[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF HYNSON, WESTCOTT AND DUNNING]

THE PREPARATION OF BISMUTH THIOGLYCOLAMIDE

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The interesting discovery that the ethyl ester of thioglycolic acid dissolves metallic oxides to form thio salts of the ester was made some years ago by Abel[1] who prepared antimony sodium thioglycolate and antimony thioglycolamide. Since that time other metallic derivatives of thioglycolic acid have been prepared by Rouiller,[2] who prepared among others triethylbismuthtrithioglycolate, and by Myers,[3] who prepared a large number of such derivatives, including bismuth sodium thioglycolate.

The antimony amide was first described as a thick, resinous, oily body.[1] The late Dr. Daniel Base, however, working in this Laboratory, succeeded in obtaining the material as white, needle-like crystals. The marked physiological properties of this compound led the authors to attempt to prepare similar metallic derivatives of thioglycolic acid.

The preparation of bismuth thioglycolamide is described in this paper.. An attempt was made to prepare arsenic thioglycolamide in a similar manner, but in every case the resulting compound was a milky, unstable oil which decomposed on standing and which resisted all efforts at crystallization. The vanadium compound was also attempted, but without success.

Experimental Part

The Preparation of Crystalline Antimony Thioglycolamide.[4]—Antimony thioglycolamide, $Sb(SCH_2CONH_2)_3$, was prepared as described by Abel.[1] Two hundred g. of the oily, resinous material obtained by this method was transferred to a 2-liter beaker, and about 1 liter of boiling water added. The oily, resinous material dissolved readily upon stirring and the slightly turbid solution was filtered at once and allowed to cool. After standing overnight in the ice box, the solution was filtered and the nearly white crystals were washed with cold water and dried, first in the air and finally at 80°. Another small crop of crystals was obtained by evaporating the filtrate on the water-bath to a small volume. Even if this is not done, however, the loss is slight, for the material is soluble in cold water only to about 0.4%. After two recrystallizations from hot

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[1] Rowntree and Abel, *J. Pharmacol.*, **2**, 108 (1910).

[2] Rouiller, THIS JOURNAL, **41**, 777 (1919).

[3] Myers, *J. Lab. Clin. Med.*, **6**, 7 (1921).

[4] The directions for preparing crystalline antimony thioglycolamide, as well as the analytical results, are taken from the unpublished notes of the late Dr. Daniel Base.

water, the crystals melted at 139° (uncorr.) and gave the following analysis.

Anal. Calcd. for $C_6H_{12}O_3N_3S_3Sb$: Sb, 30.77; S, 24.67; N, 10.58. Found: Sb, 31.36; S, 24.61; N, 10.77.

Preparation of Bismuth Thioglycolamide.—Ethyl thioglycolate was prepared by the method of Claesson.[5] Sixty g. of the moist ester thus obtained was treated with 39 g. of bismuth oxide (prepared by ignition of the sub-carbonate) according to the method described by Rouiller.[2] The yellow alcoholic solution resulting was saturated with ammonia gas at room temperature. The reaction is exothermic and no attempt was made to cool the solution as the reaction progressed. When the ammonia was no longer absorbed, the solution was cooled, allowed to stand overnight and again saturated with ammonia gas. This time there was no evolution of heat and the reaction was assumed to be complete. On cooling the solution, the bismuth thioglycolamide settled out as a dark red, viscous mass. The alcohol was decanted and the bismuth thioglycolamide remaining in solution in it was precipitated by the addition of several volumes of ether. The two lots of amide were then united and dissolved in 1 liter of water at 70–80°. Water at higher temperatures causes considerable decomposition of the amide and subsequent precipitation of bismuth sulfide. The warm solution was filtered and allowed to cool, when the amide, $Bi(SCH_2CONH_2)_3$, crystallized in shiny yellow plates. After two recrystallizations from warm water and drying at 80°, the crystals melted at 144.5° (uncorr.) and gave the following analytical results.

Anal. Calcd. for $C_6H_{12}O_3N_3S_3Bi$: Bi, 43.6; N, 8.76. Found: Bi, 43.3, 43.7; N, 9.00, 8.89.

Summary

Antimony thioglycolamide has been prepared in crystalline form. The preparation of bismuth thioglycolamide is described. The pharmacological action of bismuth thioglycolamide is being investigated.

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[5] Claesson, *Ann.*, **187**, 113 (1877).