

Some Comments on Chromium Chloride-Sulphates

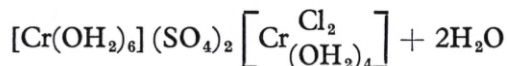
Preliminary communication

NIELS BJERRUM

Translated from *Ber.* **39** (1906) 1597-1602. The paper was received by the journal
12th April, 1906.

Recently, papers have been published by A. Werner and R. Huber¹ and also by R. F. Weinland and R. Krebs² on chromium chloride-sulphates. I have been occupied for some time with work on the chlorides of chromium and shall soon report these results in detail. In the course of this work, I have also carried out investigations on chromium chloride-sulphates, and since I have arrived at conclusions about the constitution of these compounds different from those of the above mentioned authors, I shall here briefly state my conclusions and the most important facts upon which I base them. Furthermore, I also hope to be able to show that the basis for the opinions which are described in the above mentioned papers is insufficient, or allows of another explanation.

A new chloro-sulphate has been prepared by Werner and Huber by adding sulphuric acid to a mixture of violet chromium sulphate and green chromium chloride; it is isomeric with Recoura's³ compound $\text{CrClSO}_4 \cdot 6\text{H}_2\text{O}$ and has similar properties, as regards the solubility and precipitation of the sulphate radical. I have already some time ago prepared this isomeric salt and can in all respects confirm the data given for the new salt. From the method of preparation of the salt, Werner and Huber conclude that it is apparently a di-molecular compound of which the constitutional formula can be written as follows:



Further support is gained for this constitutional formula by the preparation of an analogous compound, in which they have substituted aluminium sulphate for the chromium sulphate grouping. That this interpretation, to which I also subscribe, is correct, I was able to prove in another way. A solution (1:10) of the salt in dilute hydrochloric acid gave on saturation with hydrogen chloride

a precipitate of blue chromium chloride, which contained almost half of the chromium (calculated 0.48 g, found 0.45 g). Since a solution of blue chromium chloride is nearly quantitatively precipitated by hydrogen chloride, (at 10° C only 0.05 per cent remains in solution) this experiment shows that half the chromium is present as blue chromium ion, quite as is to be expected from Werner's formula.

Werner and Huber ascribed the same formula to Recoura's salt. Their reason for this seems to me rather unconvincing.

They succeeded in preparing a little blue chromium chloride from Recoura's chloro-sulphate, but only by repeated precipitation with hydrogen chloride and storing the precipitate on a clay disc in open air. By this procedure a part with green colour goes into the clay disc while the violet chromium chloride hydrate remains. From this experiment the authors conclude "dass die Entstehung von violetterm Chromchloridhydrat aus dem Chlorosulfat unter den beschriebenen Bedingungen sich nur dann erklären lässt, wenn man annimmt, dass sich das Radical $[\text{Cr}(\text{OH}_2)_6]$ im Chlorosulfat schon vorfindet".

Firstly, it should be pointed out that the reactions of chromium chlorides are not so well known that one can entirely exclude formation of $[\text{Cr}(\text{OH}_2)_6]$ even if it is improbable. Secondly, it is possible that a small amount of $[\text{Cr}(\text{OH}_2)_6]$, in the form of the new chloro-sulphate, has been present as an impurity in the chloro-sulphate used (no data are given on the amount of violet chromium chloride prepared). When I tried to prepare Recoura's compound from heated solutions of green chromium chloride, I always obtained such impure preparations. If, however, I prepared the salt according to Recoura's method, it was always pure. (No precipitation occurred when a solution (1:10) in hydrochloric acid was saturated with hydrogen chloride). It seemed to me, however, quite possible that the small alteration in Recoura's method of preparation which Werner and Huber had introduced (drying of the boiled hydrochloric-acid solution of violet chromium sulphate in the vacuum desiccator instead of simple storing), may have resulted in a greater yield, but a less pure salt.

That the chloro-sulphate, in a damp atmosphere, lying on a clay disc, partly deliquesces and leaves behind a little violet chromium sulphate, appears to me unconvincing as a proof of the constitution suggested by Werner.

On the other hand, I think it can be concluded from the following experiments that a fresh solution of Recoura's chloro-sulphate can contain no $[\text{Cr}(\text{OH}_2)_6]$. A solution of 1 g of Recoura's chloro-sulphate in 10 cc of hydrochloric acid gives no precipitation with hydrogen chloride during the first hours. If but a few centigrams (that is the quantity of blue chromium chloride which can be precipitated with hydrogen chloride from 10 cc of water) of blue chromium chloride had been present in the solution, precipitation would have occurred.

From this fact I concluded that Recoura's chloro-sulphate cannot be a dichlorochromium-chromium sulphate. That it really is a monochlorochromium sulphate I think I can demonstrate in the following way.

First of all, I should mention that I was able to prepare a new chromium chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, the properties of which revealed it as being the *monochlorochromium chloride*, which has so far been unsuccessfully sought. It is prepared from a concentrated, boiled solution of green chromium chloride, by precipitating by hydrogen chloride the blue chromium chloride formed, and transferring the filtrate to a large amount of ether saturated with hydrogen chloride. By this procedure the new chloride separates out, while the dichlorochromium chloride contained in the solution is transformed into compounds giving a red colour when dissolved. The monochloro compound may be recrystallized by dissolving in a mixture of ether and fuming hydrochloric acid (1:1), in which the two other chromium chlorides are insoluble, and then pouring into ether saturated with hydrogen chloride. If the chloride is freshly prepared — it is unfortunately rather unstable — exactly $2/3$ of the chlorine is precipitated by silver nitrate in nitric acid solution. From this it can be concluded that the new salt must be a monochlorochromium chloride or an equi-molecular compound of blue and green chromium chlorides. Since, however, the aqueous solution of the salt has properties differing from those of a mixed solution of blue and green chromium chlorides, for example in the presence of hydrogen chloride or concentrated sulphuric acid, the first supposition is the more probable. This new chloride can now be obtained with good yield (about 75 per cent) from Recoura's chloride-sulphate by dissolving in hydrochloric acid and pouring into a large excess of ether saturated with hydrogen chloride. Similarly a solution of the new chloride gives Recoura's chlorosulphate on treatment with concentrated sulphuric acid. From these observations it follows with great probability that Recoura's chloro-sulphate is really a monochlorochromium sulphate $[\text{CrCl}]\text{SO}_4$.

The electrical conductivity and the changes in electrical conductivity of solutions of both chloride-sulphates agree well with this type of constitution for the salts.

The paper by Weinland and Krebs is concerned with two isomeric chromium chloride-sulphates with the formula $\text{CrClSO}_4 \cdot 8\text{H}_2\text{O}$. One is green and is prepared by evaporating to dryness a solution of the green chromium chloride after adding sulphuric acid. Except for the water content, the authors found that their salt was identical with Recoura's. The second is violet. They prepare it by the addition of an equi-molecular amount of sulphuric acid to a solution of blue chromium chloride. If the solution is sufficiently concentrated, precipitation occurs immediately, otherwise it must first be evaporated.

From the properties of these salts it doubtless follows that the chlorine in the

green salt is bound complexly and in the violet in the ionic state. However, when Weinland and Krebs conclude from their experiments that all SO_4 in both salts is bound complexly, I cannot agree with them. They conclude this from the fact that barium chloride does not precipitate the SO_4 immediately from a dilute solution (less than 0.01 M) when a certain amount of nitric acid is present.

It appeared very improbable to me that the SO_4 in these salts should be complexly bound. The instantaneous precipitation of the violet chloride-sulphate from a blue-violet solution of chromium chloride makes a complex bond highly improbable, since chromium and sulphuric acid only slowly form complex linkages with one another. I sought, therefore, another explanation of Weinland and Krebs's experimental results; and I think that I have found this explanation in the fact that precipitation of barium sulphate always takes place slowly in dilute solution. It is generally known that many sulphates e.g. calcium sulphate, show the phenomenon of supersaturation to a great extent. Therefore, it is also necessary, when estimating sulphuric acid, to wait a certain time before filtering. That this phenomenon of supersaturation is sufficient to account for the slow precipitation of SO_4 in chromium chloride-sulphate, I have demonstrated by the fact that potassium sulphate shows exactly the same behaviour.

To 10 cc of 0.01 M solution of potassium sulphate, I added varying amounts of 1 N nitric acid, and after cooling in ice to about 1°C , 1 cc of 0.1 M barium chloride solution (equi-molecular amounts) was added; the following results were obtained:

Moles HNO_3 per mole K_2SO_4	Time, before the appearance of a precipitate
0	0
10	less than 1 sec.
20	about 2 sec.
50	5—10 sec.
150 (1 cc 15 N nitric acid added)	2—10 min.

Especially at higher acid concentrations, the time before the appearance of a precipitate, varied from experiment to experiment. In another experiment the same amount of nitric acid was added to 10 cc of water instead of potassium sulphate solution. After cooling in ice, about 0.03 g of chromium chloride-sulphate was dissolved which took $\frac{1}{4}$ min. 1 cc of 0.1 M barium chloride was added, and it was found that the same times elapsed before the appearance of the precipitates. These time intervals are of course somewhat irregular, as is to be expected in such phenomena, and I was not able by parallel experiments to discover whether

potassium sulphate or the different chloride-sulphates (the two prepared by Weinland and Krebs, as well as the salt prepared by Recoura) were precipitated more slowly. Sometimes potassium sulphate produced a precipitate more quickly and sometimes it produced a precipitate more slowly than the chloride-sulphates. In a solution of 0.01 M K_2SO_4 and 150 moles HNO_3 per mole K_2SO_4 to which an equivalent amount of $BaCl_2$ had been added, a precipitate appeared after 2 minutes, but only about half of the sulphuric acid had been precipitated after 10 minutes. The clear filtrate gave a copious precipitation after it had been heated and allowed to stand.

Weinland and Krebs² write: "Die Bestimmung des Molekulargewichtes bzw. des Dissoziationsgrades der Verbindungen auf kryoskopischem Wege steht mit dem angegebenen Befund der Fällbarkeit des Chlors bzw. der Schwefelsäure im Einklang". They find namely for the violet chloride-sulphate a molecular depression of the freezing point which is approximately twice as great as is to be expected for an undissociated compound. "Beim violetten Salz stimmt die gefundene Depression mit der für ein in zwei Ionen gespaltenes Salz berechneten völlig überein". For the green chloride-sulphate, they find a somewhat greater molecular depression, than was calculated for the undissociated compound. Nevertheless, the depression is not so great as is required for a compound split into two ions. The figures increase with the time; hence they attribute the too great figures to the rather rapid hydration of the compound.

In order to show that this type of conclusion is not necessary, nor even permissible, I have compared in the following table, the molecular depressions, calculated from the results of Weinland and Krebs, for the green chloride-sulphate (concentrations in moles per 1000 g water), with those found for other sulphates of divalent metals⁴ (concentrations in moles per liter).

	Molar concentration	Molar depression
Green $CrClSO_4 \cdot 8H_2O$	0.0769	2.99
—	0.1044	2.80
Green $CrClSO_4 \cdot 5H_2O$	0.0499	2.10
$MgSO_4 \cdot 7H_2O$	0.0638	2.59
$ZnSO_4 \cdot 7H_2O$	0.0689	2.45
$CuSO_4 \cdot 5H_2O$	0.112	2.17
$CdSO_4 \cdot \frac{8}{3}H_2O$	0.0417	2.59
—	0.104	2.28

The values found for the green chromium chloride-sulphate, $CrClSO_4 \cdot 8H_2O$, are not smaller, but on the contrary somewhat larger than those given for the other sulphates. That the figures are all considerably smaller than would be

expected (3.70) for a salt completely dissociated into two ions, is of course explained by the incomplete electrolytic dissociation of the compound. The fact that the anions are linked to the cations, need not imply that they are in complex combination. By analogy, the sulphate radical is not complexly bound in undissociated magnesium sulphate; and since green chromium chloride-sulphate, $\text{CrClSO}_4 \cdot 8\text{H}_2\text{O}$, behaves similarly to this compound, it is as little justifiable to assume such a combination in this case. The depression of the freezing point of the green $\text{CrClSO}_4 \cdot 5\text{H}_2\text{O}$, appears, however, to be rather small, but in this compound a part of the sulphuric acid is without doubt complexly bound.

Similar considerations can be applied to the depression of the freezing point of the violet chloride-sulphate. Just because the depression of the freezing point of this salt in 0.0822 *M* solution is approximately as great (3.98), as that calculated for a compound completely dissociated into two parts (3.70), it must be concluded that the salt is tri-ionic, and not that it is di-ionic as Weinland and Krebs believe. At the dilution used, it will certainly not be fully dissociated, and in this case it is not possible to use, as an explanation for the somewhat too large figures, the fact that the depression increases with time.

Hence the statement that the sulphuric acid in the chromium chloride-sulphate is complexly bound, must be considered as unwarranted, since Weinland and Krebs have given no other reasons for their conclusions, than the two discussed here.

REFERENCES

1. Werner, A., and Huber, R. *Ber.* **39** (1906) 329.
2. Weinland, R. F., and Krebs, R. *Z. anorg. Chem.* **48** (1906) 251.
3. Recoura, A. *Compt. rend.* **135** (1902) 163.
4. Arrhenius, S. *Z. physik. Chem.* **2** (1888) 496-97.