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A Study of the Reaction between Bismuth Bromide and Amine Hydrobromides

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Twenty five compounds were prepared by the reaction OF hydrobromic acid solutions of bismuth bromide and amide hydrobromides. The complex compounds were purified by recrystallization, analyzed for bromine and bismuth content, their melting points or decomposition temperatures determined and qualitative solubilities found. The conditions of the reactions were carefully controlled and practically identical for all preparations. The solid compounds recovered were of four different types: three $RBiBr_4$; eight R_2BiBr_5; ten R_3BiBr_6; four $R_3Bi_2Br_9$ (where R represents an amine cation).

Introduction

The preparation of $((C_2H_5)_4N)_3Bi_2Br_9$ was reported by Jorgenson.[1] $(C_5H_5NH)_3Bi_2Br_9$ was prepared by Hauser and Vanino.[2] Datta and Sen[3] reported the preparation of $((CH_3)_4N)_2BiBr_5$. $((C_2H_5)_4N)_2BiBr_5$, $(C_5H_5NH)_2BiBr_5$ and $(C_9H_7NH)_2BiBr_5$. Pugh[4] studied the reaction of hydrazinium bromide with bismuth bromide and reported the isolation of the following compounds: $N_2H_6BiBr_5 . 4H_2O$; $(N_2H_5)_3BiBr_6$; $(N_2H_5)_4BiBr_7$; $(N_2H_5)_3Bi_2Br_9$ and $(N_2H_5)_6HBi_3Br_{16}$. Dubsky, Wagonhofer and Langer[5] studied the reaction of bismuth tribromide with both quinolinium bromide and analinium bromide. They reported the compounds as $(C_9H_7NH)_2Bi_2Br_8 . 2H_2O$; $(C_9H_7NH)_3Bi_2Br_9 . H_2O$; $(C_9H_7NH)_4Bi_2Br_{10} . 6H_2O$; $C_6H_5NH_3BiBr_4 . 2H_2O$; $(C_6H_5NH_3)_4Bi_2Br_{10} . 4H_2O$; $(C_6H_5NH_3)_4Bi_2Br_{10} . 8H_2O$. They postulated a binuclear structure for five of these compounds with bismuth atoms at the center of two octahedra with two bromine atoms as bridges at the common edges of the octahedra.

Materials. Bismuth tribromide was prepared from reagent grade bismuth trioxide. Most of the amines were Eastman white label chemicals and were without further purification. All solvents were reagent grade.

Synthetic procedure. The method of preparation was almost identical for the different compounds. The bismuth tribromide solution was prepared by dissolving 233 grams (0.5 mole) in 800 ml of concentrated HBr and diluting to one liter. The resulting solution was 1.0 *M* with respect to bismuth and 7.9 *M* with respect to hydrogen bromide. The amine hydrobromide salts were prepared by adding an excess of hydrogen bromide to the amine. Fifty ml aliquots of the bismuth bromide solution were added with constant stirring to the respective hydrobromide salt solutions. The amine hydrobromide to bismuth molar ratio was approximately 5 to 1 and the bromide to bismuth ratio was about 10 to 1 in all preparations. If precipitation did not immediately occur the solution was heated to reduce the volume and cooled in an ice bath. 2-propanol and 2-propanol-ether mixtures were used to precipitate a few of the more soluble salts. The products were filtered by reduced pressure through sintered glass crucibles and rinsed with a solution of 2-propanol-hydrobromic acid (10 to 1 by volume) and finally with diethyl ether. The compounds were recrystallized from approximately 200 ml of 2-propanol-acetone (1 to 1 by volume) containing 10 ml of concentrated hydrobromic acid. The solutions were heated on a hot plate at low temperature until precipitation was initiated and then allowed to cool slowly to room temperature. The product was recovered by filtration at reduced pressure, washed successively with 2-propanol and diethyl ether and dried in a vacuum desiccator Yields varied from 50 to nearly 100% calculated in terms of the bismuth content.

Analytical Procedures. The samplas used for bismuth analysis were dissolved in a few ml of concentrated nitric acid and heated to oxidize the organic material and vaporize the hydrobromic acid. The solutions were diluted with water and the pH adjusted to 1.5 by the addition of dilute NaOH. The samples were warmed to 50°C, and titrated with standard EDTA using xylenol orange as an indicator. The results are shown in Table I.

Samples used for the analysis of bromide were dissolved in a small volume of 0.5 *M* tartaric acid to complex the bismuth and prevent the precipitation of BiOBr in basic or neutral solutions. The solutions were made basic by the addition of NaOH and heated to remove the free amine. They were then diluted and the pH adjusted to 6 by the addition of dilute tartaric acid. The bromine was determined by potentiometric titration with standard silver nitrate using

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[1] S. M. Jørgenson, *J. Pr. Chem.*, (2), 3, 328 (1871).
[2] O. Hauser and L. Vanino, *Ber. Chem. Dtsch. Chem.*, 36, 3682 (1903).
[3] R. L. Datta and J. N. Sen, *J. Am. Chem. Soc.*, 39, 750 (1917).
[4] W. Pugh, *J. Chem. Soc.*, 1385 (1954).
[5] J. V. Dubsky, E. Wagonhofer, and A. Langer, *Collection Czech. Chem. Commun.*, *11*, 441 (1939).

Table I.

		Bismuth (%)		Bromine (%)	
	M.P. Range, °C	Theoretical	Experimental*	Theoretical	Experimental*
$2{-}CH_3 . C_5H_4NHBiBr_4$	207-208	33.56	33.27±0.06	51.33	51.28±0.29
$3{-}CH_3 . C_5H_4NHBiBr_4$	220-222	33.56	33.46±0.06	51.33	51.24±0.10
$C_9H_7NHBiBr_4$	>300	31.72	31.92±0.25	48.52	48.38±0.41
$(iso{-}C_3H_7NH_3)_2BiBr_5$	285-288	28.68	28.45±0.14	54.83	55.01±0.11
$(n{-}C_4H_9NH_3)_2BiBr_5$	249-251	27.61	27.62±0.07	52.79	52.84±0.04
$(iso{-}C_4H_9NH_3)_2BiBr_5$	273-275	27.61	27.53±0.25	52.79	52.78±0.06
$(H_3CCH(CH_3)CH_2CH(CH_3)NH_3)_2BiBr_5$	260-261	25.71	25.48±0.09	49.15	49.24±0.01
$(4{-}CH_3 . C_5H_4NH)_2BiBr_5$	186-189	26.23	26.68±0.22	50.15	50.04±0.38
$(C_6H_{11}NH_3)_2BiMr_5$	d-270	25.83	25.70±0.04	49.39	49.00±0.10
$((CH_2)_5NH_2)_2BiBr_5$	d-276	26.76	26.77±0.04	51.17	51.10±0.19
$(C_5H_5NH)_2BiBr_5$	d-282	27.18	26.72±0.11	51.98	51.60±0.02
$(CH_3NH_3)_3BiBr_6$	>300	26.76	26.58±0.04	61.11	61.12±0.08
$((CH_3)_2NH_2)_3BiBr_6$	264-266	25.28	25.15±0.12	58.00	58.18±0.14
$(C_2H_5NH_3)_3BiBr_6$	231-233	25.28	25.08±0.23	58.00	57.91±0.24
$((C_2H_5)_2NH_2)_3BiBr_6$	194-195	22.94	22.76±0.07	52.64	52.65±0.26
$(n{-}C_3H_7NH_3)_3BiBr_6$	254-255	24.05	23.78±0.12	55.19	54.96±0.25
$((n{-}C_3H_7)_2NH_2)_3BiMr_6$	179-180	21.02	20.94±0.17	48.19	48.07±0.02
$((iso{-}C_3H_7)_2NH_a)_3BiBr_6$	230-232	21.02	20.89±0.19	48.19	48.18±0.25
$(H_2C{:}\ CHCH_2NH_3)_3BiBr_6$	d-259	24.22	23.93±0.17	55.58	55.56±0.11
$(C_6H_5CH_2NH_3)_3BiBr_6$	235-236	20.63	20.60±0.14	47.34	47.20±0.35
$((C_2H_5)_3NH)_3Bi_2Br_9$	102-104	28.95	28.28±0.05	49.81	49.57±0.06
$((C_2H_5)_4Bi_2Br_9$	d-295	27.36	26.72±0.17	47.07	46.86±0.36
$((iso{-}C_4H_9)_2NH_2)_3Bi_2Br_9$	161-162	27.36	27.17±0.07	47.07	47.28±0.23
$(C_6H_5CH(CH_3)N(CH_3)_2H)_3Bi_2Br_9$	260-262	26.32	25.94±0.06	45.29	45.11±0.42

* The recorded results show the average and average deviations for three determinations of each compound.

a silver indicating electrode and a mercury-mercurous sulfate reference electrode. The results are tabulated in Table I.

Physical Properties of the Compounds. The color of the compounds varied from yellow to nearly colorless. The tetrabromo and pentabromo compounds are more highly colored than the other types of compounds. The compounds are soluble in water but decompose to form BiOBr. They are soluble in the more polar organic solvents but undergo solvation reactions which either involves the dissociation of the complex ion or replacement of bromide with a molecule of the solvent. The solubility and the rate of solvation is related to the dielectric constant or Lewis base properties of the solvent. The compounds are practicallp insoluble in benzene, chloroform and carbon tetrachloride.

The melting points or decomposition temperatures of the compounds were determined using a modified Thiele-Dennis melting point tube containing Dow Corning 550 silicon oil. The melting point data are shown in Table I.

The complex compounds are sufficiently soluble in a number of the more polar organic solvents for absorption spectral study. The spectra are highly dependent upon the concentration of bromide ion and Beer's law is not obeyed unless a large, constant excess of bromide ion is present. The absorption spectra of the compounds were determined in methanol with hydrogen bromide concentration of 0.10 M. In these solutions the ratio of bromide ion to bismuth is greater than 1,000 to 1 as the concentration of the compounds were in the 10^{-5} to 10^{-4} M range. Under these conditions the absorption spectra of the compounds were identical within the limit of experimental error. The absorption spectra of four different concentrations of the salts were determined and the molar absorptivity was found to be $(7.48 \pm 0.08) . 10^3$ M^{-1} cm^{-1} at a wavelength of 355 mμ.

X-ray diffraction studies have been made of $2{-}CH_3 . C_5H_4NHBiBr_4$[6] $(C_6H_{11}NH_3)_2BiBr_5$[7] and $((CH_3)_2NH_2)_3BiBr_6$.[8] In the $BiBr_4^-$ structure it was found that each bismuth atom was surrounded by an irregular octahedron of bromine atoms and that four halogen bridges connected adjacent bismuth atoms. The two unbridged bromine atoms had practically identical Bi–Br distances but the Bi–Br distance was quite different for the bridged halogen atoms. The $BiBr_5^{2-}$ ion was a distorted octahedron of bromine atoms around bismuth, with two bromine bridges that link adjacent bismuth atoms. The $BiBr_6^{3-}$ was a slightly distorted octahedron with only slight deviations in Bi–Br distances but the angular axial deviations from 90° indicate that the octahedra are not regular. This distortion was probably caused by the pair of 6s electrons in the Bi^{III} ion. The structure of compounds of the $R_3Bi_2Br_9$ have not been determined. It would seem logical that they also have the octahedral configuration with three bromine atoms involved in bismuth-bromide bridges.

Discussion

The absorption spectral studies indicate that all of the complex bromo-bismuth ions are quite labile. In any solvent in which the different compounds could be dissolved, the spectra varied with time but achieved equilibrium rapidly and gave similar but not identical absorption spectra. When a large con-

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(6) B. K. Robertson, W. G. McPherson, and E. A. Meyers, *J. Phys. Chem.*, *71*, 3531 (1967).

(7) W. G. McPherson and E. A. Meyers, *J. Phys. Chem.*, *72*, 532 (1968).

(8) W. G. McPherson and E. A. Meyers, *J. Phys. Chem.*, *72*, 3117 (1968).

stant excess of bromide ion was present the spectra were identical within the limit of experimental error.

The formation of a particular solid compound from solution is governed by a number of factors. The final product is the specific form which produces the greatest change in the free energy of the total system. The four different types of solid compounds made in this work were not due to differences in either bismuth or bromide concentrations as they were kept practically constant in all of the preparations. There was some variation in the dielectric constant of the medium from which the original products were formed, due to the addition of nonaqueous solvents to induce precipitation, but the recrystallization conditions were constant. This work suggests that the principal factor in determining the particular bromobismuthate complex compound which forms as a solid is the lattice free energy.