Studies on the Aqueous Solutions of Some Chromic Salts. I. Spectrochemical Studies of the Chloro-aquo Compounds.

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Studies on the chromic salts were active until about 1910, but were not continued after the perfect explanation of the three isomers of chromic chloride hydrate, then discovered by A. Recoura(1) and N. Bjerrum(2), was given by Werner's co-ordination theory. For the purpose of investigating the constitution of these salts in various hydrogen ion concentrations, the author has quantitatively measured their absorption spectra in the ultra-violet region by changing the *p*H values. Such researches have not yet been systematically performed(3).

The measurements of the absorption spectra and hydrogen ion concentration are similar to those which were applied to the author's previous studies on the cobalt(4) and chromium(5) ammine-complex salts.

The absorption spectra were determined as soon as the chromic salts were dissolved, because the structural changes of these complex salts occurred after their solutions had been left standing for a long time. The thickness of the layer and the concentration of solutions were suitably chosen in the ranges of 10–50 mm. and 1/50–1/100 N (for the chromium atom), respectively. As the Lambert-Beer law holds under these conditions, $\log \varepsilon$(6) was adopted for the unit of the absorption intensity, and the details of the descriptions about the conditions of measurement were neglected. The following chromic compounds have been studied in the present work: violet chloride $[Cr(H_2O)_6]Cl_3$(7), violet sulphate $Cr_2(SO_4)_3 \cdot 17H_2O$(8), chrome alum $KCr(SO_4)_2 \cdot 12H_2O$(9), Bjerrum's salt

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(1) *Compt. rend.*, **102** (1886), 548; *Ann. chim. phys.*, **10** (1887), 34.

(2) *Z. physik. Chem.*, **59** (1907), 581.

(3) A. Byk and H. Jaffe did not obtain the absorption curves, *Z. physik. Chem.*, **68** (1909), 323.

(4) This Bulletin, **10** (1935), 50, 85; **12** (1937), 71.

(5) This Bulletin, **10** (1935), 267.

(6) ε is defined from the formula: $\log I_0/I = \varepsilon cd$, where I_0 and I represent respectively the light intensity given before and after its transmission; c, concentration of solution in normal; d, layer thickness of solution in cm.

(7) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 339.

(8) R. F. Weinland and R. Krebs, *Z. anorg. allgem. Chem.*, **49** (1906), 165.

(9) Recrystallised two times below 35°C. Merck's extra pure chrome alum.

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$⁽²⁾, $[Cr(H_2O)_5Cl]SO_4$⁽¹⁰⁾, green chromic chloride $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$⁽⁷⁾. They were prepared by referring the papers indicated in the foot notes.

I. The absorption curves and the hydrogen ion concentration of the solutions. (A) $[Cr(H_2O)_6]Cl_3$; $Cr_2(SO_4)_3 \cdot 17H_2O$; $KCr(SO_4)_2 \cdot 12H_2O$. The experiments made for the three above-mentioned salts are summarised in Table 1. Curve numbers given in the table correspond to those noted in Fig. 1.

Table 1.

	Compound	Conc.	Solvent	*p*H	Curve no.
1	$[Cr(H_2O)_6]Cl_3$	1/50 N	1/100 N HCl	1.8	I
2	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	,,	1.9	,,
3	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	1.8	,,
4	$[Cr(H_2O)_6]Cl_3$	,,	H_2O	2.7	,,
5	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	,,	2.9	,,
6	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	,,
7	$[Cr(H_2O)_6]Cl_3$	,,	1/1000 N NaOH	3.1	,,
8	,,	,,	5/1000 N NaOH	3.6	II
9	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	8/1000 N NaOH	4.1	III
10	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	4.0	,,
11	$Cr_2(SO_4)_3 \cdot 17H_2O$	,,	1/100 N NaOH	4.3	,,
12	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	,,
13	$[Cr(H_2O)_6]Cl_3$	1/100 N	,,	4.7	—
14	$KCr(SO_4)_2 \cdot 12H_2O$	,,	,,	,,	—

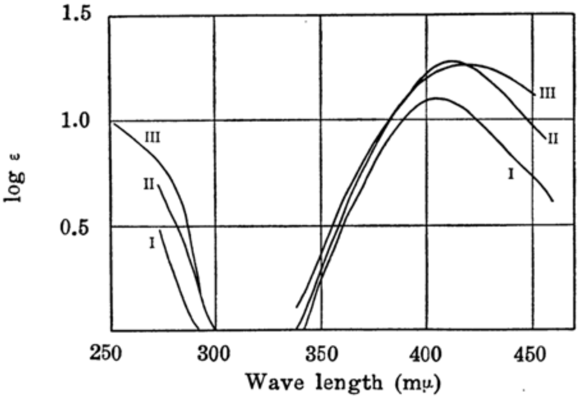

Fig. 1. The absorption spectra of $[Cr(H_2O)_6]^{+++}$

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(10) R. F. Weinland and T. Schumann, *Ber.*, **40** (1907), 3091.

As the absorption spectra of the solutions 1–7 in Table 1 are almost coincident, they are shown by a curve (curve I, Fig. 1). All these solutions are bluish-violet, but they become greener with the addition of sodium hydroxide to the solution, and their absorption curves then approach curve III in Fig. 1, that is, their absorption curves shift to the longer wave length, increasing their absorption capacities.

In the solutions containing sodium hydroxide equivalent to the chromium atom (13 and 14 in Table 1), the precipitation of chromic hydroxide was recognized when ultra-violet light was projected. The precipitation began in the part where light was projected. But, it did not occur when the solution was protected from light, even under the same conditions. It can therefore be safely concluded that this reaction is accelerated by light.

As the absorption curves of these three salt solutions were almost identical(11) in the range of pH 1.8 and 3.1, these salts must have the same chromofore. A. Werner and A. Gubster(12) gave already formula $[Cr(H_2O)_6]Cl_3$ to the violet chromic chloride hydrate, and other researchers also confirmed their opinion(13). This suggests that the violet chromic sulphate as well as the chrome alum should have the same complex ion with the above-mentioned violet chloride. A. Sénéchal(14) and W. R. Whitney(15) gave already formula $[Cr_2(H_2O)_{12}](SO_4)_3$ to the violet sulphate, but their confirmation for giving the formula to this salt seems to be weak. From the present results of the absorption spectra, the author wishes to give formulæ $[Cr(H_2O)_6]_2(SO_4)_3 \cdot 5H_2O$ and $K[Cr(H_2O)_6](SO_4)_2 \cdot 6H_2O$ to the violet chromic sulphate and the chrome alum respectively.

(B) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$; $[Cr(H_2O)_5Cl]SO_4$. For $[Cr(H_2O)_5Cl]Cl_2$ absorptions in three different pH were observed as indicated in Table 2. In this case, the absorption of the aqueous solution (curve II, Fig. 2) was not similar to that of the solution in hydrochloric acid (curve I, Fig. 2). The latter curve was, on the whole, shifted to a longer wave length than the former. On the contrary, the absorption curve of the solution with sodium hydroxide (curve III, Fig. 2) moved to the shorter

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(11) The violet chloride and sulphate indicated identical curves also in the visible region, N. Bjerrum, *Z. anorg. allgem. Chem.*, **63** (1909), 140.

(12) *Ber.*, **34** (1901), 1579.

(13) P. Pascal, "Traité de Chimie Minérale," Vol. X, 1021 (1933).

(14) *Compt. rend.*, **156** (1913), 552.

(15) *Z. physik. Chem.*, **20** (1896), 40.

Table 2.

Compound	Conc.	Solvent	pH	Curve no.
$[Cr(H_2O)_5Cl]Cl_2$	1/70 N	1/100 N HCl	1.9	I
,,	1/58 N	H_2O	3.2	II
,,	1/72 N	1/100 N NaOH	4.3	III
,,	1/110 N	9/1000 N NaOH	4.7	—
$[Cr(H_2O)_5Cl]SO_4$	1/50 N	1/100 N HCl	2.0	IV
,,	,,	H_2O	2.9	,,
,,	,,	8/1000 N NaOH	4.1	V
,,	,,	1/100 N NaOH	4.2	,,

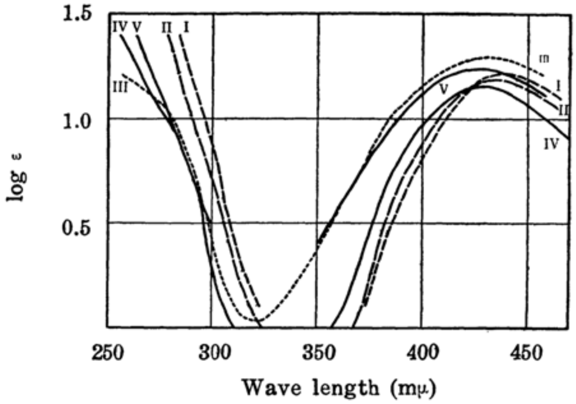

Fig. 2. The absorption spectra of $[Cr(H_2O)_5Cl]^{++}$

wave length(16). A precipitate of chromic hydroxide was observed in the solution of pH 4.7, when it was exposed to light.

As $[Cr(H_2O)_5Cl]Cl_2$ is very hygroscopic and unstable, the complex ion $[Cr(H_2O)_5Cl]^{++}$ cannot be easily studied by its absorption spectra. Similar experiments were therefore repeated with the sulphate which is more stable than the chloride. The absorption curve given by the aqueous solution of the sulphate (curve IV, Fig. 2) was identical with that observed with the solution in hydrochloric acid. The solution of this salt with sodium hydroxide showed similar absorption curves (curve V, Fig. 2) when pH was 4.1 and 4.2.

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(16) Except hydroxo-compounds, among the salts already studied by the author, this salt is the only one that shows different absorption spectra in neutral and in acidic solutions.

The wave length representing the absorption band of curve V, Fig. 2 almost coincides with curve IV, and the intensity observed in the former curve is a little stronger than that shown by the latter. But, the absorptions in the range of shorter wave length (near 300 mμ) were observed to be quite similar in these two curves. A few minutes after the end of the measurement, a precipitation of chromic hydroxide occurred in the solution of *p*H 4.2.

From the fact that the chloride and the sulphate show different absorptions in spite of the same complex ion, it can be safely assumed that either of these two salts is impure. As the chloride is unstable in solution as well as in the solid state, it can be naturally supposed to be impure. If the impurity is based on $[Cr(H_2O)_4Cl_2]Cl$ which is prepared by the transformation of $[Cr(H_2O)_5Cl]Cl_2$, the anormality in the absorption can be easily explained by assuming that the transformation of Bjerrum's salt into the green chloride is more rapid in hydrochloric acid than in the neutral aqueous solution.

(C) $[Cr(H_2O)_4Cl_2]Cl$. The results obtained with this compound are summarised in Table 3 and Fig. 3.

When the *p*H-value increased in the solution, the absorption was generally shifted to the shorter wave length, accompanying the increase of the absorption capacity in the absorption band.

As seen in (A), (B) and (C), the absorption curves shown by solutions of higher *p*H-values are similar with one another.

Table 3.

Conc.	Solvent	*p*H	Curve no.
1/50 N	1/100 N HCl	1.9	I
,,	H_2O	3.3	I
1/100 N	8/1000 N NaOH	4.3	II
,,	1/100 N NaOH	4.6	III

Table 4.

Compound	$\lambda_{max.}$ (mμ)	log ε
$[Cr(H_2O)_6]^{+++}$	405	1.10
$[Cr(H_2O)_5Cl]^{++}$	430	1.15
$[Cr(H_2O)_4Cl_2]^{+}$	443	1.24

Table 5.

The Absorption of $[Cr(H_2O)_4Cl_2]Cl$.

λ (mμ)	ε	
	(obs.)	(calc.)
400	6.8	6.3
410	10.0	11.1
420	13.2	15.9
430	15.8	19.2
440	17.4	20.1
450	16.6	17.9
460	15.1	15.3

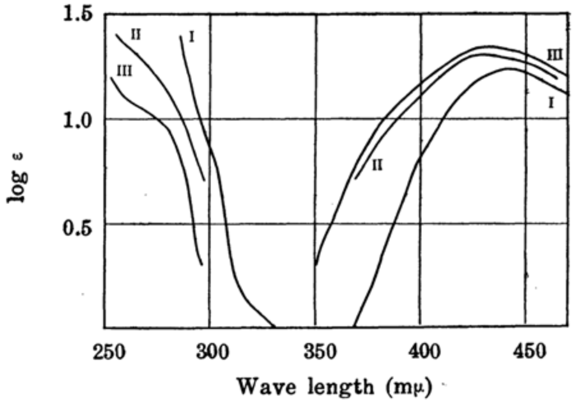

Fig. 3. The absorption spectra of $[Cr(H_2O)_4Cl_2]Cl$

II. Action of alkali on the aqueous solutions of aquo-chloro chromic salts. By the thorough investigations of the aqueous solution of violet chloride, N. Bjerrum⁽⁷⁾ confirmed the existence of the following equilibrium, and the equilibrium constant has been already determined by many authors⁽¹⁷⁾:

$$[Cr(H_2O)_6]^{+++} \rightleftarrows [Cr(H_2O)_5OH]^{++} + H^+.$$

When sodium hydroxide is added to the aqueous solution of this salt, $[Cr(H_2O)_5OH]^{++}$ must be formed, and it is quite natural that the absorption given by its solution of high pH is more similar with that given by $[Cr(H_2O)_5OH]^{++}$.

As to the aqueous solution of $[Cr(H_2O)_4Cl_2]Cl$, the following hydrolysis was suggested by A. B. Lamb⁽¹⁸⁾, who already measured its equilibrium constant⁽¹⁹⁾.

$$[Cr(H_2O)_4Cl_2]^+ + 2H_2O \rightleftarrows [Cr(H_2O)_5OH]^{++} + H^+ + 2Cl^-.$$

For the aqueous solution of $[Cr(H_2O)_5Cl]^{++}$, the hydrolysis has not yet been reported. As the absorption given by a solution of higher pH-value of this salt becomes almost the same as that represented by the solutions of $[Cr(H_2O)_6]^{+++}$ and $[Cr(H_2O)_4Cl_2]^+$ with sodium hydroxide, the addition of alkali to the solution of $[Cr(H_2O)_5Cl]^{++}$ tends to form

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(17) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 339; A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43** (1921), 1154; H. G. Denham, *J. Chem. Soc.*, **93** (1908), 53; J. N. Brönsted and K. Volgvartz, *Z. physik. Chem.*, **134** (1928), 97.

(18) *J. Am. Chem. Soc.*, **28** (1906), 1710.

(19) A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43** (1921), 1154.

$[Cr(H_2O)_5OH]^{++}$. Hereupon, the author has assumed the following equilibrium in the aqueous solution of $[Cr(H_2O)_5Cl]^{++}$ like $[Cr(H_2O)_6]^{+++}$ and $[Cr(H_2O)_4Cl_2]^{+}$.

$$[Cr(H_2O)_5Cl]^{++} + H_2O \rightleftarrows [Cr(H_2O)_5OH]^{++} + HCl.$$

III. Absorption of aquo-chloro compounds and configuration of $[Cr(H_2O)_4Cl_2]Cl$. It has already been reported⁽⁵⁾ that the absorption curve near 250 mμ, given by the chloro-ammine chromic complex salts, is regularly shifted to a longer wave length, as often as a chlorine atom enters into a complex radical. The same fact was also observed with this chloro-aquo salt, that is, the wave lengths, where $[Cr(H_2O)_6]^{+++}$, $[Cr(H_2O)_5Cl]^{++}$, and $[Cr(H_2O)_4Cl_2]^{+}$ absorbed the light by the intensity of $\log\varepsilon = 0.5$, were 273 mμ, 296 mμ, and 307 mμ.

The wave lengths and extinction coefficients of the maximum absorptions of these three salts have a certain relation with the number of chlorine atoms in a complex radical, and as indicated in Table 4, they are shifted in a definite direction in proportion to the number of chlorine atoms.

From the point of view of Werner's co-ordination theory, there should be two isomers of $[Cr(H_2O)_4Cl_2]Cl$, i.e. cis and trans. But, it has not yet been determined whether the ordinary salt has cis- or trans-configuration. Applying to this salt the hypothesis⁽²⁰⁾, which the present author already proposed, and assuming this salt to have cis-form, he has calculated the absorption of $[Cr(H_2O)_4Cl_2]^{+}$ from absorption curves given by $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]SO_4$. The calculated values show a coincidence with the observed values to the extent indicated in Table 5. But, from this comparison of values only, the author cannot give a cis-configuration to this salt, because when this salt is assumed to be trans, a better coincidence might be obtained by calculation, which, however, has as yet been impossible.

Summary.

(1) The absorption spectra of six solutions of chromic chloride and sulphate hydrates were quantitatively measured in the ultra-violet region.

(2) Violet chromic sulphate and chrome alum should respectively have the formula $[Cr(H_2O)_6]_2(SO_4)_3$ and $K[Cr(H_2O)_6](SO_4)_2$.

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(20) The hypothesis is related to the configuration of complex salts and their absorption spectra; this Bulletin, **12** (1937), 188.

(3) Chloro-aquo chromic salts were transformed into the hydroxo-pentaquo chromic salts in the solutions where the *p*H-values were higher than 4.0.

(4) The substitution of a chlorine atom for a molecule of water in these salts caused the absorption band to shift in the direction of the increasing wave length and absorption capacity.

(5) Following his method, the author has made a comparison of calculated and observed values of the absorption of green chromic chloride.

In conclusion, the author wishes to express his sincere thanks to Assist. Prof. T. Uemura of the Tokyo University of Engineering for his kind encouragement.

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