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The Synthesis and the Properties of Some New Boroarsenites

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Though heteropoly salts of boron such as borotungstates[1,2] and borotungstovanadates[3] are reported in literature, very little work has been done on boroarsenites. Lery and Curty[4] found that, borophosphoric and boroarsenic acids exist in solution provided the solutions are sufficiently concentrated, even in the presence of vigorous hydrolyzing agent such as steam. In this note the preparation of ammonium boroarsenite and there-from the boroarsenite salts of silver, lead, zinc, cadmium and iron(II) are reported. Some of the physical properties of a few of these compounds are also studied.

Experimental

Synthesis of Ammonium Boroarsenite. Boric acid (9.27 g) and arsenious oxide (9.89 g) were dissolved in aqueous ammonia separately. The solutions were mixed together and then refluxed for ten to twelve hours. The solution was then concentrated to small volume and kept in a refrigerator, when ammonium boroarsenite separated out. It was recrystallized from water two to three times and dried in a vacuum desiccator.

The other salts were prepared by adding solutions of $AgNO_3$, $Pb(CH_3COO)_2$ $Zn(CH_3COO)_2$, $Cd(CH_3COO)_2$ and $FeSO_4$ to the ammonium salts solution. The analytical results are recorded in Table 1.

Analytical. Boron was estimated by a volumetric method in the presence of mannitol using phenolphthalein as an indicator. Nitrogen was estimated by the Kjeldahl method and the percentage expressed in terms of $(NH_4)_2O$. Other metals were estimated by standard

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[1] H. Copaux, *Ann. Chim. Phys.*, **17**, 217 (1909).

[2] D. Klein, *Bull. Soc. Chim.*, **33**, 466 (1880); **34**, 23 (1880); **37**, 202 (1882); *Ann. Chim. Phys.*, **28**, 426 (1883).

[3] N. A. Polotebunova, *Uchenge. Zapiski. Kishinev*, **27**, 83 (1957).

[4] G. R. Levi and R. Curty, *Gazz. Chim. Ital.*, **68**, 376 (1938).

Table 1

Compound	% of Metal oxide		% B_2O_3		% As_2O_3		% H_2O	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$5(NH_4)_2O \cdot B_2O_3 \cdot 4As_2O_3 \cdot 25H_2O$	17.0	16.5	4.2	4.4	50.2	50.3	28.6	28.6
$5Ag_2O \cdot B_2O_3 \cdot 4As_2O_3 \cdot 21H_2O$	47.8	48.4	2.8	2.9	33.1	33.0	16.2	15.8
$5PbO \cdot B_2O_3 \cdot 4As_2O_3 \cdot 22H_2O$	46.5	47.0	2.8	2.9	34.5	33.4	16.2	16.7
$5ZnO \cdot B_2O_3 \cdot 4As_2O_3 \cdot 10H_2O$	27.3	28.0	4.6	4.8	52.9	54.7	15.2	12.4
$5CdO \cdot B_2O_3 \cdot 4As_2O_3 \cdot 6H_2O$	40.1	39.8	4.2	4.3	50.8	49.1	4.8	6.7
$5FeO \cdot B_2O_3 \cdot 4As_2O_3 \cdot 6H_2O$	27.9	27.1	5.2	5.2	57.9	59.5	8.9	8.1

methods. Water was found by difference.

Spectroscopic Studies. The infrared spectra in the range 2—15μ of ammonium boroarsenite and zinc boroarsenite were recorded on a Perkin-Elmer infrared spectrometer in KBr discs.

Discussion

It is very difficult to assign definite structures to the heteropoly acids and their salts owing to the complexity of the molecules involved. The compositions of the salts have been arrived at on the basis of analytical results. The analytical results have given the empirical formula $5(NH_4)_2O \cdot B_2O_3 \cdot 4As_2O_3 \cdot 25H_2O$ for ammonium boroarsenite. When a freshly prepared solution of this salt was subjected to ion exchange (Dowex-50 cation resin), it gave a stable free acid thus confirming the stability of boroarsenite ion in the solution. Several unsuccessful attempts were made to crystallize the acid out.

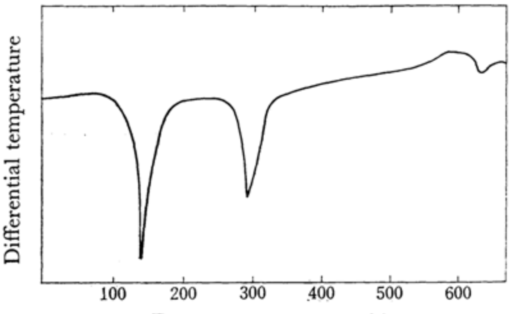

Fig. 1. Differential thermal analysis curve of ammonium boroarsenite.

The differential thermal analysis (DTA) curve reveals two endotherms one at 140°C and the other at 294°C, corresponding to the dehydration of the compound. This indicates the presence of two types of bound water molecules.

In the infrared spectra of zinc boroarsenite and ammonium boroarsenite one peak is observed in the 3μ region (3231, 3403 cm^{-1} respectively) corresponding to the –OH stretching vibrations of water molecules. The peak at 3403 cm^{-1} in case of ammonium boroasenite is broad which may due to the overlapping of –NH and –OH stretching frequencies. In the case of ammonium boroarsenite one peak is found at 1634 cm^{-1} which may be assigned as –NH bending. Peaks at 1198 cm^{-1} and 793 cm^{-1} in the case of ammonium boroarsenite and 1191 and 802 cm^{-1} in the case of zinc boroarsenite have been assigned to –BO group, though. White *et al.*[5] have reported absorption bands at 1300 and 762 cm^{-1} for –BO group in their studies on simple B_2O_3 molecule. The variation in the frequencies observed may be due to the involvement of BO group in complex formation. Bands have been observed at 1044 cm^{-1} and 1052 cm^{-1} respectively for ammonium boroarsenite and zinc boroarsenite which are attributed to As–O stretching frequency. Confirmation to this was obtained in the infrared spectrum of As_2O_3 taken by the author which showed band at 1045 cm^{-1} which can be attributed to As–O stretching frequency.

The slight differences observed in the position of the corresponding IR bands of the two salts studied may be due to the differences in their crystal structure environments.

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5) D. White, P. N. Walsh and D. E. Mann, *J. Chem. Phys.*, **28**, 508 (1958).