

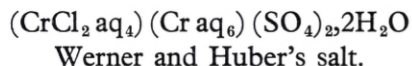
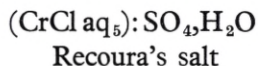
# Physico-chemical Studies on Chlorochromic Sulphates

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In 1906 I published a preliminary report on chromic chloride-sulphates<sup>1</sup>. The present paper supplements the information presented there, and further contains the results of some new investigations.

Two isomeric chlorochromic sulphates of the composition  $\text{CrClSO}_4 \cdot 6\text{H}_2\text{O}$  are known in which all chlorine is in complex and all sulphuric acid in ionogenic linkage. One of them has first been prepared by Recoura<sup>2</sup>, and more recently Weinland in collaboration with Krebs<sup>3</sup> and with Schumann<sup>4</sup> has given new and better methods of preparation. The other has been found by Werner and Huber<sup>5</sup>, and almost simultaneously by me<sup>1</sup>. In my first report, I concluded from the genetic relations between these compounds and the three chromic chlorides, that Recoura's chloro sulphate was to be regarded as monochlorochromic sulphate, while Werner and Huber's compound was dichlorochromic chromic sulphate. When we indicate the distribution of water molecules, so far as we know it, we get the formulae:



It is interesting to see that the electrical conductivity, the velocity of transformation, and the colour of these compounds agree with these formulae as shown in the following.

The agreement proves the usefulness of these physical methods and enables one to use them with more confidence in cases where the constitution cannot be established by simple chemical means.

## 1. ESTABLISHMENT OF CONSTITUTION BY MEASUREMENT OF CONDUCTIVITY

Tables 1 and 2 show the electrical conductivity of the salts.  $t$  denotes the time having passed since dissolution of the salt, and  $\lambda_t$  is the molar conductivity calculated in accordance with the formula  $\text{CrClSO}_4 \cdot 6\text{H}_2\text{O}$ , in reciprocal ohms.

Table 1. Recoura's salt in 0.0100 M solution, 25° C.

$t$ , min.	$\lambda_t$	$k$
0	140.0	
10	145.8	0.0080
20	150.0	62
40	156.0	47
60	160.5	39
80	164.3	
120	170.0	
210	178.1	
340	183.7	
660	187.0	
1400	184.1	
3170	180.6	
4220	180.1	

Table 2. Werner and Huber's salt in 0.0098 M solution, 25° C.

$t$ , min.	$\lambda_t$	$k$
0	125.0	
10	137.2	0.0137
20	147.1	127
40	159.6	0.0095
60	166.9	65
80	171.4	
360	188.7	
1420	188.6	
2080	186.2	
2720	184.9	
4180	183.5	
5830	183.6	
7400	183.6	

Note:  $\lambda_t$  ( $t = 0$ ) has been extrapolated from the values during the first five minutes.

In fig. 1 the variation of conductivity with time is shown graphically. The conductivities at first increase rapidly, then pass through maxima and begin to decrease, and finally they asymptotically approach limiting values\*. The initial rapid increase is explained by rapid liberation of the chlorine in the form of chloride ion<sup>6c</sup> while the subsequent slow decrease may be explained by the formation of sulphato complexes.

It must be possible to calculate approximately the conductivity of a monochlorochromic sulphate from the conductivity of monochlorochromic chloride by subtraction of the usual difference between the molar conductivities of chlorides and sulphates of a common divalent cation. The molar conductivity of monochlorochromic chloride at 25° C in 0.01 molar solution has formerly been found by me<sup>6j</sup> to be 208.5; and the difference between the conductivities of chloride and sulphate in the case of magnesium is 64.4; in the case of nickel and cobalt it is 74 (calculated for the same conditions<sup>7</sup>); hence, the mean value is about 70.

\* These limiting values, however, seem not to be absolute, since the conductivities begin to increase again if the observations are extended over periods of months. After 10 months  $\lambda_t$  was found to be 203 in the case of Recoura's salt. Probably an extremely slow hydrolysis takes place.

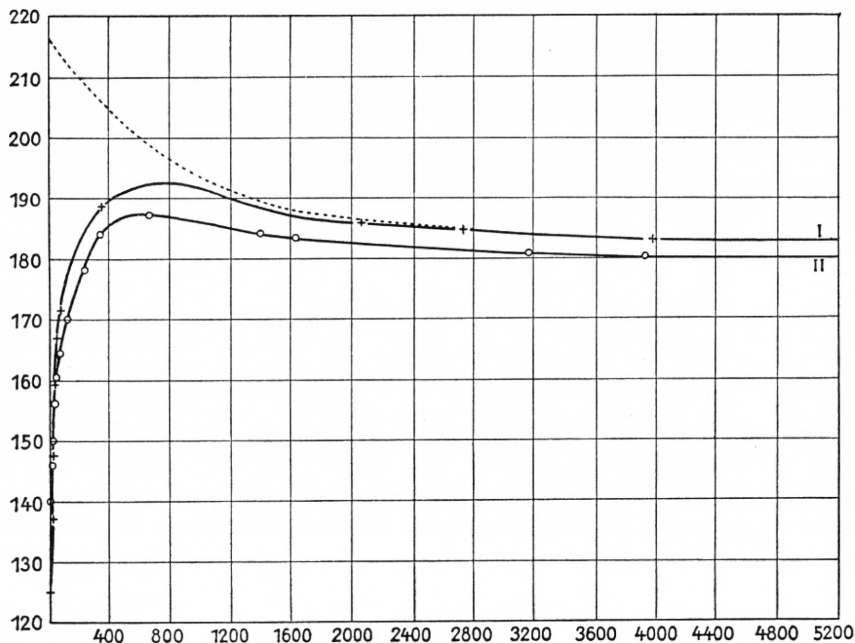


Fig. 1. Molar conductivity of: I. Werner and Huber's chlorochromic sulphate. II. Recoura's chlorochromic sulphate.

According to this the conductivity of monochlorochromic sulphate in 0.01 molar solution at 25° C should be  $208.5 - 70 = 138.5$  while, in agreement herewith, the value found with Recoura's chlorosulphate was 140.

The molar conductivity of a dichlorochromic chromic sulphate may be calculated in the following manner. It must be equal to the molar conductivity of potassium chromic sulphate<sup>8</sup> minus the difference between the molar conductivities of potassium chloride<sup>7</sup> and of dichlorochromic chloride<sup>6d</sup>. The result of this calculation is:  $283.4 - (141 - 98) = 240.4$ . One half of this value has to be compared with the molar conductivities of the chloro sulphates found when assuming their molecular formula to be  $\text{CrClSO}_4$ . Half the value is 120.2 which agrees satisfactorily with the value 125 found for Werner and Huber's chloro sulphate.

## 2. ESTABLISHMENT OF CONSTITUTION FROM VELOCITY OF TRANSFORMATION

Since the reaction in which sulphate is bound as a complex is very much slower than the liberation of chloride ions, it is possible with good approximation to calculate a velocity constant for the liberation of chloride ions from the observations during the first hour. For this purpose it is only necessary to know

the value the conductivity would have reached if the sulphate had not been complexly bound. We are able to calculate this value in the following manner. It must be equal to  $\frac{1}{3}a + \frac{1}{3}b$  where  $a$  is the molar conductivity of hexaquo-chromic chloride and  $b$  that of hexaquo-chromic sulphate, both in solutions 0.01 molar with respect to the blue chromic ion.  $a$  is equal to 343.5<sup>6a</sup> and  $b$  is 306.4<sup>8</sup>. Consequently  $\frac{1}{3}a + \frac{1}{3}b$  is 216.6. This value agrees with the curvature of the conductivity curve after completion of the liberation of chloride ions. In the figure the dotted line represents the conductivity the solution would probably have had if the chloride ions had been in a free state all the time. From this curve may be seen that the decrease of conductivity due to the sulphate during the first hour is insignificant (about two units) in comparison with the increase due to the liberation of chloride ions (20—40).

Under the heading  $k$  in tables 1 and 2 are entered the values of the velocity constants of the liberation of chloride ion calculated in accordance with the equation of a first-order reaction:

$$k = \frac{\log(216.6 - \lambda_{t_1}) - \log(216.6 - \lambda_{t_2})}{0.4343(t_2 - t_1)}$$

Let us try how far these values agree with the assumed constitutions of the salts. In an investigation of the conversion of green dichlorochromic chloride in about 0.01074 molar solution<sup>6d</sup>, the values found for the velocity constant of the liberation of chloride ion from monochlorochromic chloride were 0.0057—0.0036. These values agree well with those found for Recoura's salt, viz. 0.0080—0.0039. The high values found in the beginning with Recoura's salt originate from a period when the solution does not contain so much hexaquo-chromic salt and consequently not so much free acid as the chromic chloride solution in the period when the values 0.0057—0.0036 were found.

That the increase in the conductivity of Werner's chloro sulphate agrees with its assumed constitution may be shown in the following manner.

The transformation of dichlorochromic chromic sulphate must proceed at the same rate as the transformation of dichlorochromic chloride in a solution of the same acid content as the solution of the double salt. For the rate of change of the dichlorochromic ion depends solely on the content of free acid in the solution<sup>6i</sup>. From the value of the hydrolysis constant of hexaquo-chromic salts at 25° C ( $0.9 \cdot 10^{-4}$ ), the concentration of acid in the solution of the double salt is computed to be 0.00061 initially and 0.00091 after liberation of the chloride ion<sup>6b</sup>. Since in 0.01 molar solutions of dichlorochromic chloride in approximately 0.0004 *N* and 0.001 *N* hydrochloric acid, the concentration of free acid varies with time from 0.0004 to 0.0011 and from 0.001 to 0.0015, respectively,<sup>6g</sup> the rate of transformation of dichlorochromic chromic sulphate must be between those of di-

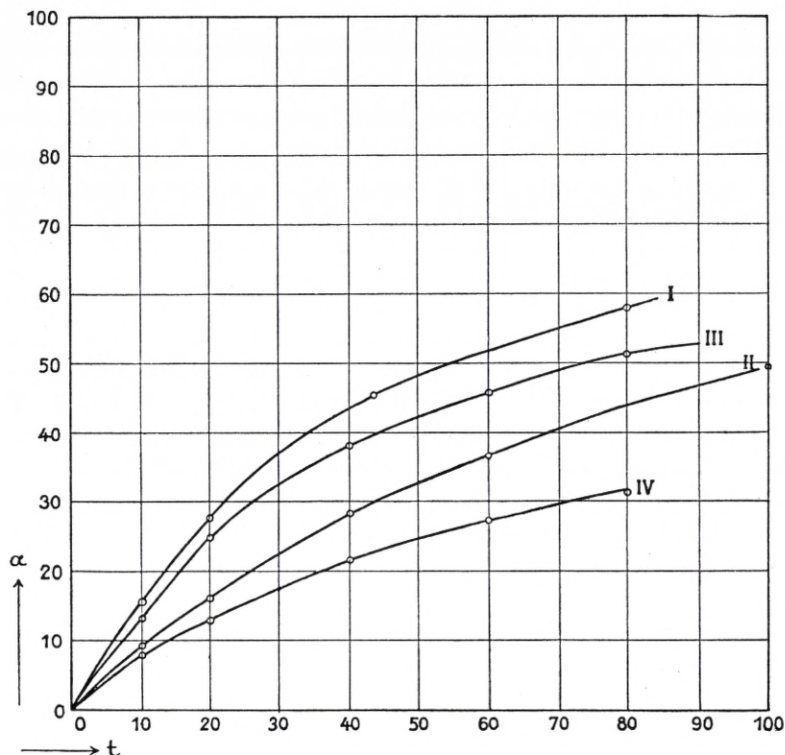


Fig. 2.

chlorochromic chloride in these solutions in hydrochloric acid. In fig. 2 the degree of transformation in per cent as computed from the conductivity data is plotted against time. Curves I and II show the transformation of dichlorochromic chloride in 0.0004 and in 0.001 *N* hydrochloric acid, respectively<sup>6c</sup>; curves III and IV show the transformation of Werner and Huber's and of Recoura's chlorochromic sulphate.

It is seen that the curve of Werner and Huber's double salt is between those of dichlorochromic chloride whereas the curve of Recoura's compound lies under both these curves. From this we may infer that only Werner and Huber's double salt can be dichlorochromic chromic sulphate.

We see then that not only the values of the conductivities in the moment of dissolution but also the changes of conductivity with time are explained by the assumed constitutions; and the differences between the two chloro sulphates are great enough to permit the use of these properties for the establishment of their constitution. The investigation of the colours of these compounds, however, affords a still finer means to this end.

## 3. ESTABLISHMENT OF CONSTITUTION BY INVESTIGATION OF COLOURS

The colour of a salt in solution is completely and exactly defined (setting aside surface and fluorescence colours) when its molar coefficients of extinction at various wave-lengths of light have been determined. The molar extinction coefficient ( $mEk$ ) is defined by the formula

$$mEk = \frac{\log I_0 / I}{lm}$$

where  $I_0$  is the intensity of incident light,  $I$  that of transmitted light,  $l$  the thickness of the absorbing layer (in cms.), and  $m$  the concentration of the coloured substance in moles per litre.

For determination of the molar extinction coefficients of my solutions I have used a König-Martens' spectrophotometer fitted out with a Rutherford prism and with an illumination system (maker Schmidt and Haensch in Berlin); the light source was a large Nernst projection lamp (220 volts, 3 amps).

First of all I wish to emphasize that it is permissible to assume that the ions of an electrolyte possess the same colour in the free and in the combined state as long as they do not form a complex compound. As early as the spring of 1906 this assumption was laid down by me as probable<sup>9</sup>. I arrived at it by combination of the available optical measurements with the recent views on the constitution of inorganic salts. In the autumn of 1907 Hantzsch has advanced the same theorem and furnished new experimental support of it. Quite recently some investigations into the colours of chromic salts have provided me with new, very good evidence in favour of the theorem. I intend to enlarge further upon these investigations elsewhere, and here I shall only state the following. According to these investigations all normal hexaquo chromic salts have exactly the same colour, namely that of the hexaquo chromic ion, even at concentrations where they are only very

Table 3. Molar extinction coefficients at  $18^\circ C \pm 2^\circ$

$\lambda$	Cr(H <sub>2</sub> O) <sub>6</sub> Cl <sub>3</sub> in 0.01 N HCl			Cr(H <sub>2</sub> O) <sub>6</sub> (NO <sub>3</sub> ) <sub>3</sub> in 0.1 N HNO <sub>3</sub>			Cr(H <sub>2</sub> O) <sub>6</sub> (SO <sub>4</sub> ) <sub>3/2</sub> in 0.2 N H <sub>2</sub> SO <sub>4</sub>		
	1 M	0.02 M	0.004 M	1 M	0.1 M	0.01 M	1 M	0.1 M	0.01 M
626 ± 15	7.08	6.87	6.88	7.07	7.10	6.99	7.24	7.11	7.00
524 ± 11	13.09	12.63	12.67	13.22	12.89	12.65	13.14	13.07	13.14
519 ± 8	6.56	6.30	6.42	6.65	6.56	6.36	6.73	6.58	6.65
486 ± 6	3.36	3.22	3.26	3.26	3.32	3.18	3.27	3.24	3.26
462 ± 8	4.63	4.16	4.39	4.36	4.42	4.16	4.47	—	4.19
440 ± 14	9.21	8.61	8.68	8.92	8.71	8.75	—	—	—

slightly dissociated into ions. This is seen clearly from table 3 showing the molar extinction coefficients of various hexaquochromic salts in various concentrations.

Within the error of the experimental method identical molar extinction coefficients have been found for all solutions.

In all the solutions tested, hydrolysis was strongly suppressed by addition of acid. In 0.1 normal acid hydrolysis at 18°C amounts only to about 0.06 per cent and in 0.01 normal acid it is about 0.6 per cent as calculated from a hydrolysis constant<sup>10</sup> of  $0.66 \cdot 10^{-4}$ .

In table 4 are given the molar extinction coefficients of the two chlorochromic sulphates, as calculated when using the formula  $\text{CrClSO}_4$ . Furthermore, the molar extinction coefficients of the hexaquochromic ion and of the dichloro-tetraquochromic ion are listed.

Table 4. Molar extinction coefficients at 18° C ± 2°

λ	Chlorochromic sulphate		$\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$	$\text{Cr}(\text{H}_2\text{O})_6^{+++}$	Calcd. for $\frac{1}{2}[\text{CrCl}_2(\text{H}_2\text{O})_4]$ $[\text{Cr}(\text{H}_2\text{O})_6](\text{SO}_4)_2$
	Recoura's salt	Werner and Huber's salt			
693 ± 24	4.26	7.61	14.87*	0.92	7.89
666 ± 19	7.44	11.04	20.86*	2.12	11.49
646 ± 16	11.64	13.88	24.38*	4.07	14.22
626 ± 15	14.80	15.11	23.61	7.07	15.34
608 ± 14	16.25	14.19	18.75	10.05	14.40
591 ± 12	15.40	12.63	13.16	12.35	12.75
564 ± 11	10.72	9.12	5.52	12.96	9.24
539 ± 9	6.24	6.51	2.95	9.75	6.35
519 ± 8	3.98	4.83	3.14	6.55	4.84
501 ± 7	3.48	5.17	6.02	4.15	5.09
486 ± 6	4.92	7.30	11.04*	3.26	7.15
473 ± 5	8.24*	9.81	16.16*	3.18	9.67
462 ± 8	12.03*	12.16	20.39*	4.34	12.36

\* In these cases the wave-length interval was twice that indicated in the first column.

If Werner and Huber's chloro sulphate is to be regarded as dichlorotetraquo-chromic hexaquochromic sulphate the molar extinction coefficients of this substance calculated in accordance with the formula  $\text{CrClSO}_4$  must be mean values of the figures pertaining to dichlorotetraquo-chromic ion and to hexaquo-chromic ion, for the molar extinction coefficients are additive properties.

In the sixth column these means are listed and by comparison with the figures in column 3 it is seen that the means agree within experimental error with the

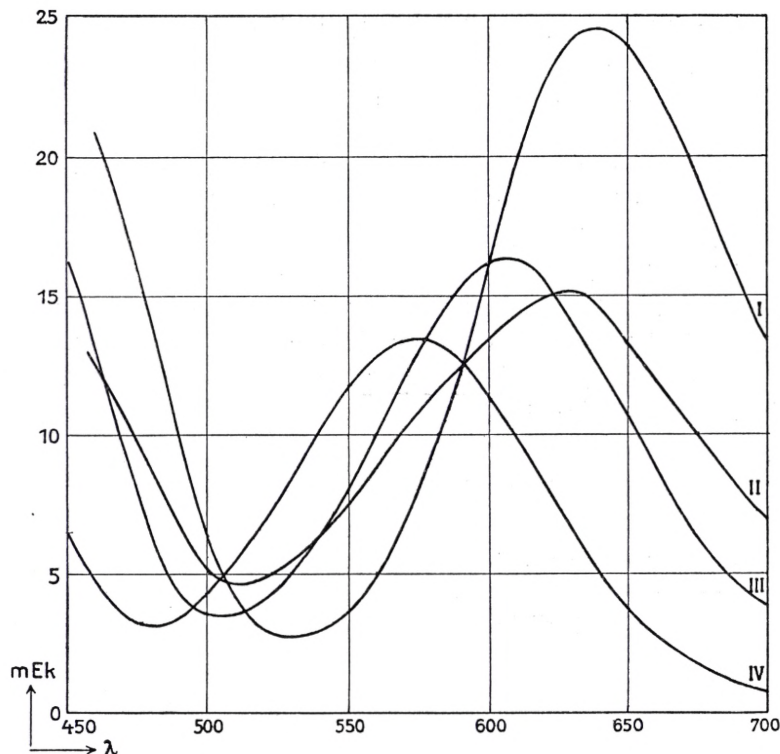


Fig. 3.

values of Werner and Huber's compound\*. In contrast the values found with Recoura's chloro sulphate deviate significantly from the means. Thus we may conclude that Werner and Huber's compound actually is dichlorotetraquochromic hexaquo chromic sulphate while Recoura's compound must have another constitution.

In fig. 3 the experimental values are represented graphically. Curve I represents the dichlorotetraquo ion, curve IV the hexaquo chromic ion. Curve II corresponds to Werner and Huber's and curve III to Recoura's chloro sulphate. It is worth noticing how well curve II goes through the points of intersection of the curves I and IV. Curve III (Recoura's chloro sulphate) in another respect occupies an intermediary position between I and IV. Its maximum is between the maxima of curves I and IV and has an intermediate value. The same applies to the minima. The intermediate values, however, are not exact means.

\* The comparatively great differences found with the two highest wave-lengths (3.5 and 4 per cent, respectively) may perhaps be explained by the fact that in these cases the band widths have not been identical throughout. However, they may just as well be considered due to experimental error.



Table 5. Molar extinction coefficients for 0.05 molar dichlorochromic chloride in 1 normal hydrochloric acid at about 18° C.

$\lambda$	$t$	$t$ min. after dissol.	1 hour later	3 days later	16 days later	extrapol. to the time 0	$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{SO}_4$
693 ± 24	12	14.75	14.02	5.83	—	14.87	4.26
666 ± 19	16	20.55	19.32	9.22	7.47	20.86	7.44
646 ± 16	20	23.95	22.59	13.13	—	24.38	11.64
626 ± 15	25	23.24	22.35	15.75	14.75	23.61	14.80
608 ± 14	29	18.59	18.26	16.41	—	18.75	16.25
591 ± 12	33	13.26	13.45	15.28	15.31	13.16	15.40
564 ± 11	37	5.84	6.36	9.88	10.60	5.52	10.72
539 ± 9	41	3.13	3.40	5.74	—	2.93	6.24
519 ± 8	45	3.22	3.33	3.83	4.02	3.14	3.98
501 ± 7	49	5.93	5.82	3.97	—	6.02	3.48
486 ± 6	54	11.10	10.78	6.18	5.03	11.40	4.92
473 ± 5	58	16.07	15.98	9.76	—	16.16	8.24
462 ± 8	63	19.99	19.63	14.44	12.48	20.39	12.03

The molar extinction coefficients of chloro compounds given in table 4 were all determined in 1 normal hydrochloric acid because hydrochloric acid makes the chlorochromic compounds much more stable<sup>6c</sup>. In the cases of dichloro-tetraquo-chromic chloride and of Werner and Huber's chloro-sulphate it was necessary to extrapolate the observed values to the time zero; this was easily done by observation of the changes during the following hour. In table 5 my measurements of the time-changes in the molar extinction coefficient of a 0.05 molar solution of dichlorochromic chloride in 1 normal hydrochloric acid are listed. The figures of this table give us a determination of the velocity of transformation of dichlorochromic chloride in 1 normal hydrochloric acid. During one hour about 9 per cent was converted into monochloro chloride. This gives the value 0.0016 of the velocity constant

$$k_1 = \frac{\log 100 - \log 91}{0.4343 \cdot 60}$$

Previous experiments<sup>6h</sup> on solutions not more than 0.01 normal with respect to hydrochloric acid gave the following formula for the same velocity constant at 25° C.

$$k_1 = 0.00272 + \frac{0.0000161}{s}$$

where  $s$  is the normality of free hydrochloric acid present. A rather bold extrapolation using this formula leads to the value  $k_1 = 0.00274$  in 1 normal hydrochloric acid at 25° C. This value obviously agrees well with the value 0.0016

found above at room temperature (the temperature during the hour when the experimental  $k_1$  was determined, was  $21^\circ$ ). After three days about 84 per cent monochloro chloride had been formed, and after 16 days the molar extinction coefficients showed that the solution contained exclusively monochlorochromic chloride (compare the columns 6 and 8). This also agrees well with my earlier investigations in very dilute solutions for, according to the formulae laid down then<sup>6f-g</sup>, the conversion of dichlorochromic chloride into monochlorochromic chloride in 1 normal hydrochloric acid should proceed about 1000 times as fast as the conversion of monochlorochromic chloride into the pure hexaquo compound. The first liberation of chloride ions may therefore be practically complete before the second liberation is noticeable. In the weakly acid solutions studied formerly, the situation was quite different.

After these experiments it lies near to prepare monochlorochromic sulphate by the following method, a variant of Weinland's method.

One part of dichlorochromic chloride is dissolved in one part of 1 normal hydrochloric acid, and after two weeks it is precipitated with concentrated sulphuric acid. In this way I have obtained a yield of 30 per cent of pure salt. This is somewhat more than I have obtained using Weinland's method (20—25 per cent); the difference, however, is not great.

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