433. *Ammines. Part X. Cobaltous and Cupric Compounds from Tris-(β-hydroxyethyl)amine. New Method of Formation of Ammino-cupric Salts.*

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THE behaviour of tris-(β-hydroxyethyl)amine (triethanolamine) (I) with salts of the commoner metals has been examined. Only ferric, cobalt, and cupric compounds gave unusual results; ferric chloride and hydroxide yielded no definite compound. Cobaltous salts gave purple crystalline compounds, *acidocobaltotris-*(β-*hydroxyethyl*)*amine* (II), but nickel chloride yielded only the blue crystalline addition *compound*, $NiCl_2,2N(CH_2{\cdot}CH_2{\cdot}OH)_3$. Although decomposed by warm water the chlorocobaltous compound (II; X = Cl) dissolved in 20% sodium hydroxide and from this solution brown crystals of a *sodium* derivative of *hydroxocobaltotris-*(β-*hydroxyethyl*)*amine* separated (II; X = ONa). The reactions, analytical data, and method of formation all support formula (II) and are against these

$$N(CH_2{\cdot}CH_2{\cdot}OH)_3 \quad \text{(I.)}$$
$$X - Co - O{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}OH)_2 \quad \text{(II.)}$$
$$Cu(OH)_2,N(CH_2{\cdot}CH_2{\cdot}OH)_3 \quad \text{(III.)}$$

compounds being addition compounds composed of (I) and basic cobaltous salts.

Although cupric salts yielded deep blue solutions with (I) in water, no crystalline compound could be separated. Cupric hydroxide dissolved easily in aqueous solutions of (I) and dark blue crystals of *tris-*(β-*hydroxyethyl*)*aminocupric hydroxide* (III) were obtained. The solution of (III) in water was strongly alkaline and looked like ammoniacal cupric hydroxide solution; it was reduced to cuprous oxide when boiled with glucose. Attempts to prepare salts of the base (III) led always to basic cupric salts containing no (I). An alcoholic solution of (III) liberated ammonia from its salts, and the reaction has led to a new method of preparation of several ammino-cupric salts from ammonium salts of organic acids.

EXPERIMENTAL.

Chlorocobaltotris-(β-*hydroxyethyl*)*amine* (II; X = Cl) separated in small purple plates when $N(CH_2{\cdot}CH_2{\cdot}OH)_3$ (30 c.c.) was stirred into $CoCl_2,6H_2O$ aq. (10 g. in 30 c.c. H_2O) at 40°, and the mixture then cooled (Found: Co, 24·2; Cl, 14·5; N, 5·8. $C_6H_{14}O_3NClCo$ requires Co, 24·3; Cl, 14·6; N, 5·8%). In the same manner $CoBr_2$ produced minute purple crystals of the corresponding *bromo*-compound (II; X = Br) (Found: Co, 20·5; Br, 27·3; N, 4·9. $C_6H_{14}O_3NBrCo$ requires Co, 20·5; Br, 27·9; N, 4·9%). The *thiocyanato*-compound (II; X = SCN) was obtained in minute purple crystals when 1 vol. of (I) was stirred into a mixture of 1 vol. of $CoCl_2$ aq. (5%) and 1 vol. of

KSCN aq. (5%) (Found : Co, 22·2; SCN, 21·5; N, 10·45. $C_7H_{14}O_3N_2SCo$ requires Co, 22·2; SCN, 21·9; N, 10·6%). The three foregoing compounds are insol. in cold H_2O. Addition of hot H_2O causes hydrolysis, but evaporation to dryness regenerates the original compound. All are sol. in NaOH aq., forming purple solns.

The *sodium* derivative of *hydroxocobaltotris-(β-hydroxyethyl)amine* (II; X = ONa) separated in brown plates of the *dihydrate* after saturation of 20% NaOH aq. at 50° with the chloro-compound (above), heating for ½ hr. at 100°, filtering, and cooling (Found : Co, 20·5; Na, 8·2; N, 4·6; H_2O, 13·2. $C_6H_{14}O_4NNaCo,2H_2O$ requires Co, 20·9; Na, 8·2; N, 4·9; H_2O, 12·8%). This compound forms an alkaline soln. in H_2O; on exposure to air it becomes black, and decomposes to Co_3O_4.

Ditris-(β-hydroxyethyl)aminonickel chloride, $NiCl_2,2N(CH_2{\cdot}CH_2{\cdot}OH)_3$, was obtained as a blue cryst. ppt. on addition of EtOH to a mixture of $NiCl_2$ aq. (10 g. $NiCl_2$ in 20 c.c. H_2O) and 20 c.c. of (I) (Found : Ni, 13·6; Cl, 16·6; N, 6·6. $C_{12}H_{30}O_6N_2Cl_2Ni$ requires Ni, 13·7; Cl, 16·6; N, 6·5%). The compound gives a blue soln. in H_2O and green in NaOH aq. Boiling causes decomp.

Tris-(β-hydroxyethyl)aminocupric hydroxide (III) was obtained in dark blue crystals as follows : Freshly pptd. moist $Cu(OH)_2$ was dissolved to saturation in 50% aq. soln. of $N(CH_2{\cdot}CH_2{\cdot}OH)_3$ and 9 vols. of acetone were added to the filtered soln. (Found : Cu, 25·8; N, 5·7. $C_6H_{17}O_5NCu$ requires Cu, 25·8; N, 5·7%). Attempts to form salts of the base (III) by adding 1 or 2 equiv. of acid led only to basic cupric salts, and addition of NH_4 salts resulted in evolution of NH_3.

Amminocupric Salts.—Addition of (III) (3 g. in 30 c.c. EtOH) to solns. of organic NH_4 salts (2 g. in 8 c.c. H_2O) yielded the following cryst. amminocupric salts on addition of more EtOH or acetone.

Diamminocupric thiocyanate, $2NH_3,Cu(SCN)_2$, pale blue crystals (Found : Cu, 29·2; N, 26·0. Calc. : Cu, 29·8; N, 26·2%).

Diamminocupric formate, $2NH_3,Cu(HCO_2)_2$, dark blue needles (Found : Cu, 33·9; NH_3, 18·2. Requires : Cu, 33·9; NH_3, 18·1%).

Diamminocupric succinate, $2NH_3,CuC_4H_4O_4,2H_2O$, purple needles (Found : Cu, 25·5; NH_3, 13·6. Requires : Cu, 25·7; NH_3, 13·8%).

Triamminocupric maleate, $3NH_3,CuC_4H_2O_4,2H_2O$, purple needles (Found : Cu, 24·6; NH_3, 19·1. Requires : Cu, 24·4; NH_3, 19·3%).

Diamminocupric fumarate, $2NH_3,CuC_4H_2O_4,H_2O$, dark blue needles (Found : Cu, 27·1; NH_3, 15·2. Requires : Cu, 27·7; NH_3, 14·8%).

All the above ammino-salts are hydrolysed by H_2O to basic cupric salts and NH_3.

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[*Received, October 22nd*, 1932.]