

LXVII.—*Ammoniacal Double Chromates and Molybdates.*

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IN a previous paper (Trans., 1903, 83, 391), a number of double chromates were described belonging to a series having the general formula  $M_2^I M^{II} (RO_4)_2, 2NH_3$ .

Since the majority of the comparatively small number of ammoniacal double salts which have been prepared are halides or cyanides, it seemed worth while to make a more complete examination of this series, and compounds have been obtained in which  $M^I$  represents  $NH_4$  or K;  $M^{II}$  is Cu, Zn, Cd, Ni, or Co; and R is Cr or Mo. Numerous attempts to prepare the corresponding tungstates were unsuccessful.

The double salts are characterised by considerable stability. They may be heated at  $150^\circ$  without undergoing any change, and in some cases ammonia is not given off at temperatures above  $200^\circ$ . Decomposition always occurs below  $300^\circ$ , the ammonia being partially oxidised at the expense of the acid radicle.

The stability of the double salts is in marked contrast to the readiness with which ammonia is evolved from many ammonio-metallic compounds, such as  $CuCrO_4, 3\frac{1}{2}NH_3, \frac{1}{2}H_2O$ ,  $CuMoO_4, 2NH_3, H_2O$ , and  $CuWO_4, 4NH_3$ , which are described in the present paper. A further distinction between the two classes of substances is presented in their respective colours. The double salt  $(NH_4)_2Cu(MoO_4)_2, 2NH_3$  is bright blue, similar in tint to hydrated copper sulphate, whereas the compound  $CuMoO_4, 2NH_3, H_2O$  has the deep blue shade usually associated with cuprammonium compounds. Again, although ammonio-nickel compounds are generally blue or violet, the double salt  $(NH_4)_2Ni(MoO_4)_2, 2NH_3$  is green.

*Chromates.*

*Ammonio-copper potassium chromate*,  $K_2Cu(CrO_4)_2, 2NH_3$ , crystallises out when an ammoniacal solution of copper chromate to which a large amount (3 to 4 equivalents) of potassium chromate has been added is allowed to lose its free ammonia by exposure to the air.

Copper carbonate (12.5 grams) was dissolved in a small quantity of water containing 25 grams of chromium trioxide, and the solution added to a mixture of 75 c.c. of water and 125 c.c. of concentrated aqueous ammonia. A second solution containing 20 grams of potassium hydroxide and 150 grams of potassium chromate in 280 c.c. of water was then added, and the liquid filtered. The function of the potassium hydroxide was to diminish the concentration of the

ammonium ions, and thus prevent as far as possible the formation of an isomorphous mixture of potassium and ammonium salts.

After the filtrate had remained for a few days in an open dish, the compound separated in large, hard rosettes of thin, brown plates closely set together. These were broken up, washed by decantation with the mother liquor to remove any basic salt, then with dilute ammonia, and finally dried with alcohol and ether.

	Found.	Required.
CuO.....	19.34	19.44 per cent.
CrO <sub>3</sub> .....	49.06	49.16 „
NH <sub>3</sub> .....	8.8	8.4 „

The compound was decomposed by water and dissolved readily in dilute ammonia. When heated at 250° it gave off a little ammonia and decomposed rapidly at 280°.

*Ammonio-copper chromate*,  $\text{CuCrO}_4 \cdot 3\frac{1}{2}\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , was obtained from the same solution in large, greenish-black crystals, when the potassium chromate present was insufficient for the formation of the double salt  $\text{K}_2\text{Cu}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ . Its preparation was accomplished by dissolving 14 grams of copper carbonate and 25 grams of chromium trioxide in a small amount of water, pouring the solution into a mixture containing 125 c.c. of concentrated ammonia, 50 c.c. of water, and 15 grams of potassium hydroxide, and exposing the filtered liquid to the air.

	Found.		Required.
	I.	II.	
CuO.....	31.95	32.23	32.01 per cent.
CrO <sub>3</sub> .....	40.16	40.10	40.30 „
NH <sub>3</sub> .....	23.86	23.72	24.01 „

The crystals, which readily evolve ammonia at the ordinary temperature, are easily soluble in dilute ammonia, but are decomposed by water. Although several ammoniacal copper chromates have been previously described, this is the first one known containing the acidic and basic oxides in equivalent proportion (1 : 1).

#### *Molybdates.*

The double salts of ammonium molybdate belonging to this series, like the chromates, are well-defined, crystalline substances, readily obtained in a state of purity; they are decomposed by water but dissolve easily in dilute ammonia, in which they appear to be resolved to some extent into their components.

*Ammonio-copper ammonium molybdate*,  $(\text{NH}_4)_2\text{Cu}(\text{MoO}_4)_2 \cdot 2\text{NH}_3$ .— Fifty grams of ammonium molybdate in 60 c.c. of water were added

to a solution of 20 grams of ordinary copper sulphate in 50 c.c. of water and 70 c.c. of concentrated ammonia, the liquid being then made up to 210 c.c. After leaving the solution in an open dish for five days, the large, bright blue crystals were collected, washed with dilute ammonia, and dried with alcohol and ether.

	Found.	Required.
CuO .....	17.46	17.49 per cent.
MoO <sub>3</sub> .....	63.58	63.52 „
NH <sub>3</sub> .....	15.12	15.02 „

*Ammonio-copper molybdate*, CuMoO<sub>4</sub>.2NH<sub>3</sub>.H<sub>2</sub>O, crystallises in deep blue prisms on exposing to the air an ammoniacal solution of copper sulphate and ammonium molybdate which contains too small an amount of molybdate or is too dilute for the formation of the double salt. For its preparation, 24 grams of copper sulphate in 30 c.c. of water were added to 13 grams of ammonium molybdate in 15 c.c. of water and 40 c.c. of strong ammonia, the whole solution being made up to 350 c.c.

	Found.		Required.
	I.	II.	
CuO.....	28.75	28.74	28.87 per cent.
MoO <sub>3</sub> .....	52.66	52.53	52.29 „
NH <sub>3</sub> .....	—	12.53	12.37 „

The habit of the crystals varies greatly with the proportion of copper sulphate and ammonium molybdate present in the solution, an excess of the latter being accompanied by a large development of certain faces which remain insignificant when a considerable amount of the former is used. The compound evolves ammonia at the ordinary temperature; it is soluble in dilute ammonia, from which it may be re-crystallised either by allowing a warm saturated solution to cool, or by exposing a more dilute solution to the air.

*Ammonio-cadmium ammonium molybdate*, (NH<sub>4</sub>)<sub>2</sub>Cd(MoO<sub>4</sub>)<sub>2</sub>.2NH<sub>3</sub>, was prepared in the same way as the corresponding copper compound.

	Found.	Required.
CdO .....	25.69	25.49 per cent.
MoO <sub>3</sub> .....	57.72	57.36 „
NH <sub>3</sub> .....	13.47	13.56 „

When heated quickly, the colourless crystals evolved ammonia and water giving 78.6 per cent. of a black residue, whereas 2CdMoO<sub>4</sub>.Mo<sub>2</sub>O<sub>3</sub> requires 78.1 per cent. The black residue containing molybdenum sesquioxide on further heating in the air was oxidised, becoming white (residue found = 81.3; CdMoO<sub>4</sub>.MoO<sub>3</sub> requires 82.8 per cent.). This decomposition is similar to, but not so complete as, that of the salt

$(\text{NH}_4)_2\text{Cd}(\text{CrO}_4)_2, 2\text{NH}_3$ , which on heating gave  $\text{CdO}, \text{Cr}_2\text{O}_3$  (*loc. cit.*). At a higher temperature a molecule of molybdic anhydride sublimed, leaving cadmium molybdate (found  $\text{CdMoO}_4 = 54.4$ , required  $54.2$  per cent.).

*Ammonio-nickel ammonium molybdate*,  $(\text{NH}_4)_2\text{Ni}(\text{MoO}_4)_2, 2\text{NH}_3$ .—Twenty grams of hexahydrated nickel chloride dissolved in 15 c.c. of water were added to 50 grams of ammonium molybdate in 70 c.c. of strong ammonia and 50 c.c. of water. The deep blue liquid when left in an open dish deposited green crystals of the double salt.

	Found.	Required.
NiO .....	16.79	16.70 per cent.
MoO <sub>3</sub> .....	64.24	64.14 „
NH <sub>3</sub> .....	15.00	15.18 „

*Ammonio-cobalt ammonium molybdate*,  $(\text{NH}_4)_2\text{Co}(\text{MoO}_4)_2, 2\text{NH}_3$ .—A solution made up from 20 grams of cobalt sulphate, 50 grams of ammonium molybdate, 50 c.c. of strong ammonia, and 90 c.c. of water oxidised rapidly in the air; and consequently in order to obtain the cobaltous double salt it was placed over sulphuric acid in a vacuum desiccator connected with a water-pump, which was kept in action until the excess of ammonia had been evolved. The double salt was deposited in small, violet crystals, which were collected, washed with dilute ammonia, and dried with alcohol and ether.

	Found.	Required.
CoO.....	17.03	16.70 per cent.
MoO <sub>3</sub> .....	64.30	64.14 „
NH <sub>3</sub> .....	14.8	15.2 „

If the solution was allowed to oxidise in the air, it deposited a large quantity of brilliant crimson needles, which dissolved in dilute ammonia, but were slightly decomposed by water; they were easily soluble in potassium hydroxide, and the solution on boiling evolved ammonia, the cobalt being precipitated. An analysis gave  $\text{CoO} = 14.85$ ,  $\text{MoO}_3 = 55.65$  and  $55.72$ ,  $\text{NH}_3 = 19.66$ , these figures corresponding with ammonium aquopentamminocobaltic molybdate,

$(\text{NH}_4)_2\text{MoO}_4 \cdot \{ \text{Co}(\text{NH}_3)_5, \text{H}_2\text{O} \}_2 (\text{MoO}_4)_3 \cdot 2\text{H}_2\text{O}$ , which requires  $\text{CoO} = 14.47$ ,  $\text{MoO}_3 = 55.57$ , and  $\text{NH}_3 = 19.73$  per cent., but the examination of the compound was not sufficiently complete to justify any conclusions with regard to its constitution.

#### *Tungstates.*

The following new substances were obtained during the unsuccessful experiments made with the object of preparing ammoniacal double tungstates.

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The *copper* compound  $\text{CuO}, 4\text{WO}_3, 6\text{NH}_3, 8\text{H}_2\text{O}$  separated as a dirty-blue, microcrystalline mass when an ammoniacal solution of copper sulphate and ammonium tungstate gave off its excess of ammonia. If the evolution of ammonia was very slow, the compound was obtained in small, bright blue needles.

Tungstic acid corresponding with 20 grams of tungstic anhydride, obtained by precipitating a solution of sodium tungstate,  $\text{Na}_2\text{WO}_4$ , with nitric acid, was dissolved in 20 c.c. of cold concentrated ammonia, 5 grams of copper sulphate in 7.5 c.c. of water and 7.5 c.c. of concentrated ammonia were added, and the filtered solution placed in an open vessel. The large crystals were used for analysis.

	Found.	Required.
$\text{CuO}$ .....	6.43	6.35 per cent.
$\text{WO}_3$ .....	73.93	74.01    "
$\text{NH}_3$ .....	8.18	8.15    "
$\text{H}_2\text{O}$ .....	11.46 (by difference)	11.48    "

The crystals were almost insoluble in dilute ammonia and insoluble in water.

*Ammonio-copper Tungstate,  $\text{CuWO}_4, 4\text{NH}_3$ .*

(1) Copper sulphate (7.5 grams) was precipitated in hot solution with 10 grams of dihydrated sodium tungstate,  $\text{Na}_2\text{WO}_4, 2\text{H}_2\text{O}$ , the precipitated copper tungstate washed by decantation and thoroughly drained, after which it was dissolved in 20 c.c. of cold concentrated ammonia.

(2) Dihydrated sodium tungstate (13 grams) was precipitated with nitric acid, and the washed tungstic acid, after being drained, was dissolved in 20 c.c. of strong ammonia, the solution being added to the ammoniacal solution of copper tungstate. The mixture was then filtered into a bottle, and a layer of alcohol allowed to diffuse slowly into it during several weeks, the bottle remaining tightly stoppered. The experiment was arranged in this way with the object of preventing the ammonia from being given off to such an extent as would result in the formation of polytungstates. This end was achieved, only the normal tungstate being obtained, but no double salt was observed even when three times as much ammonium tungstate was present as in the experiment under consideration. The compound  $\text{CuWO}_4, 4\text{NH}_3$  separated in both cases.

	Found.	Required.
$\text{CuO}$ .....	20.80	20.96 per cent.
$\text{WO}_3$ .....	61.16	61.09    "
$\text{NH}_3$ .....	18.15	17.95    "

The deep blue crystals, which dissolved in a small amount of water and were easily soluble in dilute ammonia, gave off ammonia very readily at the ordinary temperature.

*Ammonio-zinc tungstate*,  $\text{ZnWO}_4 \cdot 4\text{NH}_3 \cdot 3\text{H}_2\text{O}$ , crystallised in large, transparent tetrahedra often exhibiting twinning; it readily evolved ammonia at the ordinary temperature.

	Found.	Required.
ZnO .....	18.49	18.66 per cent.
WO <sub>3</sub> .....	54.0	53.3 „
NH <sub>3</sub> .....	15.61	15.65 „

It was prepared like the foregoing copper salt, the zinc tungstate being precipitated in the cold, since that which comes down from hot solutions is not easily soluble in ammonia.

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