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The Existence of Chlorobromoantimonates

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Received May 3, 1971

Recent reviews[1,2] have stated that chlorobromoantimonates, $SbCl_nBr_{6-n}^-$, do not apparently exist. Thus reaction of, for example, $SbCl_4^+$ and Br^- ions under appropriate conditions is said[3] to lead to mixtures of hexachloro- and hexabromoantimonates; X-ray powder studies on crystalline tetraethylammonium salts and ultraviolet spectra measurements on acetonitrile solutions are cited as evidence. This is surprising in view of the known existence[4] of the analogous phosphorus anion PCl_5Br^-, of antimony–fluorochloro compounds,[2] and of the halogenotrifluoromethyl antimonates[1] $Sb(CF_3)_3X_3^-$, X = Cl, Br. In this note we present evidence for the preparation of two compounds containing the pentachlorobromoantimonate anion, $SbCl_5Br^-$.

Table I
Analytical Data for $(C_2H_5)_4NSbCl_5Br$ and $PSbCl_9Br$

	% P		% Sb		% Cl		% Br	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$(C_2H_5)_4NSbCl_5Br$	...	...	23.9	23.8	34.8	34.9	15.7	15.7
$PSbCl_9Br$	5.6	5.4	22.1	22.4	57.8	57.6	14.5	14.8

Preparation and Characterization of the $SbCl_5Br^-$ Ion.—The two syntheses are summarized by the equations

$$PCl_3 + Br_2 + SbCl_5 \xrightarrow{\text{liquid HCl}} PSbCl_9Br\ (A) + HBr$$

$$(C_2H_5)_4NBr + SbCl_5 \xrightarrow{\text{dichloromethane}} (C_2H_5)_4NSbCl_5Br\ (B)$$

In each synthesis the mole ratio of reactants was unity. After precipitation of compound A, the HCl was removed by pumping at ambient temperatures for 2 hr, and the resultant yellow powder subsequently stored and manipulated under strictly anhydrous conditions. Compound B, a yellow solid, was filtered on a glass sinter before pumping and storing. Analytical results (Alfred Bernhardt, Munich, Germany) are summarized in Table I.

Raman Spectra.—Raman spectra of A and B in the solid state were recorded using a Cary 81 Raman spectrometer with 6328-Å helium–neon excitation; results are listed in Table II.

The presence of the PCl_4^+ ion in A is clearly shown by the position of bands at 660, 458, 251, and 182 cm^{-1}; these correspond to PCl_4^+ bands in the spectra of authentic samples of $[PCl_4][BCl_4]$ and also $[PCl_4][SbCl_6]$ prepared and run in this laboratory. Inspection of Table II shows that, apart from bands at 667 and 422 cm^{-1} in B, due to the tetraethylammonium ion, the spectra of A and B match extremely closely. Only two weak bands (396 and 363 cm^{-1} in A) are not common to both; the same anionic species is therefore inferred. Consideration of comparison spectra of compounds containing the ions $SbCl_6^-$, PCl_6^-, and PCl_3Br^+ eliminate the possibilities that A might be formulated as $[SbCl_3Br][PCl_6]$ or as $[PCl_3Br][SbCl_6]$. That $SbBr_6^-$ was not present was shown by the absence of a strong band at 194 cm^{-1} previously observed in the spectrum of a sample of $[(C_2H_5)_4N][SbBr_6]$ prepared in this laboratory. The remaining formulation, consistent with both analytical and Raman evidence, is $[PCl_4][SbCl_5Br]$, and B is hence established as $[(C_2H_5)_4N][SbCl_5Br]$. Infrared spectra, run as Nujol mulls, on both A and B are completely consistent with the above interpretation; a detailed presentation of the vibrational spectra will be given elsewhere.

Table II
Raman Shifts (cm^{-1}) for $PSbCl_9Br$ and $(C_2H_5)_4NSbCl_5Br$[a]

$PSbCl_9Br$ (A)	$(C_2H_5)_4NSbCl_5Br$ (B)	Assignment
	677 w	Et_4N^+
660 w		PCl_4^+
458 s		PCl_4^+
	422 w	Et_4N^+
396 w		?
363 w, sh		?
332 vs	332 s	$SbCl_5Br^-$
310 m	308 m	$SbCl_5Br^-$
290 m	289 m	$SbCl_5Br^-$
251 s		PCl_4^+
222 s, br	223 s, br	$SbCl_5Br^-$
182 sh		PCl_4^+
175 s	173 m, br	$SbCl_5Br^-$
157 w	158 w	$SbCl_5Br^-$

[a] Abbreviations: Et, $(C_2H_5)_4$; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

Differential Scanning Calorimetry.—To substantiate further that A was not a 5:1 (mole) mixture of $SbCl_6^-$ and $SbBr_6^-$ species, differential scanning calorimetric (dsc) measurements were made on $[(C_2H_5)_4N][SbCl_6]$ (a), on $[(C_2H_5)_4N][SbBr_6]$ (b), on a freshly prepared 5:1 molar mixture of a and b, and on B, using sealed pans, from ambient temperature to *ca.* 280°. The thermogram from the mixture exhibited features associated with the individual components, and, in particular, reversible endothermic phase changes near 60° (a) and 158° (b). The thermogram of B differed from that of the mixture; no evidence for the 158° endotherm was found, in contrast to the mixture.

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(1) L. Kolditz, *Advan. Inorg. Chem. Radiochem.*, **7**, 13 (1965).
(2) L. Kolditz, *Halogen Chem.*, **2**, 133 (1967).
(3) L. Kolditz and G. Heuthe, unpublished results, quoted in ref 2.
(4) L. Kolditz and A. Feltz, *Z. Anorg. Allg. Chem.*, **293**, 286 (1957).

Hence the conclusion that B was a compound is further indicated.

Acknowledgment.—We thank Mr. S. Ashdown and Mr. R. Coley for help with the preparation of samples and with dsc measurements, respectively. We are greatly indebted to the Monsanto Research Corp., Prime Contractor on Air Force Contract F 33615-171-C-1132, for financial support during this investigation.

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Solubility of Potassium Halides in Fused Acetamide

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Received June 4, 1971

A chief drawback with fused inorganic salts is the necessity of maintaining a high operating temperature. Fused acetamide has been shown by several investigators[1,2] to exhibit good solvent properties for electrolytes. Acetamide melts at 80° and boils at 222°. Its dielectric constant is 60.6 at 94°.[3] Undoubtedly its strong solvent power for salts is attributed principally to its high dielectric constant.

Jander and Winkler[3] have utilized fused acetamide as a reaction medium for several inorganic reactions. Wallace and Bruins[4] have reported that potassium halide–acetamide solutions make excellent cell electrolytes for thermal salt cells. (A thermal salt cell produces electrical energy of long duration on application of heat. The electrolyte of this batter is solid and nonconducting at ordinary temperatures, but when external heat is applied, the solid melts and becomes conducting.) Recently, the electrical conductance and viscosity of potassium halide salts in dilute acetamide solutions have been measured.[5] Unfortunately, a search of the literature reveals that there are no quantitative solubility and heat of solution data for potassium halide salts in fused acetamide.

Consequently, in this work, the solubilities of potassium halide salts in acetamide have been measured as a function of temperature between 80 and 130°. From these solubility data, experimental heats of solution were also calculated. The order of decreasing solubility in fused acetamide, KI > KBr > KCl, has the same order as that found for these halides in water and *N*-methylacetamide.

Experimental Section

Apparatus.—A 500-ml Pyrex tube was fitted with a glass stopper, a 0.1° calibrated thermometer, and a glass stirrer. The stirrer was bent into a ring at its lower end. It was moved up and down vigorously during each solubility determination. This whole apparatus was clamped in position in a large electric oven. Titrations were made by a 50-ml Teflon-tipped buret.

(1) **Acetamide.**—Analytical grade acetamide crystals (Mallinckrodt Chemical) were further purified by recrystallization in pure benzene. The resulting solvent (mp 80.0–80.5°) had a mean specific conductance of 8.5×10^{-6} ohm^{-1} cm^{-1} at 94°.

(2) **Halides.**—Analytical grade KI, KBr, and KCl (Mallinckrodt Chemical) were recrystallized from distilled water and fused.

(3) **Standardized Solutions.**—Standard 0.100 *N* silver nitrate and 0.119 *N* potassium thiocyanate solutions were prepared. A saturated solution of ferric ammonium sulfate, made to 0.3 *N* acidity with nitric acid, served as the indicator for the titrations.

Procedure.—Purified acetamide containing an excess of the solid potassium salt in the Pyrex tube was heated to the desired temperature and allowed to equilibrate. All solubility measurements were made with the tube held in a silicone oil bath maintained at a constant temperature to within 0.1°. Aliquot portions of the supernatant liquid were drawn off with a pipet at the same temperature and were placed in a 250-ml erlenmeyer flask. The solution was then weighed, dissolved in water, and titrated according to the Volhard titration method.[6]

Results and Discussion

In Table I are presented the solubilities in grams of potassium halide salt in 100 g of acetamide. The solubility of each solution was corrected for loss of acetamide by weighing the sample before and after each determination, and the data represent averages of duplicate or triplicate determinations. For KCl, the solubility ranged from 2.45 g at 80° to 2.74 g at 130°; for KBr, 10.3 g at 80° to 11.6 g at 130°; and for KI, 32.3 g at 80° to 33.6 g at 130°. It is noted that KI is much more soluble in acetamide than either KBr or KCl.

TABLE I
SOLUBILITY OF POTASSIUM HALIDE SALTS IN MOLTEN ACETAMIDE

KCl		KBr		KI	
Temp, °C	Solubility, g/100 g of acetamide	Temp, °C	Solubility, g/100 g of acetamide	Temp, °C	Solubility, g/100 g of acetamide
80	2.45	81	10.3	80	32.3
86	2.52	90	10.5	85	32.5
103	2.58	100	10.8	97	32.8
115	2.62	110	11.0	118	33.2
120	2.68	120	11.2	130	33.6
130	2.74	130	11.3		

The series of decreasing solubilities in molten acetamide, KI > KBr > KCl, has the same order as that found for these halides in *N*-methylacetamide[7] and water.[8] The position of the iodide ion in this series shows that it is highly solvated in fused acetamide. Our solubility data can also be represented as a function of temperature by the following: for KCl, $\log s = 9.50 \times 10^{-4}t + 0.313$; for KBr, $\log s = 9.40 \times 10^{-4}t + 0.937$; and for KI, $\log s = 3.33 \times 10^{-4}t + 1.484$, where s is solubility, in grams per 100 g of molten acetamide, and t is temperature.

Heats of solution in the temperature range between 80 and 130° were determined from the van't Hoff equation

$$\frac{\mathrm{d}\ln m}{\mathrm{d}(1/T)} = \frac{\Delta H_{\mathrm{soln}}}{R}$$

where m is molality, in moles per 1000 g of acetamide, T is the absolute temperature, R is the gas constant,

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[1] O. Stafford, *J. Amer. Chem. Soc.*, **55**, 3987 (1933).

[2] L. Yntema and L. Audrieth, *ibid.*, **52**, 2693 (1930).

[3] G. Jander and G. Winkler, *J. Inorg. Nucl. Chem.*, **9**, 24 (1959).

[4] R. Wallace and P. Bruins, *J. Electrochem. Soc.*, **114**, 212 (1967).

[5] R. Wallace, *J. Phys. Chem.*, **75**, 2687 (1971).

[6] I. Kolthoff and K. Stenger, "Volumetric Analysis," Vol. 2, Interscience, New York, N. Y., 1947, p 250.

[7] L. R. Dawson in "Chemistry in Nonaqueous Ionizing Solvents," Vol. IV, G. Jander, H. Spandaw, and C. Addison, Ed., Friedr Vieweg & Sohn, Braunschweig, Germany, 1963, p 266.

[8] "Handbook of Chemistry and Physics," 43rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 1821.