194. *Some New Co-ordination Compounds of Chromic Chloride.*

By D. R. Chesterman.

Piccini (*Z. anorg. Chem.*, 1895, **8**, 115) showed that hydrated green chromic chloride, $[CrCl_2,4H_2O]Cl,2H_2O$, when dissolved in acetone or ethyl alcohol is not ionised, although in methyl alcohol it is. He made no attempt to investigate the reason for this anomaly.

Modern work has shown that chromic chloride can co-ordinate not only with water, but also with certain organic compounds. When the hydrated salt is dissolved in a suitable organic solvent, there is a possibility that the water round the chromium ion will be ousted by the excess of this new liquid, which will then take its place as the co-ordinating molecule. It is therefore probable that Piccini's results involve the ionisation, not of hydrated chromic chloride, but of a new co-ordination compound of the salt.

Of the three possible new compounds, one, *viz.*, that with ethyl alcohol, has already been prepared nearly pure. It is a red substance of composition $CrCl_3,3EtOH$ (Koppel, *Z. anorg. Chem.*, 1901, **28**, 461); here, chromium is almost certainly exerting its maximum co-ordination value of six, and the compound is $[CrCl_3,3EtOH]$, being un-ionised. This confirms Piccini's observation, although apparently Koppel did not recognise this.

It seemed of interest, therefore, to prepare the compounds with acetone and with methyl alcohol. The latter was prepared comparatively easily by a modification of Koppel's method, *viz.*, by the action of hydrogen chloride on a suspension of powdered metallic chromium in pure methyl alcohol. The pure *salt* crystallised in green cubes having the formula $CrCl_3,4MeOH$. This goes further to confirm Piccini's work, for, with chromium still exerting its co-ordination value of six, the true formula would be $[CrCl_2,4MeOH]Cl$. This salt should therefore be ionised in methyl-alcoholic solution, and this deduction was confirmed by the usual methods—instant reaction with silver nitrate to precipitate the chloride, and conductivity measurement.

The simple acetone compound has not yet been isolated in the solid state, but by refluxing acetone with the hexahydrate a red salt of approximate composition

$Cr_2Cl_5OH,2CH_3{\cdot}CO{\cdot}CH_3$ was obtained; in view of the different conditions of preparation, this formula is not strictly analogous to those of the alcohol compounds. The results were extended by making resistance measurements of dilute solutions of green chromic chloride in acetone at 25·05°; the resistance gradually increased with time to a constant and very high value. At the same time the colour of the solution changed from green to purple. It was shown quantitatively that the change took place relatively more rapidly the more dilute the solution. This would be expected from the laws of mass action. These resistance values also support Piccini's observation that no ionisation takes place: an un-ionised co-ordination compound had been formed with the acetone.

It is probably the greater size of the methyl alcohol molecules in $[CrCl_2,4MeOH]Cl$ which prevents two extra loosely held molecules from being present as in the compound $[CrCl_2,4H_2O]Cl,2H_2O$, with which it is otherwise analogous. However, the methyl alcohol molecule is small enough to allow four molecules to be co-ordinated with the chromic chloride, making it possible for one chlorine atom to be ionised. The still greater size of the ethyl alcohol molecule makes this impossible, at least in the solid state. Since only three molecules co-ordinate, the salt is necessarily un-ionised, so long as the co-ordination number of six is maintained.

By slight modifications of the previous methods, the *compounds* with propyl and with *iso*propyl alcohol were obtained in a state of purity. It was thought that the symmetrical arrangement of the groups in *iso*propyl alcohol might lower the co-ordination number to form a compound $[CrCl_3,Pr^{\beta}OH]$, but both compounds were actually very similar, and both contained three molecules of the alcohol. An attempt was also made to prepare the compound with butyl alcohol, and red needles were obtained similar to those of the propyl and ethyl compounds. Owing to the oily nature and high boiling point of butyl alcohol, the crystals were not obtained sufficiently dry to justify an analysis. They were insoluble in water and had the same crystalline form as $[CrCl_3,3PrOH]$; their reactions were also similar.

Koppel (*loc. cit.*) states that the reaction between hydrogen chloride, chromium, and ethyl alcohol did not yield any indication of a chromous salt. Although these salts are unstable, they should be the first products of a reaction such as the above, and the experiment was carefully repeated. There is a latent period before chromium commences to react (this was found with all the alcohols examined); during this time a very rapid stream of hydrogen chloride was passed through the apparatus to remove all the air, and the chromium then started to dissolve to form a very pale blue solution. If a stream of dry air was bubbled through it, however, the colour at once flashed over to the usual dark permanganate-red colour. It is therefore obvious that a chromous salt is the first product of the reaction. Even in absence of air, this changed slowly into the chromic salt, as the solution became more concentrated.

Since the compound with methyl alcohol has the formula $[CrCl_2,4MeOH]Cl$ it should exist in a *cis*- and a *trans*-form. The compound obtained formed small green cubes, but the solution from which these were crystallised was dark red, being green only at the beginning of the reaction before much chromium had dissolved. It is proposed to attempt the isolation of the red isomeride and to determine its structure.

Experimental.

The alcohols were the purest obtainable, and were dried over lime and redistilled immediately before use. The *iso*propyl alcohol, however, was specially purified by Boots' and was used as supplied. A.R. Acetone was used without further purification.

Compounds with Alcohols.—Hydrogen chloride, from concentrated sulphuric acid and pure sodium chloride, was washed by concentrated sulphuric acid and then bubbled through 10—20 c.c. of the alcohol in which was placed a small piece of metallic chromium or a suspension of the powdered metal. The apparatus was constructed entirely of glass, the flasks having ground glass necks, and access of moisture was prevented by a final sulphuric acid bubbler. After reaction had ceased, excess chromium was filtered off in a desiccator, but this was unnecessary if a lump of metal had been used, for the solution remained quite clear. After several days crystals began to appear in the liquid, which was then rapidly transferred to a vacuum desiccator

over sulphuric acid. When the higher alcohols were used, repeated evacuations and replacements of the acid were necessary.

The crystals were repeatedly washed with pure dry ether, a preliminary experiment in the same apparatus having shown that this did not react with chromic chloride. The ether was removed by re-evacuation, and the crystals were then analysed for chromium (as Cr_2O_3) and chloride (as AgCl), a tight-fitting weighing bottle being used [Found: (i) Cr, 18·24; Cl, 37·16. $CrCl_3$,4MeOH requires Cr, 18·14; Cl, 37·22%. (ii) Cr, 15·18; Cl, 31·64. $CrCl_3$,3Pr$^{\alpha}$OH requires Cr, 15·36; Cl, 31·42%. (iii) Cr, 15·53; Cl, 31·40. $CrCl_3$,3Pr$^{\beta}$·OH requires Cr, 15·36; Cl, 31·42%].

Properties of the Compounds with Alcohols.—The *compound* $CrCl_3$,4MeOH formed green hygroscopic cubes, which dissolved readily in water and methyl alcohol to give green solutions. When heated, the crystals swelled enormously, and methyl alcohol was evolved. The purple residue was converted into green chromic oxide on further heating.

The two propyl alcohol *compounds* were odourless and un-ionised, and in common with many other un-ionised salts they were insoluble in water, but after a few minutes' contact with water they suddenly decomposed, giving a green solution having the smell of the alcohol.

They dissolved in their respective alcohols to give a pinkish solution which slowly became green; silver nitrate then gave a precipitate of the chloride, showing that ionisation had taken place. According to Koppel, the compound with ethyl alcohol behaves similarly. Probably an extra molecule of alcohol is added on, and the ionised compound is formed by an isomeric change:

$$[CrCl_3,3PrOH] + PrOH \rightleftharpoons [CrCl_2,4PrOH]^+Cl^-.$$

Compound with Acetone.—This compound could not be prepared from metallic chromium, since acetone in the presence of hydrogen chloride condenses to mesityl oxide, etc. A red co-ordination compound was isolated, but this was contaminated with oily material. The use of chlorine instead of hydrogen chloride led to formation of dichloroacetone. Preliminary experiments having shown that hydrated chromic chloride co-ordinated readily with acetone, the two were refluxed together and distilled under reduced pressure at 100°; some decomposition took place, but a red salt was obtained of approximate composition $Cr_2Cl_5OH,2CH_3{\cdot}CO{\cdot}CH_3$. This was also obtained by starting with the partially dehydrated salt $Cr_2Cl_5OH,4H_2O$ (Olie, *Z. anorg. Chem.*, 1907, **52**, 62).

The changes in resistance (R, ohms) with time (mins.) of solutions of chromic chloride hexahydrate in acetone are shown in the tables. The measurements were made in conductivity cells in a thermostat at 25·05° ± 0·05°, a previously calibrated bridge and resistance box being used.

Resistance measurements of solutions of green chromic chloride in acetone.

0·0403% Solution. Cell constant = 2·212.

Time	0	3	6	12	20	23	26	30	38	70
$R \times 10^{-3}$	40·0	49·9	63·0	98·7	132·9	137·1	140·0	141·5	142·5	142·5

0·751% Solution. Cell constant = 0·1453.

Time	0	6	12	18	30	42	51	54	57	63	80
R	2725	3480	4665	5915	7840	8645	8870	8930	8965	9020	9020

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