

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

## THE ABSORPTION SPECTRA OF THE CHROMIUM AMMINE HYDRATES<sup>1</sup>

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### Introduction

The aquo ammino chromic salts have been regarded by Werner<sup>2</sup> as indicating the close relationship between chromic ammine complexes and chromic salt hydrates. Schwarz<sup>3</sup> mentions the interesting colors exhibited by these compounds, noting that the color changes from yellow through red to violet as ammonia molecules are replaced by water molecules in hexamine chromic salts. Shibata, together with his co-workers,<sup>4,5</sup> and Luther and Nikolopoulos<sup>6</sup> have published absorption spectra observations on several of the aquo ammino chromic salts though data for the complete series were not obtained. These investigators agreed that the substitution of a water molecule for an ammonia molecule in these amines causes the visible absorption band (of the compound in solution) to shift in the direction of increasing wave length. Since their data were not precise enough to furnish an estimate of the magnitude of this shift, this research was undertaken to obtain the desired information.

**Preparation of Compounds.**—The compounds used in this investigation were prepared by standard methods described in the literature.<sup>7</sup>

**Apparatus.**—The absorption spectra measurements were obtained by the use of a Nutting Polarization Photometer in conjunction with a Constant Deviation Spectrometer. Both instruments were made by Wm. Gaertner and Co. For a description and method of operation of this

<sup>1</sup> This paper is based on part of a dissertation submitted by Robert Irving Colmar to the Faculty of the Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Original manuscript received August 19, 1931.

<sup>2</sup> Werner, "Neue Anschauungen auf dem Gebiete der anorganische Chemie," 4th ed., Braunschweig, 1920.

<sup>3</sup> Schwarz, "The Chemistry of the Inorganic Complex Compounds," translated by Bass, John Wiley and Sons, Inc., New York, 1928, p. 38.

<sup>4</sup> Urbain and Shibata, *Compt. rend.*, **152**, 593 (1913); Shibata, *J. College Sci. Imp. Univ. Tokyo*, **37**, Art. 2 (1915).

<sup>5</sup> Shibata and Matsuno, *ibid.*, **41**, Art. 6, Mar. 20 (1920).

<sup>6</sup> Luther and Nikolopoulos, *Z. physik. Chem.*, **82**, 361 (1913).

<sup>7</sup> Biltz, "Laboratory Methods of Inorganic Chemistry," by Heinrich and Wilhelm Biltz, translated by Hall and Blanchard, John Wiley and Sons, Inc., New York, 1928; Christensen, *J. prakt. Chem.*, **23**, 27 (1881); Pfeiffer, *Ber.*, **38**, 3592 (1905); Pfeiffer, *ibid.*, **40**, 3126 (1907); Werner, *ibid.*, **43**, 2290 (1910); Reisenfeld, *ibid.*, **37**, 3059 (1905); Nordenskjöld, *Z. anorg. Chem.*, **1**, 126 (1892); Werner and Klein, *Ber.*, **35**, 277 (1902).

spectrophotometer, Wagner's book<sup>8</sup> may be consulted. The absorption cells consisted of various lengths (about 1.5 cm. diameter) of hollow cylinders with polished ends over which were slipped circular end-plates. Measurements were taken at room temperature, no form of temperature control being employed.

Molecular extinction coefficients were calculated from the formulas

$$\text{Molecular extinction coefficient} \equiv \text{M. E. C.} = -\log_{10} T/cd$$

where  $T$  was the transmission of a tube of solution, of concentration  $c$  molar, and a length of  $d$  centimeters. The value of  $T$  was obtained from the equation

$$T = \frac{\sin^2 \alpha}{\sin^2 \alpha^0}$$

where  $\alpha$  was the value of the photometer disk angle necessary to produce a balance in the photometric field when the solution being measured was in the path of the light beam of the photometer and  $\alpha^0$  was the value of the photometer disk angle when no absorption cell was in place.

**Precision of Measurements.**—The average deviation of the mean of the M. E. C. was kept at about  $\pm 1$  unit throughout the visible spectrum by varying the number of observations. In the violet part of the spectrum, ten readings at each point were taken because of poor visibility and low illumination; otherwise, five readings were satisfactory. By using copper sulfate and potassium chromate solutions, which are accepted spectrophotometric standards, recognition of constant or residual errors was possible. From a consideration of the results obtained by comparing observations on these solutions with those furnished by the Bureau of Standards, the author believes that the precision measure of the M. E. C. is 5%, which is a good value for this type of measurement.

### Results

By plotting the molecular extinction coefficient versus wave number (see Tables I and II; also Figs. 1 and 2) for each solution, a value of the wave number at which the extinction coefficient is a maximum, is obtained. These maximum values of the M. E. C. are plotted *versus* molecules of water replacing molecules of ammonia in the complex (see Fig. 3). On examining these curves, the following generalizations may be noted. (1) On substituting a water molecule for an ammonia molecule in either a chromium or cobalt complex (up to four substitutions) the wave number at which maximum absorption of light occurs is decreased  $610 \text{ mm.}^{-1}$  (Fig. 3). (2) On substituting a water molecule for an ammonia molecule in a chromium complex, the value of the molecular extinction coefficient at the maximum of the absorption band is decreased successively 4.9 units (Fig. 4). (3) In the cobalt complexes an anomaly to the previous rule for

<sup>8</sup> Wagner, "Experimental Optics," John Wiley and Sons, Inc., New York, 1929, p. 158.

TABLE I  
MOLECULAR EXTINCTION COEFFICIENTS

Wave length in Ångström units	Wave number in $\text{mm.}^{-1}$	Hexamino-chromic chloride	Aquo-pentamino-chromic chloride	Diaquo-tetramino-chromic chloride	Triquo-triamino-chromic chloride	Tetraquo-diamino-chromic chloride	Hexaquo-chromic chloride
4500	22220	36.1	26.7	19.7	12.2	10.0	..
4550	21980	38.8	28.6	21.0	..	..	..
4600	21740	40.8	31.9	22.8	16.5	10.5	..
4650	21500	40.1	32.8	24.8	..	..	..
4700	21280	39.2	34.1	26.6	18.7	11.9	..
4750	21060	36.8	35.6	28.5	..	..	..
4800	20840	33.8	35.4	30.5	22.0	14.2	2.8
4850	20620	30.8	35.1	30.8	..	..	..
4900	20410	27.5	34.4	30.9	25.6	16.3	3.4
4950	20200	24.4	33.1	30.8	25.4	17.9	..
5000	20000	19.7	31.5	30.6	26.1	19.1	3.6
5050	19800	15.2	29.5	29.5	26.4	19.1	..
5100	19610	12.6	27.8	28.1	25.4	20.1	4.3
5150	19420	9.5	25.6	..	25.0	20.4	..
5200	19230	8.4	21.9	24.0	24.8	20.6	5.0
5250	19050	..	20.0	..	23.0	20.6	..
5300	18870	..	17.2	19.8	22.0	20.2	5.8
5350	18690	..	15.3	..	..	20.3	..
5400	18520	..	12.1	14.4	19.7	19.3	6.7
5450	18350	..	..	..	..	..	..
5500	18180	..	9.4	10.0	16.7	16.7	7.4
5550	18020	..	..	..	..	..	7.8
5600	17860	..	6.8	7.3	14.3	14.1	8.5
5650	17700	..	..	..	..	..	8.7
5700	17540	..	5.4	..	..	11.9	8.9
5750	17390	..	..	..	..	..	..
5800	17240	..	3.9	..	8.4	10.5	8.8
5850	17090	..	..	..	..	..	8.8
5900	16950	..	..	..	..	..	8.2
5950	16810	..	..	..	..	..	8.1
6000	16670	..	3.1	..	3.6	6.6	8.1
6050	16530	..	..	..	..	..	..
6100	16390	..	..	..	..	..	6.9
6150	16260	..	..	..	..	..	..
6200	16130	..	..	..	1.6	4.7	6.3
6250	16000	..	..	..	..	..	..
6300	15870	..	..	..	..	..	5.1
6350	15750	..	..	..	..	..	..
6400	15630	..	..	..	..	..	4.2
6600	15150	..	..	..	..	..	2.5

chromium complexes exists, for a decrease in the molecular extinction coefficient takes place on the substitution of the first molecule of water for ammonia but an *increase* is noted for the second entering water molecule. However, the shift in wave number (as in Rule 1) holds true (Fig. 4).

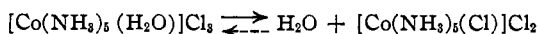
TABLE II  
 MOLECULAR EXTINCTION COEFFICIENTS

Wave length in Ångström units	Wave number in mm. <sup>-1</sup>	Hexamino- cobaltic chloride	Aquo- pentamino- cobaltic chloride	Diaquo- tetramino- cobaltic chloride	Chloro- pentamino- cobaltic chloride	Chloro- pentamino- chromic chloride
4500	22220	46.1	34.9	22.4	24.2	20.6
4550	21980	50.8	37.9	..	26.2	..
4600	21740	53.8	40.8	30.4	30.4	23.6
4650	21500	54.5	42.5	..	31.0	..
4700	21280	56.1	45.5	36.4	33.4	26.2
4750	21060	56.1	46.0	..	35.5	..
4800	20840	55.5	46.5	44.9	37.5	29.8
4850	20620	54.0	47.6	..	39.2	..
4900	20410	49.1	47.9	49.5	40.9	33.1
4950	20200	44.4	46.5	51.9	41.9	..
5000	20000	33.6	45.5	52.9	43.1	35.1
5050	19800	..	44.5	53.1	44.9	..
5100	19610	..	42.8	51.5	46.1	35.8
5150	19420	..	..	50.4	47.1	..
5200	19230	18.9	39.2	49.1	47.5	34.2
5250	19050	..	..	47.5	46.8	..
5300	18870	..	..	44.7	46.4	32.4
5350	18690	..	..	..	45.6	..
5400	18520	5.7	25.9	39.3	44.0	27.6
5450	18350	..	..	..	..	..
5500	18180	..	..	32.0	40.5	21.6
5600	17860	0.4	13.6	26.4	34.6	16.2
5700	17540	..	..	..	25.6	..
5800	17240	..	6.5	15.8	19.3	6.9
5900	16950	..	..	..	13.5	..
6000	16670	..	3.4	8.4	..	3.4
6100	16390	..	..	..	6.5	..
6200	16130	..	..	..	..	..
6300	15870	..	..	..	3.4	..

(4) Referring to Fig. 3 it will be noted that the lines for chromium salts and cobalt salts are parallel. This would seem to indicate that the substitution of a cobalt atom for a chromium atom in a complex as in  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  to  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  or in  $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$  to  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$  causes the wave number at which maximum absorption of light occurs to decrease 510  $\text{mm}^{-1}$ . In order to verify this assumption  $[\text{Cr}(\text{NH}_3)_5(\text{Cl})]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{Cl})]\text{Cl}_2$  were prepared and their absorption spectra studied. The difference between their wave numbers at maximum absorption was 500  $\text{mm}^{-1}$ , a value not much different from that predicted by the above generalization. (5) The molecular extinction coefficients at maximum absorption for all cobalt compounds have higher values than those of the corresponding chromium compounds (Fig. 4). (6) The substitution of chlorine for an ammonia molecule decreases the wave number at maximum absorption 1970  $\text{mm}^{-1}$ .

### Discussion

Shibata<sup>4</sup> believes that in solution the following equilibrium is rapidly established



the chloro-pentammino salt being formed almost exclusively. As the reason for this belief he points out that, according to his measurements, the absorption spectra of the aquo and chloro compounds are nearly identical. The author finds that this is not the case, since aquo-pentammino-cobaltic chloride has a wave number at maximum absorption of 20,570, while chloro-pentammino-cobaltic chloride has a wave number of 19,200, a difference quite beyond the possibility of experimental error.

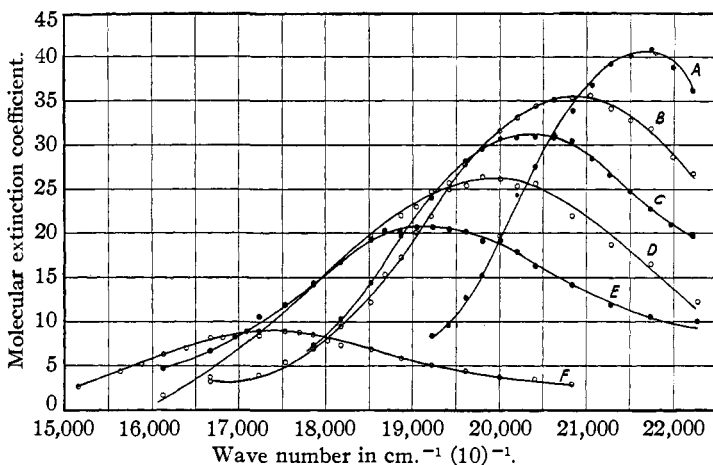


Fig. 1.—Absorption spectra of the chromium ammine hydrates: Curve A, hexammino-chromic chloride; B, aquo-pentammino-chromic chloride; C, diaquo-tetrammino-chromic chloride; D, triaquo-triammino-chromic chloride; E, tetraquo-diammino-chromic chloride; F, hexaquo-chromic chloride.

A similar difference is observed for the corresponding chromium salts. It is therefore believed that the absorption spectra furnish no evidence for such an hydrolysis (in freshly prepared solutions). However, the author has noticed that aquo-pentammino-chromic chloride changes into chloro-pentammino-chromic chloride in about a week, even if stored in the dark and over phosphorus pentoxide. It is therefore extremely likely that if a considerable interval elapsed between the preparation of the salts and their optical examination, erroneous results would be obtained.

**Physical Theory.**—From the fact that changes of the central atom produce variations in molecular extinction coefficients and wave numbers, it is evident that at least some (if not the greater part) of the color must be due to the central atom, or, strictly speaking, the central ion. This idea

furnishes a starting point in formulating a theory to explain the observed regularities.

For a basis the following principle, having wide application in spectroscopy, has been applied. If a molecule contains a number of energy absorbing units, capable of absorbing quanta denoted by  $h\nu_1, h\nu_2, h\nu_3$ , etc., then absorption of radiation energy, whose frequency is  $\nu_1, \nu_2, \nu_3$  and  $\nu_1 + \nu_2 + \nu_3 + \dots$ , etc., may occur.

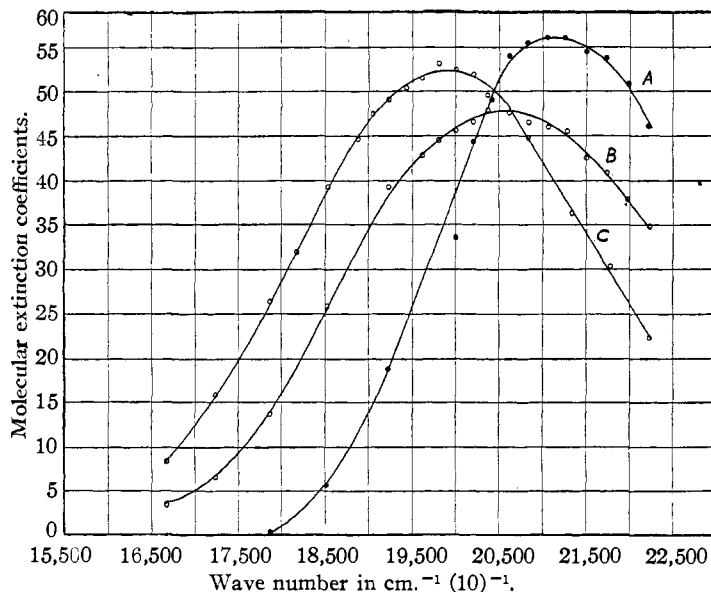


Fig. 2.—The absorption spectra of the cobaltic ammine hydrates: Curve A, hexammino-cobaltic chloride; B, aquo-pentammino-cobaltic chloride; C, diaquo-tetrammino-cobaltic chloride.

In any molecular group there may be a number of possibilities; these have been enumerated by Taylor:<sup>9</sup> (1) electronic transitions within individual atoms; (2) vibrations of the atoms within chemical groups; (3) rotation or quasi-rotation of the group as a whole.

Thus part of the light absorption capacity is attributed to the chromic ion or the cobaltic ion, because of an electronic transition within these ions. Another part is attributed to the internal vibrations of the atoms and ions making up the complex. Here, because of the great number of degrees of freedom possible in the system, many modes of vibration are possible, though it seems reasonable to expect that one or two modes will predominate.

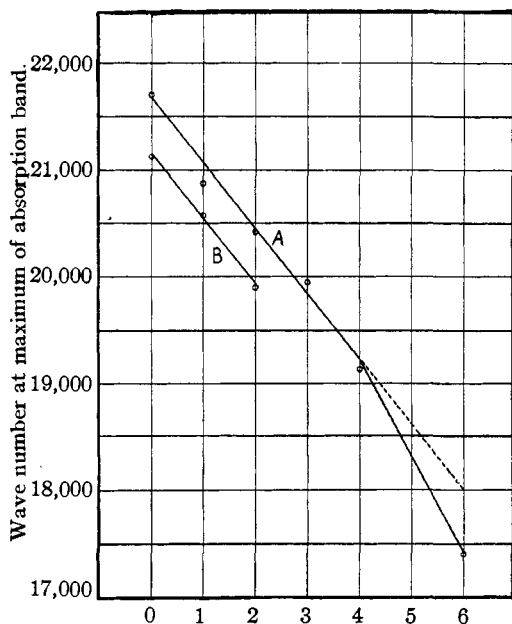
The vibrational frequency (which is proportional to wave number) must be proportional to some function of the binding forces between the

<sup>9</sup> Taylor, *Trans. Faraday Soc.*, **25**, 860 (1929).

vibrating bodies and inversely proportional to some function of their masses.

The rotational frequencies are small, compared with electronic and vibrational frequencies, and are therefore neglected.

From the foregoing considerations, the absorption spectra of these complexes should show a strong absorption line (corresponding to  $\nu_1 + \nu_2 + \nu_3 + \dots$ , etc.) surrounded by fine line structure (since there is a series of vibrational levels); instead a continuous band is observed. A number of reasons may be advanced for this, one of the most important being that given by Sidgwick,<sup>10</sup> who states "the broadening of the absorption lines of an ion in solution is due to the electric fields of neighboring atoms, which break up each line into components, whose separation depends on the strength of the field (Stark effect); as the ions present are thus affected in various degrees, the result is to spread the sharp lines into a band." The rotational frequencies must also contribute to the blurring of the lines as well as the collisions of the absorbing bodies in solution.



Molecules of water replacing ammonia in complex.  
Fig. 3.—Curve A, chromic ammine hydrates; Curve B, cobaltic ammine hydrates.

Consider the compounds



Since (1) and (3) have the same central ion, their electronic term must be the same and the shift in frequency, which is 1830 (10)<sup>10</sup> [the product of the velocity of light in centimeters and the difference between the wave numbers at maximum absorption of compounds (1) and (3)], is due to a change in the vibrational spectral terms. Since the masses of the ammonia and water molecules are approximately the same (17 and 18), it seems reasonable to attribute the change in vibrational frequency to a loosening of the binding forces which connect the ammonia and water groups to the central ion. This effect should be observed in an x-ray crystal analysis

<sup>10</sup> Sidgwick, "The Electronic Theory of Valency," The Clarendon Press, Oxford, England, 1927.

of these compounds. The hexammino salt should have the most compact structure, while the substitution of ammonia for water should loosen the crystal structure. The effect also should parallel the shifts in frequency: an anomaly should be observed for the hexaquo salt. Other evidence which supports this point of view comes from considerations of the chemical stability. The hexammine salts are the most stable, with the stability decreasing as water is substituted for ammonia, which is what would be expected from the binding forces becoming weaker.

The vibrational frequencies are affected by change of mass also, since the substitution of chlorine for ammonia causes a shift in frequency of 5910 units while a change of water for ammonia causes a shift in frequency of 1830 units. This also is to be expected on the basis of the theory.

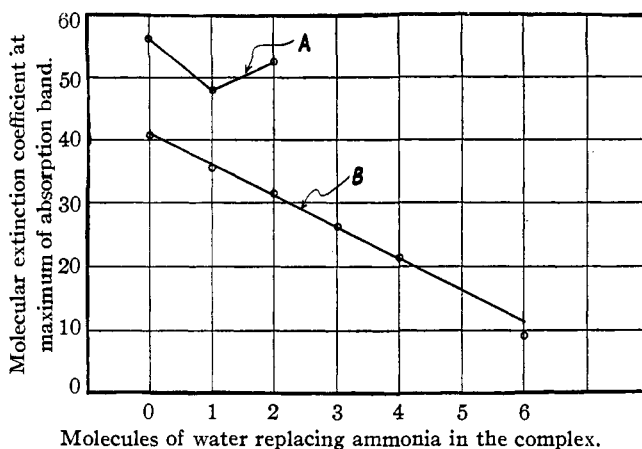


Fig. 4.—Curve A, cobaltic ammine hydrates; Curve B, chromium ammine hydrates.

Considering Compounds (1) and (2), the generalizations previously mentioned state that a decrease of 1530 units is to be expected on changing from Cr to Co. Since this difference of 1530 is constant for all compounds whose only difference is the central ion and the shift in frequency (1830) due to the substitution of water for ammonia remains the same for cobalt compounds, the only way to account for this is to assume that the vibrational terms for these compounds are the same or always differ by a constant amount. This attributes all change of color in these compounds to differences in the electronic terms. Since this electronic transition is a property of the central ion only, all complexes of cobalt and chromium, whose only difference in structure is a change of central ion, should show this same constant difference.

The explanation of the decrease in the value of the molecular extinction coefficients at the wave number of maximum absorption with the number of



substitutions of water for ammonia is related to the probability of electronic transitions within the group.

**Acknowledgment.**—This investigation was under the co-direction of Dr. Frederick William Schwartz, Professor of Inorganic Chemistry, and Dr. Robert Alexander Patterson, Professor of Physics, at the Rensselaer Polytechnic Institute. The author is deeply grateful to these men and others, who, by their interest and aid, contributed to the advancement of this research.

### Summary

1. The visible absorption spectra of some chromamines and cobalt-ammines have been measured.
2. Certain empirical generalizations have been deduced from these measurements.
3. A theory has been put forth to account for the light absorption of complex compounds.
4. As a test of the theory, a prediction of the x-ray crystal analysis of a series of chromamines has been recorded.

TROY, NEW YORK

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

## THE PRECISION WITH WHICH THE CONCENTRATIONS OF SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE MAY BE DETERMINED WITH THE IMMERSION REFRACTOMETER

BY E. ROGER WASHBURN AND ALLEN L. OLSEN

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The refractive index of solutions varies with the concentration. A curve may be prepared showing this variation and then if the refractive index of an unknown solution is determined, the concentration may be read from the curve, or calculated from the equation of the curve. In order to make an accurate determination, it is necessary that the solution contain no measurable amount of impurity and that the temperature at which the reading is taken be the same as that for which the curve and equation were determined. Since refractive index may be easily and accurately determined, it has been suggested<sup>1</sup> that the refractometer be used as a means of determining the concentrations of various standard solutions used in analytical chemistry.

The results of previous work on concentration-refractive index relation-

<sup>1</sup> H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **2**, 201 (1930); C. A. Clemens, *J. Ind. Eng. Chem.*, **13**, 813 (1921); B. Wagner, *Z. angew. Chem.*, **33**, 249 (1920).