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A Study of the Reaction Between Antimony(III) Chloride and Amine Hydrochlorides

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Twenty compounds were prepared by the reaction of antimony(III) chloride with amine hydrochlorides in the presence of a large excess of hydrochloric acid. The melting point ranges and densities of the compounds were determined. Qualitative solubilities of the compounds were observed and the absorption spectra in different concentrations of hydrochloric acid were studied. Although practically identical precipitating and recrystallization conditions were maintained, four different types of compounds were prepared. Ten of the compounds had chlorine to antimony ratios of 5 to 1; six of the compounds had chlorine to antimony ratios of 6 to 1; two of the compounds had chlorine to antimony ratios of 4 to 1; two of the compounds had chlorine to antimony ratios of 9 to 2.

Introduction

Few compounds have been reported of the type $R_xSb_yCl_z$, where R represents an aliphatic or aromatic amine cation. $C_5H_5NHSbCl_4$, $C_9H_7NHSbCl_4$, $C_6H_5N(CH_3)_3SbCl_4$, and $3\text{-Cl}.C_6H_4N(CH_3)_3SbCl_4$ were prepared by Pfeiffer and Schneider.[1] Pugh[2,3] prepared $(N_2H_5)_2SbCl_5$, $(N_2H_5)_3SbCl_6$ and $(CH_3)_2C{:}N.N{:}C(CH_3)_2HSbCl_4$. Lamchen, Pugh and Stevens[4] made $((n\text{-}C_4H_9)NH_2)_2SbCl_5$. Compounds of the type $R_3Sb_2Cl_9$ have not been reported previously.

Experimental Section

Materials. Antimony trichloride was prepared from Baker and Adamson reagent grade antimony trioxide. The amines were Eastman white label, Merck's Mallinkrodt's and Matheson Coleman and Bell and were purfied by vacuum distillation. All solvents were reagent grade.

Procedure. The antimony trichloride solutions were prepared by dissolving 0.5 mole of antimony trioxide in concentrated hydrochloric acid with sufficient excess acid added to make a volume of one liter. The amine hydrochlorides were prepared by adding an excess of concentrated hydrochloric acid to about 0.25 mole of the amine in an ice bath. Fifty ml aliquots of the antimony chloride solutions were added to the respective amine hydrochloride solutions with vigorous stirring. The amine salt to antimony ratio was about 5 to 1 and the chloride to antimony ratio was about 20 to 1 in all preparations. Since precipitation was initiated almost immediately in most cases, the actual concentration ratios of amine salt to antimony and chloride to antimony were much higher than 5 to 1 and 20 to 1 in the medium at the time of precipitation. The lower molecular weight aliphatic amine salts were exceptions and precipitated very slowly, several days were required for the separation of reasonable amounts of product. The yields ranged from twenty to eighty percent (calculated in terms of the antimony used). The salts were separated from their mother liquor by vacuum filtration through sintered glass crucibles and washed several times with concentrated hydrochloric acid. The products were placed in a vacuum desiccator and dried over calcium chloride and sodium hydroxide at reduced pressure until no odor of hydrochloric acid could be detected. The salts were recrystallized from concentrated hydrochloric acid unless the initial product gave a correct analysis for a relatively pure compound.

Analytical Methods. Samples for analysis were dissolved in a small volume of methanol and 50 mls of 0.2 *M* tartaric acid was added. The antimony content of the samples was determined by oxidation with standard potassium bromate using Brilliant Ponceau 5R as an indicator. Some of the aromatic amines tended to react with the indicator and the antimony content of these compounds was determined iodometrically. The samples used for the chloride determination were buffered to pH of 6 and titrated with standard silver nitrate by potentiometric methods using a silver electrode as the indicating electrode and a mercury-mercurous electrode as the reference electrode. The results of the analysis are shown in Table I.

Physical Properties of the Compounds. Most of the compounds are white crystalline solids. The quinolinium salt is pale yellow and some of the aromatic amine compounds have a light brown tinge. This slight discoloration is apparently due to the oxidation of the aromatic amines. The compounds are decomposed by water forming a white precipitate of SbOCl. They are soluble in the more polar organic solvents such as methanol and acetone but quite insoluble in such non-

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[1] P. Pfeiffer and K. Schneider, *Ber. Chem. Dtsch. Chem.*, *68B*, 50 (1935).
[2] W. Pugh, *J. Chem. Soc.*, 3445 (1953).
[3] W. Pugh, *J. Chem. Soc.*, 1385 (1954).
[4] M. Lamchen, W. Pugh, and A. M. Stephens, *J. Chem. Soc.*, 4418 (1954).

Table I.

	Density g/cm^3	m.p. Range (°C)	Antimony (%)		Chloride (%)	
			Theoretical	Experimental	Theoretical	Experimental
$(C_2H_5)_3NHSbCl_4$	1.39±0.02	95 - 98	33.29	32.6±0.1	38.77	38.7±0.1
$4\text{-}CH_3 . C_5H_4NHSbCl_4$	1.64±0.02	135 - 139	34.04	35.5±0.1	39.65	39.7±0.1
$(C_5H_5NH)_2SbCl_5$	1.64±0.03	217 - 219	26.51	25.8±0.1	38.60	36.5±0.1
$(C_9H_7NH)_2SbCl_5$	1.51±0.02	175 - 178	21.77	22.5±0.1	31.70	31.9±0.1
$(2\text{-}CH_3 . C_5H_4NH)_2SbCl_5$	1.40±0.01	113 - 115	24.99	25.1±0.1	36.38	35.3±0.2
$(3\text{-}CH_3 . C_5H_4NH)_2SbCl_5$	1.31±0.06	141 - 144	24.99	25.2±0.1	36.38	35.5±0.1
$(iso\text{-}C_3H_7NH_3)_2SbCl_5$	1.28±0.02	164 - 166	29.04	29.0±0.1	42.28	42.6±0.1
$((CH_3)_2NH_2)_2SbCl_5$	1.74±0.04	d 204	31.12	31.2±0.1	45.32	45.4±0.1
$((CH_2)_5NH_2)_2SbCl_5$	1.08±0.01	251 - 253	25.83	25.5±0.1	37.61	37.2±0.2
$(C_6H_{11}NH_3)_2SbCl_5$	1.27±0.03	d 181	24.38	24.4±0.1	35.50	34.8±0.1
$(n\text{-}_3H_7NH_3)_2SbCl_5$	1.36±0.01	145 - 147	29.04	29.1±0.1	42.28	42.7±0.1
$(4\text{-}CH_3 . C_6H_4NH_3)_2SbCl_5$	1.30±0.03	151 - 153	23.63	23.8±0.2	34.40	34.2±0.1
$(4\text{-}Cl . C_6H_4NH_3)_3SbCl_6$	1.19±0.01	d 208	16.91	17.0±0.2	29.53	29.4±0.2
$(C_6H_5CH_2NH_3)_3SbCl_6$	0.98±0.02	d 189	18.48	18.5±0.1	32.29	32.6±0.2
$((C_2H_5)_2NH_2)_3SbCl_6$	1.23±0.03	128 - 130	21.87	21.6±0.1	38.18	38.4±0.2
$(C_2H_5NH_3)_3SbCl_6$	1.39±0.02	d 173	25.77	26.7±0.1	45.00	45.0±0.1
$((n\text{-}C_3H_7)_2NH_2)_3SbCl_6$	1.07±0.01	d 162	19.00	18.7±0.2	33.16	32.6±0.2
$((n\text{-}C_4H_9)_2NH_2)_3SbCl_6$	1.01±0.01	104 - 106	16.79	16.4±0.2	29.31	28.8±0.2
$(CH_3NH_3)_3Sb_2Cl_9$	1.67±0.03	311 - 315	36.96	37.0±0.1	48.44	48.1±0.2
$((CH_3)_3NH)Sb_2Cl_9$	1.37±0.02	220 - 222	32.78	32.7±0.1	42.95	42.8±0.1

polar solvents as benzene, carbon tetrachloride and chloroform. The extent of solubility seems to be directly related to the dielectric constant of the solvent. Attempts to recrystallize these salts from either single organic solvents or mixtures of two different solvents were unsucessful. The solid product was apparently always a mixture of two or more compounds. The results seemed to indicate that the lower dielectric constant solvents tended to decompose the higher charged species. If this conclusion is correct, it might be possible to control the type of product to a greater extent by using non-aqueous systems in their preparation. The melting point or decomposition temperatures were reasonably sharp and are given in Table I. While no definite conclusions can be drawn from so few cases, it seems that the R_2SbCl_5 and R_3SbCl_6 have melting temperatures in similar ranges while the $RSbCl_4$ compounds have lower melting points and the $R_3Sb_2Cl_9$ have quite high melting points. The densities of the compounds were determined and are reported in Table I. No correlation between the densities and the type of salt was observed but the densities of the compounds are roughly inversely proportional to the size of the amine cation. An absorption maximum occurs at 228 mμ in 6 to 12 molar hydrochloric acid solutions. The molar absorptivity is $2.3\times10^4 L/M$-cm. In more dilute hydrochloric acid solutions the maximum is shifted to shorter wavelengths and decreases in magnitude.

Results and Discussion

The relative concentrations of antimony and chloride ions in the several preparations was maintained as constant as possible. The principal variation was due to the differences in the solubility of the products. The antimony chloride solutions were added slowly with constant stirring to the amine salt solutions. If the product precipitated almost immediately, the chloride to antimony ratio of the total volume was extremely high, however in the immediate vicinity of the nucleation process the chloride to antimony ratio was probably somewhat less due to the lower concentration of chloride in the amine salt solutions. In general the chloride to antimony ratio was probably in excess of 10 to 1. The fact that four different types of salts were produced in the solid state indicates that the relative concentrations was not the single factor which determined the type of product produced. These results indicate that the stability constants of $SbCl_4^-$, $SbCl_5^{2-}$, and $SbCl_6^{3-}$ differ by small amounts and all three ions are present in appreciable amounts in the same solutions. This conclusion is in agreement with the work of Pantani and Desideri[5] in their study of the polarographic behavior of Sb^{III} in solutions in which the chloride concentrations were varied from 0.01 M/L to 10 M/L. Their work indicated the progressive change from Sb^{3+} to $SbCl_6^{3-}$ and they calculated constants for the stepwise equilibria. Using their constants the relative concentration of the respective ions in 10 M hydrochloric acid would be: $SbCl_6^{3-}$ - -70%; $SbCl_5^{2-}$ - -27%; $SbCl_4^-$ - -3%. Fifty percent of the salts produced were $(R_4N)_2SbCl_5$, thirty percent were $(R_4N)_3SbCl_6$ with ten percent each of the types R_4NSbCl_4 and $(R_4N)_3Sb_2Cl_9$. The form in which the salts separate as solids is in part a function of the relative concentrations modified by the structural requirements of the crystal lattice. The product which is isolated is that which will give the minimum free energy for all of the processes involved.

Two of the compounds had chlorine to antimony ratios of 4 to 1. The complex ions in these compounds could be either tetrahedral or planar. Ten of the compounds had chlorine to antimony ratios of 5 to 1. Edstrand, Inge, and Ingre[6] studied the structure of $(NH_4)_2SbCl_5$ by x-ray diffraction methods. They found the $SbCl_5^{2-}$ ion to be a deformed octahedron with an unshared pair of electrons occupying one corner and five chlorines at the other corners of the octahedron. Bystrom and Wilhelmi[7] found a similar structure for SbF_5^{2-}. It is probable the similar conmpounds prepared

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(5) F. Pantani and P. G. Desideri, *Gazz. Chim. Ital.*, *89*, 1360 (1959).

(6) M. Edstrand, M. Inge, and N. Ingri, *Acta Chem. Scand.*, 9, 122 (1955).

(7) A. Bystrom and K. Kilhelmi, *Arkiv Kemi*, 3, 461 (1952)

in this study have the same form. Six of the compounds had chlorine to antimony ratios of 6 to 1 and probably contain octahedral $SbCl_6^{3-}$ ions. Two of the compounds had chlorine to antimony ratios of 9 to 2. The complex ions in these compounds probably consist of two octahedra, face to face, with two antimony atoms at the center of the octahedra and a bridge of three chlorine atoms. Similar bromine compounds were found by Whealy and Yeakley[8] and the corresponding iodine compounds were prepared by Whealy and Blackstock.[9] X-ray diffraction studies of a number of similar compounds have been reported: $K_3W_2Cl_9$ by Brosset[10] and by Watson and Waser;[11] $K_3Cr_2Cl_9$ by Wessel and Ijdo;[12] $Cs_3As_2Cl_9$ and $Cs_3Ti_2Cl_9$ by Hoard and Goldstein. All of these compounds were found to have this binuclear structure.

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(8) R. D. Whealy and R. L. Yeakley, *J. Inorg. Nucl. Chem.*, *25*, 365 (1963).

(9) R. D. Whealy and J. B. Blackstock, Jr., *J. Inorg. Nucl. Chem.*, 26, 243 (1964).

(10) C. Brosset, *Arkiv Mineral Geol.*, *12A*, No. 4 (1935); *Chem. Abstr.*, *29*, 6812 (1935).

(11) W. H. Watson, Jr. and J. Waser, *Acta Cryst.*, *11*, 689 (1958).

(12) G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, *10*, 466 (1957).

(13) J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, 3, 117, 199 (1935).