

CXLIX.—*The Hydrates of Chromic Nitrate.*

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TWEEDY.

IN the course of investigations on chromium salts, it was necessary to prepare crystals of chromium nitrate. Chromic hydroxide, precipitated from cold, saturated chrome alum solution, and washed with hot water, was dissolved in the least possible quantity of cold nitric acid (about 4*N*; compare Loewel, *J. Pharm. Chim.*, 1845, 7, 321, 401). The dark green dichroic solution thus obtained was allowed to crystallise in an open dish; after a few days it turned violet, and was then transferred to a stoppered bottle. Some three months later, it had deposited reddish-violet crystals and reverted to its original green colour. The crystals were not deliquescent and appeared through the microscope to be octahedral. After drying between filter-paper, they gave Cr, 11.2, 11.15; N, 9.0, 9.0% (determined by reduction with Devarda's alloy; very low results are obtained if the reaction is not allowed to finish in the cold after the initial warming necessary to start it) [ $\text{Cr}(\text{NO}_3)_3, 12\frac{1}{2}\text{H}_2\text{O}$  requires Cr, 11.2; N, 9.1%]. Large crystals were also grown.

The "normal" chromic nitrate described in text-books (*e.g.*, Roscoe and Schorlemmer, 1923, vol. ii, p. 1084) forms deliquescent rhombohedra,  $\text{Cr}(\text{NO}_3)_3, 9\text{H}_2\text{O}$ . By allowing a solution of chromic hydroxide in dilute nitric acid to evaporate spontaneously, Halse (*Chem.-Ztg.*, 1912, 36, 962) obtained from a violet solution crystals of a hydrate,  $\text{Cr}(\text{NO}_3)_3, 7\frac{1}{2}\text{H}_2\text{O}$ , m. p. about 100°, which he considered to be identical with a brown, crystalline hydrate obtained by Jovitschitsch (*Monatsh.*, 1912, 33, 9), who heated ignited chromic anhydride with nitric acid (*d* 1.4) in a sealed tube for 1½ hours at 160°. It seems, however, that the crystals obtained by Halse are identical with those obtained by us and contain  $12\frac{1}{2}\text{H}_2\text{O}$ . Our crystals turned black (viewed by reflected light) at 95° and melted to a dark green liquid at 104—105°. Halse remarks that these crystals, since they are formed by the action of an acid on a hydr-

oxide, should be considered as the "normal" form of chromium nitrate in preference to the nonahydrate, which is only obtained under special conditions.

On one occasion, in a repetition of Halse's experiment, the liquid evaporated to a dark green syrup which retained its colour both on boiling and on dilution. Attempts were made to precipitate the green form of chromic nitrate from the syrup. Anhydrous ether and ether mixed with nitric acid were ineffectual, but addition of excess of absolute alcohol threw out a light green precipitate which, after drying between filter-paper, had a m. p. about 74°. No precipitation occurred on the addition of 96% alcohol. A quantity of the substance is being prepared with a view to future investigation.

We repeated Jovitschitsch's preparation with pure chromic anhydride prepared by the action of sulphuric acid on potassium dichromate (Traube, *Annalen*, 1848, **66**, 165) and purified by grinding with concentrated nitric acid, draining and heating at 80° in a current of dry air. The bomb tubes used in the preparation of the nitrate are very liable to burst during the heating. On only one occasion a brown solution was obtained which deposited brown crystals on keeping in a vacuum desiccator over potassium hydroxide. On all other occasions, the ordinary blue-violet dichroic solution of chromic nitrate was obtained, which yielded crystals of the nonahydrate. The factors controlling the production of the brown solution were not discovered. The brown crystals gave a brownish-green dichroic aqueous solution; the filtrate obtained after precipitating with ammonia was pale yellow, indicating that a small portion of the chromium is present in the crystals as chromate [Found: Cr, 13.3. Calc. for  $\text{Cr}(\text{NO}_3)_3, 7\frac{1}{2}\text{H}_2\text{O}$ : Cr, 13.9%]. No crystals were available for checking this figure, or for determining the nitrogen.

Jovitschitsch remarks that the brown crystals on drying over potassium hydroxide and even over calcium chloride lose both nitric acid and water; later, he says that, after 5 days over calcium chloride,  $\text{Cr}(\text{NO}_3)_3, 4\frac{1}{2}\text{H}_2\text{O}$  is formed. We kept 0.2522 g. of the crystals over sodium hydroxide; after 4 days they turned a dull violet and weighed 0.2222 g., this weight remaining constant for 12 days [Found: Cr, 15.1; N, 12.35. Calc. for  $\text{Cr}(\text{NO}_3)_3, 4\frac{1}{2}\text{H}_2\text{O}$ : Cr, 16.3; N, 13.1%].\* None of these figures is to be regarded as final.

The viscosities,  $\eta$ , of solutions of the nonahydrate of chromium nitrate (Kahlbaum's pure; see below) were determined by the

\* Dr. A. D. Mitchell has pointed out to us that the values found are very nearly those required for  $\text{Cr}(\text{NO}_3)_3, 6\text{H}_2\text{O}$ .

comparative flow method at 18° and 25°. The modified Ostwald viscosimeter described by Martin was used (*Bull. Soc. chim. Belg.*, 1925, 34, 81); we have found this instrument to give very consistent results. The viscosimeter was standardised with freshly-prepared conductivity water obtained from a Bousfield still and stored in a Pyrex flask; water similarly prepared was used for making the solutions. Each viscosity ratio represents at least a dozen consecutive identical time readings or else the mean of a dozen or more readings the extreme variation of which is 0.5 second. The time of flow for water was 31.5 seconds at 25° and 36.5 seconds at 18°.  $w$  is the weight of anhydrous salt in 100 g. of water.

Temperature 18°.			Temperature 25°.		
$w$ .	$\eta/\eta_{H_2O}$ .	$\eta$ .	$w$ .	$\eta/\eta_{H_2O}$ .	$\eta$ .
29.11	1.8219	0.01948	25.37	1.6428	0.01498
26.58	1.7055	0.01823	18.58	1.4048	0.01281
23.62	1.5616	0.01669	12.61	1.2302	0.01122
19.73	1.4247	0.01523	10.98	1.1984	0.01093
15.07	1.2841	0.01373	8.99	1.1508	0.01050
9.56	1.1422	0.01221	6.05	1.1032	0.01006
7.16	1.0960	0.01172	5.93	1.0952	0.00999
4.99	1.0582	0.01131	3.58	1.0556	0.00963
3.55	1.0308	0.01102	3.18	1.0476	0.00953
			1.91	1.0238	0.00934

Measurements at higher dilutions are unsatisfactory with the method used.

The figures given in the third and sixth columns represent the absolute viscosities, obtained by multiplying  $\eta/\eta_{H_2O}$  by  $\eta_{H_2O}$ . Thorpe and Rodger (*Phil. Trans.*, 1894, 185, 397) give 0.00891 and 0.010563 dyne/cm.<sup>2</sup> at 25° and 18°, respectively, for  $\eta_{H_2O}$ ; we have used the more recent values determined by Leroux (*Ann. Physique*, 1925, 4, 163), namely, 0.00912 and 0.01069 dyne/cm.<sup>2</sup>, the former figure being calculated on the assumption that the viscosity varies linearly with the temperature over the range 23.2° to 26.4°, for which  $\eta = 0.00949$  and 0.00883 dyne/cm.<sup>2</sup>, respectively. The above values for the viscosities of chromium nitrate solutions lie on smooth curves.

Kahlbaum's pure chromic nitrate crystals,  $Cr(NO_3)_3 \cdot 9H_2O$  (Found: Cr, 13.0; N, 10.7. Calc.: Cr, 13.0; N, 10.5%), freed from adhering nitric acid by pressing between filter-paper, melted to a dark green liquid at 66–66.5°; there were no signs of fusion at the previously recorded m. p., 36.7° (Ordway, *Amer. J. Sci.*, 1850, 9, 30). The fused salt on cooling passed through an indefinite pasty stage extending from about 37° to 20°, and gradually changed in colour to a greyish-green. On continual stirring, the temperature rose to 30–33° and slow crystallisation set in. The crystals were violet. These temperatures are slightly different from

those recorded by Ordway, who found that the green liquid first deposited crystals at  $24^{\circ}$ , the temperature rising gradually to  $34^{\circ}$ . A crystal picked out of the green paste melted sharply at  $66.5^{\circ}$  and was evidently, therefore, a crystal of nonahydrate. Apparently no transition to a second hydrate takes place at the m. p.

Chromic nitrate nonahydrate crystals may be readily prepared by dissolving violet chromic chloride in slightly more than the theoretical quantity of hot strong nitric acid and storing in a vacuum desiccator over sodium hydroxide. If excess of the chloride is used, the product contains small quantities (0.1%) of chlorine. No chromic chloride nitrate similar to that prepared by Schiff by dissolving basic chromic chloride in nitric acid (*Annalen*, 1862, **124**, 177) was obtained.

An X-ray examination of chromium nitrate and other chromium salts is being undertaken. It is expected that information of importance for the theory of co-ordination will be obtained with the three isomeric hexahydrates of chromic chloride, all of which have been prepared.

#### *Summary.*

1. The solution obtained by dissolving chromic hydroxide in nitric acid yields crystals of  $\text{Cr}(\text{NO}_3)_3 \cdot 12\frac{1}{2}\text{H}_2\text{O}$ , m. p.  $104\text{--}105^{\circ}$ , and not  $\text{Cr}(\text{NO}_3)_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ , as previously described.

2. The viscosities of some chromic nitrate solutions at  $18^{\circ}$  and  $25^{\circ}$  are recorded.

3. Chromic nitrate nonahydrate crystals melt at  $66\text{--}66.5^{\circ}$ , no transition to a second hydrate occurring at this temperature.

4. Chromic nitrate nonahydrate crystals may be prepared by dissolving violet chromic chloride in hot nitric acid and allowing the solution to crystallise in a vacuum desiccator.

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