199. *Chromic Picrate.*

By Herbert J. S. King.

Normal chromic picrate has not previously been isolated. Silberrad and Phillips (J., 1908, **93**, 486) attempted to prepare it by concentrating the filtrate from equivalent quantities of barium picrate and chromic sulphate, but the product was a basic picrate of approximate composition $Cr(C_6H_2O_7N_3)_3,2CrO(C_6H_2O_7N_3)$.

The normal picrate has now been prepared by treating a solution of violet hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, with 3 mols. of silver picrate. From the filtrate, by concentration at room temperature, yellowish-green needles of the *octahydrate* were obtained; these yielded on dehydration dark brown anhydrous *chromic picrate*, which sintered with decomposition at 94° and exploded feebly at 240°. The readiness with which dehydration occurs differentiates hydrated chromic picrate from hexa-aquochromic chloride, which can be kept indefinitely over sulphuric acid without loss in weight.

The picrate radical in an aqueous solution of the hydrated picrate was immediately and completely precipitated in the cold by hexa-amminochromic nitrate. However, the values obtained for the molecular conductivity of the octahydrate at 0° were 20% lower than those expected for hexa-aquochromic picrate, based on the values recorded by Bjerrum (*Z. physikal. Chem.*, 1907, **59**, 336) for the molecular conductivity of hexa-aquochromic chloride, and by Ferguson and Vogel (*Phil. Mag.*, 1927, **4**, 239) for the mobility of the picrate ion. These observations suggest that the aqueous solution of the octahydrate contains an equilibrium mixture of $[Cr(H_2O)_6](C_6H_2O_7N_3)_3$ with $[Cr(H_2O)_5(C_6H_2O_7N_3)](C_6H_2O_7N_3)_2$ or $[Cr(H_2O)_4(C_6H_2O_7N_3)_2](C_6H_2O_7N_3)$.

An attempt to prepare dichlorotetra-aquochromic picrate from dichlorotetra-aquochromic chloride and 1 mol. of silver picrate yielded green needles which, however, contained no chlorine and proved to be essentially chromic picrate.

When hexa-aquochromic chloride was treated with 3 mols. of silver nitrite, the resulting violet solution of hexa-aquochromic nitrite evolved oxides of nitrogen when left in a vacuum over sulphuric acid, and chromic nitrite could not be isolated from it.

Experimental.

Hexa-aquochromic chloride was prepared by Higley's method (*J. Amer. Chem. Soc.*, 1904, **26**, 620). Silver picrate was obtained by boiling excess silver oxide with picric acid; it was an orange monohydrate, not the yellow anhydrous salt as stated by Silberrad and Phillips (*loc. cit.*) (Found: H_2O, 5·1. Calc. for $C_6H_2O_7N_3Ag,H_2O$: H_2O, 5·1%). The monohydrate was stable if air-dried, and yielded the yellow anhydrous salt when heated at 85° for 20 minutes.

Chromic Picrate.—Octahydrate. Hexa-aquochromic chloride (5 g.) was mixed with 18·9 g. of silver picrate and 25 c.c. of water in an ice-cooled mortar, and left for ½ hour, with occasional trituration. After being filtered from silver chloride, the dark brown solution was concentrated at room temperature over sulphuric acid in a vacuum. When practically all the water had been removed, long yellowish-green needles separated, and were recrystallised from water at 25°, 10 g. dissolving in 4 c.c. On cooling in ice, the yellowish-green needles were again obtained, and were dried on plate over soda–lime in a vacuum [Found: Cr, 6·0; N, 14·2; H_2O, 16·4. $Cr(C_6H_2O_7N_3)_3,8H_2O$ requires Cr, 5·9; N, 14·3; H_2O, 16·4%].

The conductivity data at 0° were as follows :

v	64	128	256	512	1024	2048
λ_{0°	89·4	103·9	117·1	130·6	143·7	159·2

When the solution of chromic picrate was concentrated by boiling, it yielded green needles of a basic picrate, sparingly soluble in cold water. *Anhydrous salt.* At 85° the octahydrate lost 5 mols. of water in 15 minutes, and was completely dehydrated in 24 hours. Dehydration for a month over sulphuric acid also afforded the *anhydrous* salt [Found : Cr, 7·0; N, 17·0. $Cr(C_6H_2O_7N_3)_3$ requires Cr, 7·1; N, 17·1%]. Its ignition point (*i.e.*, the lowest temperature at which immediate ignition occurred on dropping a small portion into a tube heated in a metal-bath) was 240°. It dissolved readily and completely in cold dry acetone and pyridine to deep brown solutions, was sparingly soluble in alcohol, and insoluble in benzene and in ether. It was decomposed by cold water into picric acid and green basic chromic picrate.

When anhydrous chromic picrate was treated with liquid ammonia, and the excess ammonia allowed to evaporate, a mixture of chromammine picrates was obtained, in which 3·5 mols. of ammonia were associated with each atom of chromium.

Action of Hexa-amminochromic Nitrate (1½ *Mols.*) *on Hydrated Chromic Picrate.*—On mixing the cold aqueous solutions, bright yellow needles were immediately precipitated. No further precipitate was produced on adding more of the nitrate to the filtrate and leaving it over-night {Found : Cr, 7·6; NH_3, 15·0; N, 26·8. $[Cr(NH_3)_6](NO_3)(C_6H_2O_7N_3)_2$ requires Cr, 7·7; NH_3, 15·2; N, 27·1%}. Hexa-amminochromic tripicrate is precipitated only in presence of excess of picrate (see King, J., 1924, **125**, 1333).

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