indicated by the bright yellow-orange color which develops following the first stages of the mechanical grinding Under nitrogen, melts are stable for a short time even when maintained at temperatures just above their melting points and, under these conditions, systems showed reproducible spectroscopic results when subjected to melting-and-cooling cycles The relatively low stability of the melts induced us to focus on the characterization of antimony-thiocyanate species occurring in solidified samples for which infrared information can be fruitfully complemented by Mössbauer results

The most relevant features in the vibrational spectra originate both from absorptions characteristic of the thiocyanate groups as well as from those assignable to Sb-F motions Therefore, the strong covalent Sb-F bonds are maintained even at the lowest SbF_3/NCS^- ratio Within each potassium or ammonium thiocyanate system, essentially the same features are observed once allowance is made for the contributions from free thiocyanate The involvement of the ammonium cation in hydrogen bonding is evidenced by shifts and/or modifications of its typical absorption bands Although the hydrogen bonding is expected to affect the Sb-F vibrations, the differences observed in the ν(SbF) region between potassium and ammonium samples seem better explained by the presence of different antimony-fluoro species KNCS samples show three principal resolved bands at 570, 510 and 440 cm^{-1} and a strong feature at 290 cm^{-1} whereas the ammonium ones show an unresolved envelope with principal components at about 590, 565, 480 and 450 cm^{-1} The pattern observed for the potassium systems closely resembles that reported for $KSbF_3NO_3$ and $CsSbClF_3$ characterized by the absence of fluorine bridges as shown by structural and vibrational data [6,7] For these species, the absorption band at 290 cm^{-1} is assigned to the ν_2 bending vibration of a SbF_3 skeleton having an effective C_{3v} local symmetry Spectral data for the ammonium systems show similarities with those reported for a number of salts of the type MSb_xF_y (M = alkali or alkali-like cations, x,y = 1,4, 2,7, 3,10) and are therefore more consistent with the presence of fluoro-antimonate polymers [8-11]

The examination of the characteristic NCS^- absorptions reveals in the ν(CN) range a number of spectral features, superimposed on the spectrum of free thiocyanate, attributable to coordinated groups These are located at

2105, 2085 and 2070 cm^{-1} for the potassium systems, while only two absorptions at 2075 and 2055 cm^{-1} are found for the ammonium ones. In both cases, the ν(CS) vibration appears made up of several components spanning the 770-720 cm^{-1} range. The strong ν(SbF) envelopes are sensibly masking the δ(NCS) range; however, in the case of the potassium systems, two weak features at 940 and 920 cm^{-1} are recognized as overtones of this mode originating from bonded thiocyanate groups.

Following accepted criteria for deciding the thiocyanate bonding type [12], present data, although not straightforwardly, can be interpreted as indicating a N-coordination in the case of the ammonium matrix while for the potassium systems they could reflect both bridging as well as S-bonded thiocyanate groups. On the other hand, S-bonded thiocyanate seems unlikely. In fact, while antimony(III) can be possibly regarded as borderline between "class A" and "class B" elements, bonding to fluorines is expected to enhance its "class A" character; moreover, analogies are expected with tin(II) systems for which infrared results have shown that $Sn(NCS)_2$ is bridged while many $Sn(NCS)_3^-$ containing salts are solely N-bonded [13].

Antimony-121 systems give Mössbauer spectra consisting of an unresolved envelope of eight lines (twelve if the asymmetry parameter (η) is different from zero). Different sites can be occasionally distinguished provided the isomer shift values are sufficiently different. Our spectra consist of only one asymmetric absorption centered at about

14 mms^{-1} Their fit, performed assuming the presence of one mainly contributing antimony(III) site (and allowing the independent variation of the isomer shift (IS), quadrupole coupling constant (eQV_{zz}), half width (Γ) and η parameters), gave in all cases acceptable outputs However, inspection of the data (see Table) reveals half width values larger than normally found for pure antimony(III) compounds, and are possibly reflecting antimony(III) centers experiencing slightly different chemical environments Such uncertainty should in some way affect the isomer shift and quadrupole coupling constant values which nevertheless can provide some information on the antimony-containing species in the thiocyanate matrix

TABLE
Mössbauer parameters

Mixture		IS[a] (mm/s)	eQV_{zz} (mm/s)	Γ (mm/s)
	molar ratio			
SbF_3/NH_4NCS	1 7	-14 2	20 5	3 9
	1 2	-14 1	20 0	3 8
	1 1	-14 3	19 9	3 7
$SbF_3/KNCS$	1 7	-15 2	23 6	4 3
	1 2	-14 2	16 2	3 0

[a] relative to the $Ca^{121m}SnO_3$ source

Again, differences can be noted between potassium and ammonium systems The latter show essentially similar spectral parameters for all the compositions and a close similarity with data reported for a number of fluoro antimonate derivatives, including SbF_3 [14,15] These findings are in agreement with the infrared results in suggesting that the environment at antimony is mainly provided by fluorine atoms and possibly resulting in polynuclear arrangements in which terminal, N-bonded, thiocyanate groups are present

Mössbauer data for the potassium system indicate some modification in the chemical nature of antimony as the SbF_3/KNCS ratio changes which could not be evidenced from the infrared spectra The narrower Γ value and the reduction of the quadrupole coupling constant obtained with the 1 2 sample, seems indicative of a rather defined environment at Sb Despite our failure in synthesizing salts such as for example $KSbF_3NCS$ or $K_2SbF_3(NCS)_2$, it seems that present spectroscopic data point to the actual formation of species of this type, possibly characterized by having bridging thiocyanato groups The 1 7 sample suggests the presence in the system, for larger NCS^- concentration, of a number of different chemical species This is mainly inferred from the larger gamma value and, in this respect, no precise meaning should be attached to the fairly large quadrupole coupling constant The more negative isomer shift obtained is, however, probably reflecting the contribution from species actually experiencing a larger s-electron density at the antimony nucleus The latter can be tentatively imputed to an increased coordination number as well as to the presence of sulfurs in the coordination sphere

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