

XXXVI.—*The Preparation of Some Metallic Chromates.*

By SAMUEL HENRY CLIFFORD BRIGGS.

THE normal chromates of copper, zinc, and cadmium were first obtained by Schulze (*Z. anorg. Chem.*, 1895, **10**, 148) in an insoluble anhydrous form by heating solutions of the dichromates with the corresponding hydroxides in sealed tubes. The author has confirmed these results and also prepared the normal chromates of nickel and cobalt (*ibid.*, 1908, **56**, 246; 1909, **63**, 325). Britton (J., 1926, 134) studied the precipitation of basic zinc chromate and, apparently without attempting to repeat Schulze's experiments, made the following statement: "An insoluble normal zinc chromate has been stated to exist by Schulze and by Briggs, but the latter's data are unconvincing." In view of this criticism the previous work has been repeated, and the existence of the normal zinc chromate described by Schulze has once more been confirmed.

During attempts to obtain other normal chromates by various modifications of Schulze's method, the following crystalline compounds were prepared: $9\text{ZrO}_2, 5\text{CrO}_3, 12\text{H}_2\text{O}$; $3\text{Al}_2\text{O}_3, 2\text{CrO}_3, 6\text{H}_2\text{O}$; $2\text{Fe}_2\text{O}_3, 4\text{CrO}_3, \text{H}_2\text{O}$; $3\text{SbO}_2, 2\text{CrO}_3$; and also the chromites $2\text{Sb}_2\text{O}_3, \text{Cr}_2\text{O}_3$ and $3\text{Bi}_2\text{O}_3, 2\text{Cr}_2\text{O}_3$. With the exception of the complex iron compounds of Hensgen (*Ber.*, 1879, **12**, 1300), no definitely crystalline chromates of aluminium, iron, or antimony appear to have been previously described.

The normal chromates of copper, cadmium, and cobalt have also been obtained in an insoluble hydrated form by the action of sodium chromate on a large excess of highly concentrated solutions of the corresponding dichromates. The normal chromates of nickel and zinc could not be prepared by this method, in accordance with Britton's observations on zinc chromate (*loc. cit.*).

EXPERIMENTAL.

Zinc Chromate.—By an alteration in the proportions of the reagents the normal chromate of zinc was obtained free from the

basic salt present in the earlier preparations. Chromium trioxide (5 g.) was mixed with 4.5 g. of zinc carbonate (ZnO , 70%) and 5 c.c. of water in a glass tube, and the mixture warmed until evolution of carbon dioxide ceased. The tube was then sealed and heated for 4 hours at 200—210°. After being washed with cold water and dried, the product was a yellow, satiny powder (Found: ZnO , 45.4; CrO_3 , 54.7. Calc.: ZnO , 44.9; CrO_3 , 55.1%). Under the microscope it appeared homogeneous and consisted of a felted mass of acicular crystals. It was sufficiently soluble in water to give a distinctly yellow solution.

Zirconium Chromate, $9\text{ZrO}_2, 5\text{CrO}_3, 12\text{H}_2\text{O}$.—Crystallised zirconium nitrate (7 g.) in 50 c.c. of water was added to 10 g. of potassium dichromate in 80 c.c. of water. The precipitate was filtered off after 1 day, washed with a little water, and dried in a vacuum. The dried, powdered product (2.5 g.) was heated in a sealed tube for $3\frac{1}{2}$ hours with 6 g. of chromium trioxide and 6 c.c. of water at 190°. An orange-red, homogeneous, crystalline powder was obtained, which was insoluble in water (Found: ZrO_2 , 60.7; CrO_3 , 27.0; $\text{ZrO}_2 + \text{Cr}_2\text{O}_3$, 81.2. $9\text{ZrO}_2, 5\text{CrO}_3, 12\text{H}_2\text{O}$ requires ZrO_2 , 60.7; CrO_3 , 27.4; $\text{ZrO}_2 + \text{Cr}_2\text{O}_3$, 81.6%).

Aluminium Chromate, $3\text{Al}_2\text{O}_3, 2\text{CrO}_3, 6\text{H}_2\text{O}$.—4 G. of hydrated aluminium chloride in 25 c.c. of water were added to a solution of 15 g. of sodium chromate in 30 c.c. of water, and the mixture was heated for 1 hour on the water-bath. The filtered precipitate was washed with a little water and dried in a vacuum. The finely powdered product (1.8 g.) was heated in a sealed tube for 4 hours at 200—210° with 2 g. of chromium trioxide and 2 c.c. of water. A crystalline, insoluble, lemon-yellow powder was obtained (Found: Al_2O_3 , 49.6; CrO_3 , 32.3. $3\text{Al}_2\text{O}_3, 2\text{CrO}_3, 6\text{H}_2\text{O}$ requires Al_2O_3 , 49.8; CrO_3 , 32.6%).

Ferric Chromate, $2\text{Fe}_2\text{O}_3, 4\text{CrO}_3, \text{H}_2\text{O}$.—This compound was prepared from 5 g. of ferric chloride, the procedure and the quantities of the other reagents being exactly the same as with the aluminium salt; it was a brownish-black, insoluble solid (Found: Fe_2O_3 , 43.7; CrO_3 , 53.7. $2\text{Fe}_2\text{O}_3, 4\text{CrO}_3, \text{H}_2\text{O}$ requires Fe_2O_3 , 43.3; CrO_3 , 54.2%). Under the microscope it was seen to consist of shining, black crystals mixed with a trace of a lighter-coloured substance, evidently of a more basic character as shown by the analysis. The formula may also be written $2(\text{FeCrO}_4)_2\text{O}, \text{H}_2\text{O}$, and the compound is therefore analogous to the dichromate $(\text{FeCr}_2\text{O}_7)_2\text{O}$ described by Calcagni (*Gazzetta*, 1925, 55, 396).

Antimony Chromate, $3\text{SbO}_2, 2\text{CrO}_3$.—Antimony oxychloride, $2\text{SbOCl}, \text{Sb}_2\text{O}_3$ (3.5 g.), was heated for 4 hours in a sealed tube at 200° with 6 g. of chromium trioxide and 6 c.c. of water. On

opening the tube, a trace of a straw-coloured sublimate was observed, probably an oxychloride, and an orange-coloured deposit present in the liquid was found to consist of crystalline, spherical aggregates, insoluble in water but slowly soluble in nitric acid. The compound was analysed by decomposition with concentrated sulphuric acid, followed by digestion on the water-bath with a solution of tartaric acid until it was completely dissolved. The antimony was precipitated with hydrogen sulphide, and the filtrate evaporated and ignited, leaving the chromium as sesquioxide (Found : SbO_2 , 69.53; CrO_3 , 30.52. $3\text{SbO}_2, 2\text{CrO}_3$ requires SbO_2 , 69.76; CrO_3 , 30.24%). Several attempts to repeat the preparation of this compound failed, the following chromite being obtained. It is proposed to make a further investigation of the chromates of antimony.

Antimony Chromite, $2\text{Sb}_2\text{O}_3, \text{Cr}_2\text{O}_3$.—The oxychloride $2\text{SbOCl}, \text{Sb}_2\text{O}_3$ (3.5 g.) was heated as before for 5 hours at 200° with 8 g. of chromium trioxide and 8 c.c. of water. The chromic acid was partly reduced, and there was formed a brown powder mixed with a dark-coloured liquid which had a strong odour of chlorine. The solid, after being thoroughly washed and dried, had the appearance of powdered stone (Found : Sb_2O_3 , 80.0; CrO_3 , 19.9. $2\text{Sb}_2\text{O}_3, \text{Cr}_2\text{O}_3$ requires Sb_2O_3 , 79.3; CrO_3 , 20.7%). It was totally insoluble in alkalis, water, or acids, including aqua regia.

Bismuth Chromite, $3\text{Bi}_2\text{O}_3, 2\text{Cr}_2\text{O}_3$.—This was prepared (5 g. BiOCl ; 6 g. CrO_3 ; 6 c.c. water) in the same way as the antimony chromite, which it resembled in appearance and properties (Found : Bi_2O_3 , 82.7; Cr_2O_3 , 18.0. $3\text{Bi}_2\text{O}_3, 2\text{Cr}_2\text{O}_3$ requires Bi_2O_3 , 82.1; CrO_3 , 17.9%).

An attempt was made to prepare a normal chromate from bis-methyl dichromate by a similar method, but only unchanged material was recovered.

Copper Chromate, $\text{CuCrO}_4, 2\text{H}_2\text{O}$.—A solution of 4.5 g. of crystallised sodium chromate (73% Na_2CrO_4) in 20 c.c. of water was added in the cold to a solution of 17 g. of copper carbonate in 30 c.c. of water containing 30 g. of chromium trioxide. The reddish-brown precipitate was filtered off and washed with cold water. It weighed 2 g. and under the microscope it was seen to be crystalline and homogeneous (Found : Cu, 29.7; CrO_3 , 46.6. Calc. : Cu, 29.5; CrO_3 , 46.4%).

Cobalt Chromate, $\text{CoCrO}_4, 2\text{H}_2\text{O}$.—This was prepared in exactly the same way as the copper compound, and obtained as a black, microcrystalline powder (Found : Co, 28.1; CrO_3 , 47.4. Calc. : Co, 27.9; CrO_3 , 47.4%).

Cadmium Chromate, $\text{CdCrO}_4, \text{H}_2\text{O}$.—This was prepared in the

same way and consisted of a bright yellow, crystalline powder (Found : Cd, 45.3; CrO_3 , 40.9. Calc. : Cd, 45.6; CrO_3 , 40.6%).

The water molecules in the normal chromates of copper, cobalt, and cadmium are very firmly attached and are not evolved in a vacuum over sulphuric acid.

Nickel Chromates.—When an attempt was made to prepare a normal chromate of nickel in the same way as for copper, a clear solution was obtained, from which at the summer temperature a deep red compound crystallised very slowly, 1.9 g. having separated after 4 days. The red *compound* appeared homogeneous under the microscope, but had a very complex constitution [Found : Ni, 25.9; CrO_3 , 49.7; loss, after twelve days in a vacuum over sulphuric acid, 4.1; Na, 5.2. $2\text{Na}_2\text{CrO}_4, 7\text{NiCrO}_4, \text{Ni}(\text{OH})_2, 10\text{H}_2\text{O}$ requires Ni, 25.8; CrO_3 , 49.5; $4\text{H}_2\text{O}$, 4.0; Na, 5.1%].

In another experiment a solution of 40 g. of chromium trioxide in 40 c.c. of water was saturated with nickel carbonate; 15 g. of sodium chromate in 25 c.c. of water were then added with vigorous stirring and the mixture was cooled to 0° . In spite of inoculation with nickel sulphate and magnesium chromate, no crystals of normal nickel chromate separated, but a slight brown deposit having approximately the composition $2\text{NiO}, \text{CrO}_3, 5\text{H}_2\text{O}$ had formed after 2 hours (Found : Ni, 34.9; CrO_3 , 28.9; $3\text{H}_2\text{O}$, loss after five months over sulphuric acid in a vacuum, 15.9. Calc. : Ni, 34.6; CrO_3 , 29.4; $3\text{H}_2\text{O}$, 15.9%).

[Received, December 11th, 1928.]