LXVIII.—*The Hexahydrated Double Chromates.
Magnesium and Nickel Compounds.*

By SAMUEL HENRY CLIFFORD BRIGGS.

THE double chromates $M_2^I M^{II}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, which are of some interest on account of their analogy with the corresponding double sulphates, have been but slightly investigated, only two members of the series having been hitherto prepared, namely, magnesium ammonium chromate, $(\text{NH}_4)_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Grailich, *Sitzungsber. Akad. Wissen. Wien.*, 1857, 27, 175), and nickel ammonium chromate (Briggs, *Trans.*, 1903, 83, 391).

The continuation of the experiments described in the previous paper (*loc. cit.*) has led to the isolation of nickel potassium chromate, $\text{K}_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, a compound which is very efflorescent at the ordinary temperature.

It was shown by Tutton (*Trans.*, 1896, 69, 521) that, in the case of the double sulphates the stability of those compounds which contain the same bivalent metal increases with the increase in the atomic weight of the alkali metal. Thus the double salt $\text{K}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ could not be prepared, $\text{Rb}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was very efflorescent, and $\text{Cs}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ much less so at the ordinary temperature. Consequently, it seemed probable that a similar increase in stability from the potassium to the caesium compounds would hold good for the double chromates, and for this reason the rubidium and caesium salts were examined, with the result that the latter was found to be quite stable at 10° , whereas the former became slightly discoloured after

being kept for two months. Nickel ammonium chromate occupies an intermediate position between the two in agreement with the place in the alkali series assigned to ammonium by Tutton in a recent paper on the morphological and physical properties of ammonium sulphate (Trans., 1903, 83, 1049).

The double salts of magnesium chromate have also been prepared, and the same differences in stability observed. From the readiness with which magnesium potassium chromate and nickel potassium chromate give off their water at the ordinary temperature, it seems likely that all the potassium compounds of this group would be efflorescent if they could be obtained, since Tutton (Trans., 1896, 69, 521) found that nickel potassium sulphate was one of the most stable potassium double sulphates which he examined.

EXPERIMENTAL.

Nickel Potassium Chromate, $K_2Ni(CrO_4)_2 \cdot 6H_2O$.

Eight grams of potassium chromate in 14 c.c. of water were added to 8 grams of nickel acetate in 27 c.c. of water, both solutions having been previously cooled to -6° in a mixture of ice and salt. If the temperature rises much above this, basic salts separate, these substances also being deposited if the solution is left for any length of time in the freezing mixture. In order to obtain a good yield, it is therefore necessary to induce crystallisation by vigorous stirring. Working in this way, 3.2 grams of the double salt were prepared in the form of small, yellowish-green crystals; these were collected at the pump, washed with a very small quantity of cold water, and dried with alcohol and ether.

Two different preparations gave the following analytical results:

	Found.		Required.
	I.	II.	
CrO_3	41.5	41.3	41.95 per cent.
NiO	16.0	15.9	15.65 „

The compound, when kept in a stoppered bottle at 10° for a few hours, evolved water and was converted into a damp, brownish-yellow mass. After exposing a portion of each preparation to the air until the weight was constant, the residues contained 47.67 and 47.81 per cent. of chromium trioxide respectively; a loss of three molecules of water requires 47.30 per cent.

Nickel Rubidium Chromate, $Rb_2Ni(CrO_4)_2 \cdot 6H_2O$.—This double salt separated readily when a solution of rubidium chromate (5 grams in 7 c.c. of water) was added to a solution of nickel acetate (4.3 grams

in 13 c.c. of water) at 10° . The yellowish-green crystals (3.5 grams) were washed with water and dried with alcohol and ether.

	Found.	Required.
NiO	13.28	13.12 per cent.
CrO ₃	34.85	35.14 „

Nickel rubidium chromate is very slightly efflorescent at the ordinary temperature.

Nickel caesium chromate, $\text{Cs}_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, was prepared in the same way as the rubidium compound, 3.8 grams being obtained from 5 grams of caesium chromate and 3 grams of nickel acetate.

	Found.	Required.
NiO	11.30	11.26 per cent.
CrO ₃	30.25	30.11 „

The crystals were unaltered after having been kept for two months. The salt dissolves in cold water without much change, but is decomposed by warm water; nevertheless, it may be partially recrystallised from a solution saturated at $35-40^{\circ}$, after filtering off the precipitate of basic salt. The potassium compound is much more readily decomposed by water.

Magnesium Potassium Chromate, $\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$.—Dammer states (*Handbuch Anorg. Chem.*), on the authority of v. Hauer (*Sitzungsber. Akad. Wissen. Wien.*, 1860, 39, 440), that magnesium potassium chromate never crystallises with $6\text{H}_2\text{O}$. The hexahydrate appears to be formed, however, in a solution of its components, if the temperature is sufficiently low. For its preparation, very concentrated solutions of potassium chromate and magnesium chromate were cooled to -10° , and then mixed. The double salt was deposited in very small, lemon-yellow crystals, which were dried with alcohol and ether.

	Found.	Required.
MgO	9.42	9.12 per cent.
CrO ₃	45.36	45.25 „
H ₂ O	23.93	24.39 „

The compound is efflorescent, and a portion on exposure to the air at $8-10^{\circ}$ lost 14.92 per cent. of water, a loss of $4\text{H}_2\text{O}$ requiring 16.25 per cent. The efflorescence did not appear to take place quite so readily as in the case of the corresponding nickel compound.

Magnesium rubidium chromate, $\text{Rb}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, separated in brilliant lemon-yellow crystals, permanent at the ordinary temperature, when solutions of its components were mixed in the cold.

680 BRIGGS: THE HEXAHYDRATED DOUBLE CHROMATES.

	Found.	Required.
MgO	7.88	7.54 per cent.
CrO ₃	37.04	37.39 „
H ₂ O	20.10	20.17 „

Magnesium caesium chromate, Cs₂Mg(CrO₄)₂.6H₂O, was prepared like the rubidium compound, which it closely resembled.

	Found.	Required.
MgO	6.80	6.40 per cent.
CrO ₃	31.64	31.75 „
H ₂ O	17.26	17.15 „

Comparison of Stabilities.

Nickel Compounds.—The potassium salt being efflorescent at the ordinary temperature, only the rubidium, ammonium, and caesium compounds were dealt with in these experiments.

(1) Approximately equal quantities of the caesium and rubidium salts were heated together for 12 hours in an air-bath at 40°, after which the rubidium compound had become slightly brown, having lost 0.5 per cent. of water, whereas the caesium compound was unchanged. After further heating for 1 hour at 60°, the caesium compound was also slightly discoloured. The temperature was therefore lowered to 50° for 4 hours, when the rubidium salt had lost 2.4 molecules of water and the caesium salt only 0.15 molecule.

(2) When the ammonium and rubidium compounds were heated together for 2 hours at 53°, the former lost 0.78 molecule and the latter 2 molecules of water. A repetition of the experiment gave exactly the same result.

(3) The ammonium and caesium salts were heated together for 1 hour at 56°. The ammonium compound lost 0.41 molecule of water, becoming brown, whereas the change in weight of the caesium compound was imperceptible.

The order of increasing stability is evidently potassium, rubidium, ammonium, and caesium; but, as is seen from the above experiments, the difference between the potassium and rubidium compounds is more marked than that between the rubidium and caesium salts.

Magnesium Compounds.—The caesium and rubidium salts were heated together for 12 hours at 55°. The caesium salt remained unchanged, whilst the rubidium compound lost only 0.16 per cent. of water. The heating was therefore continued for 3 hours at 65°, after which the caesium compound had lost 0.18 and the rubidium derivative 1.6 molecules of water respectively.

Here again the order of increasing stability coincides with the increase in the atomic weight of the alkali metal, the magnesium compounds being somewhat less readily decomposed than their nickel analogues.