On the Relation between the Configuration of Metallic Complex Salts and their Absorption Spectra.⑴

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Introduction. Many valuable but qualitative conclusions on the absorption spectra of metallic complex salts have already been obtained by Y. Shibata⑵. By means of quantitative studies, R. Luther and A. Nikolopulos⑶, R. I. Colmar and F. W. Schwartz⑷ and A. Mead⑸ have also found that whenever a certain substitution occurs in a complex radical, a constant change of the maximum absorption is consequently produced. But, as these authors did not take notice of the position of those substituents, their point of view cannot generally apply to all complex salts. I. Lifschitz⑹, expressing his interest in his work about the relation between the absorption and the stereoisomer, could not obtain any conclusion on it. A. Uspenski and A. Bamdas⑺ have recently measured the absorption of some isomers, and have only reported that the position of maximum absorption of cis-salts corresponds to that of the minimum absorption of trans-salts. In fact, no papers have as yet appeared in which the absorptions of complexes were quantitatively discussed with a stereochemical consideration.

Thereupon, it seemed very interesting to the author to study this question. In the present research, I have found a new relation between the configuration of nitro-ammine-cobaltic salts and their absorption spectra, and have applied it to the other series of complex salts.

Nitro-ammine-cobaltic complex salts. As these salts are comparatively stable and prepared in a pure state forming a most perfect series of compounds, they are the best materials for the author's purpose of study. Although their absorption spectra have been individually

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(1) Summarized the author's two reports already published in Japanese: *J. Chem. Soc. Japan*, **57** (1936), 406, 542.

(2) Y. Shibata, *J. Coll. Sci., Tokyo Imp. Univ.*, **37** (1915), Art. 2.

(3) *Z. physik. Chem.*, **82** (1913), 361.

(4) *J. Am. Chem. Soc.*, **54** (1932), 3204.

(5) *Trans. Faraday Soc.*, **30** (1934), 1053.

(6) "Spektroskopie u. Kolorimetrie", 2. Aufl., 228 (1927).

(7) *Trans. Inst. Pure Chem. Reagents* (U.S.S.R.), No. 13 (1933), 48; *Chem. Abstracts*, **27** (1933), 4736.

measured by many authors⁽⁸⁾, only Y. Shibata has studied all nitro-compounds of the series. H. Ley and Y. Shibata have discovered that *trans*-dinitro-tetrammine-cobaltic salts have an absorption band at 4000 mm.$^{-1}$ of the wave number, i.e. the third band, that is wanted in the cis-isomers. Y. Shibata has also indicated that two of the nitro-radicals in trinitro-triammine- and tetranitro-diammine-cobaltic salts must occupy the trans-position on account of the existence of this third band. Still, I have studied on the absorption band in the neighbourhood of 320–350 mμ of wave length, i.e. the second band, and have found that this band changes owing to the position and the number of nitro-radicals in the complex salts.

Comparison of the absorption curves⁽⁹⁾. (1) $[Co(NH_3)_5(NO_2)]Cl_2$ and *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$. The absorption curves of both salts (curves A and B in Fig. 1) are similar except in their extinction coefficients: both have their maximum absorption at 325 mμ of wave length. The comparison of their extinction coefficient shows that the absorption power of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ is about double that of $[Co(NH_3)_5(NO_2)]Cl_2$. This absorption curve of pentammine-salt is different from that given in the paper of R. Samuel⁽⁸⁾, but similar to that of $[Co(NH_3)_5(NO_2)]SO_4$ obtained by R. Samuel and M. Uddin⁽¹⁰⁾.

(2) *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ and *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$. The maximum absorption of these salts is different from each other, i.e. that of cis-salt is found at 325 mμ showing log $\varepsilon = 3.46$ (ε denotes an extinction coefficient) at this wave length, but the trans-salt (curve C in Fig. 1) gives its maximum absorption at 347 mμ and log $\varepsilon = 3.55$ at that wave length. The trans-salt is more hyperchromic and more bathochromic than the cis-salt, and this is analogous to the Ley's curves measured qualitatively. In spite of the difference of position and intensity of the absorption bands, both absorptions are found to be almost coincident at 270–280 mμ of wave length⁽¹¹⁾.

(3) $[Co(NH_3)_3(NO_2)_3]$. This salt has the maximum absorption near 340 mμ of wave length where log ε is 3.65 (curve D in Fig. 1). For

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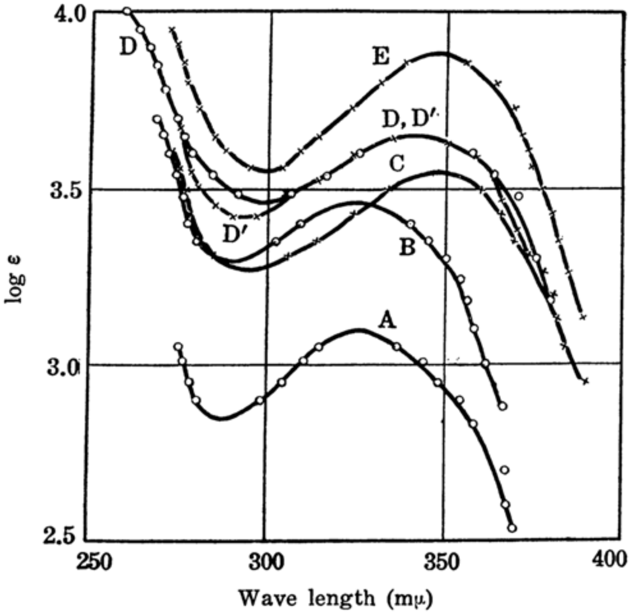
(8) A. Hantzsch, *Z. physik. Chem.*, **70** (1910), 372; H. Ley and H. Winkler, *Ber.*, **45** (1912), 372; A. Piutti, *Ber.*, **45** (1912), 1830; R. Luther and A. Nikolopulos, *Z. physik. Chem.*, **82** (1913), 361; Y. Shibata, *J. Chem. Soc. Japan*, **30** (1915), 1243; R. Samuel, *Z. Physik*, **70** (1931), 43.

(9) Measured by the author, this Bulletin, **12** (1937), 71.

(10) *Trans. Faraday Soc.*, **31** (1935), 423.

(11) The author thinks that the electric valencies of complex ions have a certain relation with their absorption which exists in their shorter wave length as in this case. Refer also to the paper: T. Uemura and H. Sueda, this Bulletin, **10** (1935), 267.

a reason which will be explained later, I have arbitrarily selected fifteen wave lengths between 275 mμ and 380 mμ by using the absorption coefficients of *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ and that of $[Co(NH_3)_5(NO_2)]Cl_2$, and the extinction coefficients corresponding to these selected wave lengths were added to form a curve D′ in Fig. 1. Curve D′ is therefore traced by mixing one mol of each salt, and it should be assumed as a curve expressing one mol. Curves D and D′ in Fig. 1 show a good coincidence in the position and the intensity of the absorption band, but a slight difference can be seen only in the shorter wave length below 300 mμ.



A $[Co(NH_3)_5(NO_2)]Cl_2$
B *cis* $[Co(NH_3)_4(NO_2)_2]Cl$
C *trans* $[Co(NH_3)_4(NO_2)_2]Cl$
D $[Co(NH_3)_3(NO_2)_3]$
D′ A+C
E K $[Co(NH_3)_2(NO_2)_4]$

Fig. 1.

(4) *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ and $K[Co(NH_3)_2(NO_2)_4]$. The curves given by these two salts are similar except their absorption power: both have the maximum absorption at 347 mμ. The relation of the absorption powers shown by both salts is perfectly the same as in case (2), i.e. the absorption power of $K[Co(NH_3)_2(NO_2)_4]$ is double that of *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$.

Discussion. It is generally accepted that an absorption of the co-ordinatedly saturated complex ion is due to a mutual action produced between a central ion and co-ordinated atomic groups. In the above comparison, cobalt is selected as the central atom and only ammonia molecules and nitro-radicals are co-ordinated in the complex ion, so the difference which occurs in the absorption can be considered in connection with the configuration of complex ions, whatever the mechanism of the light absorption may be. It is convenient to say that the absorption capacity due to the ammonia molecules which are co-ordinated with cobalt atom is very weak in comparison with that of nitro-radicals, i.e. the extinction coefficient of the maximum absorption given by $[Co(NH_3)_6]Cl_3$ is only about 40 (at 336 mμ) (12), while that given by $[Co(NH_3)_5(NO_2)]Cl_2$, the weakest absorbent of nitro-ammines, expresses 1260 (at 325 mμ). As an additivity can apply to the intensity of light absorption, an absorption given by nitro-ammine-cobaltic salts may be supposed only with the nitro-radicals, in neglecting the influences due to ammonia molecules.

According to Werner's co-ordination theory, we can safely conclude that any groups co-ordinated with the hexacovalent central ion can have no positions but cis and trans.

In comparison (1), the complex ion containing two nitro-radicals in cis-position shows that its absorption band is situated almost similarly to that given by the complex which has only one nitro-radical, but the absorption capacity of the former is nearly double that of the latter. In this case, no change on the position of the absorption band and the increase in extinction coefficients can tell me that the mutual actions between the cis-co-ordinated groups are themselves so weak that they are negligible. It is also true that the action upon the central atom of two co-ordinated groups which occupy cis-position is nearly identical when the groups is alone in a complex radical, and they show only the additivity. An analogous case can be found in organic dyes which contain several identical chromophores in the molecule, and these chromophores cannot be supposed to react one upon another from the constitution. J. D. Piper and W. R. Brode(13) have recently reported that, in such a case, the absorption band does not change its position, and its absorption capacity is increased in proportion to the number of chromophores.

From comparison (2), when two nitro-radicals take the trans-position in a complex radical, the position of the absorption band due to these

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(12) T. Uemura and H. Sueda, this Bulletin, **10** (1935), 50; R. Samuel, *loc. cit.*; J. Kranig, *Arch. phys. biol.*, **7** (1929), 148.

(13) *J. Am. Chem. Soc.*, **57** (1935), 135.

radicals is different from that given by a cis-compound, and the absorption capacity is also slightly different in these cases. It can be proved that these spectrochemical differences based on stereoisomers are produced by the central ion and co-ordinated groups and also by the stereochemical configuration that must be taken into account. When these co-ordinated groups are supposed to take a position at every corner of a regular octahedron having some influences upon the central ion, the influence of a co-ordinated group upon the centre may be said to have the deepest relation to that which is situated on its opposite side. The consequence of this consideration is that the most important factor to control the position of an absorption band must be a pair of co-ordinated groups situated in trans-position. The existence of a characteristic absorption band due to such a pair of groups which occupy the trans-position may be assumed, and the author has provisionally given the name of "characteristic absorption" to such an absorption. On the other hand, as the influence against an absorption given by cis-group is not found on the position of bands but only an additivity can be observed, we can make the following assumption: an absorption due to a metallic complex ion is represented by the sum of characteristic absorption given by the pair of groups occupied in trans-position in a co-ordinated complex. It is very important to analyse an absorption spectrum of a solution to give it a theoretical meaning, and Y. Shibata and K. Harai(14) as well as others(15) have already studied this question. Although the idea proposed by the present author is somewhat hypothetical, yet, it may also be recognized as a kind of analysis for an absorption spectrum of complex salt solutions.

With this assumption, the absorption spectra of nitro-ammine salts can be explained as follows: the absorption of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ is assumed as a sum of three characteristic absorptions, i.e. $(NH_3\text{-}Co\text{-}NH_3)$(16) and $2(NH_3\text{-}Co\text{-}NO_2)$ (see Fig. 2). The absorption of $[Co(NH_3)_5(NO_2)]Cl_2$ can also be resolved into $2(NH_3\text{-}Co\text{-}NH_3)$ and $(NH_3\text{-}Co\text{-}NO_2)$. Since $(NH_3\text{-}Co\text{-}NH_3)$ can be neglected in comparison with $(NH_3\text{-}Co\text{-}NO_2)$, as described before, the absorption given by both salts shows therefore that, due to the number of $(NH_3\text{-}Co\text{-}NO_2)$ contained,

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(14) *J. Chem. Soc. Japan*, **56** (1935), 1.

(15) W. R. Brode, *Proc. Roy. Soc.* (London), A, **118** (1928), 286; *J. Am. Chem. Soc.*, **56** (1934), 1842.

J. P. Mathiue (*Bull. soc. chim.*, [5], **3** (1936), 463) has recently reported a very interesting relation between the constitution of co-ordinated complex salts and the separation of their absorption bands.

(16) This symbol represents the characteristic absorption assumed to be produced by two ammonia molecules in trans-position having cobalt as the central ion.

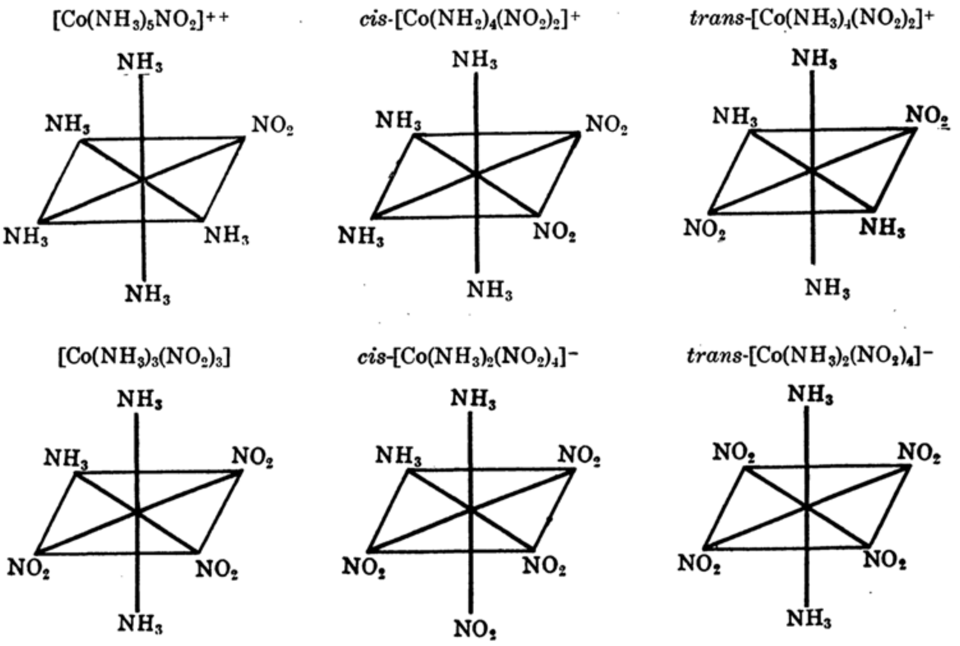

Fig. 2.

the former cis-compound has double the absorption intensity of the latter pentammine-complex showing similar curves. With regard to the *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$, its absorption may be considered as the sum produced by $2(NH_3\text{-}Co\text{-}NH_3)$ and $(NO_2\text{-}Co\text{-}NO_2)$, and it is almost the same with $(NO_2\text{-}Co\text{-}NO_2)$.

This point of view is also held in comparison (3). Y. Shibata has already determined the configuration of $[Co(NH_3)_3(NO_2)_3]$ as described in Fig. 2, i.e. two of nitro-radicals are in trans-position. Its absorption can therefore be resolved into $(NH_3\text{-}Co\text{-}NH_3)$, $(NH_3\text{-}Co\text{-}NO_2)$ and $(NO_2\text{-}Co\text{-}NO_2)$. So, it is expected that the absorption might be represented as a sum of those given by $[Co(NH_3)_5(NO_2)]Cl_2$ and *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ by neglecting the effect of $(NH_3\text{-}Co\text{-}NH_3)$ as before. Curve D′ in Fig. 1, traced by taking this sum, shows a good coincidence especially in the band with the observed curve D obtained from the complex $[Co(NH_3)_3(NO_2)_3]$.

The configuration of $K[Co(NH_3)_2(NO_2)_4]$ has not yet been determined. Y. Shibata, T. Maruki(17) and W. Thomas(18) have already

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(17) *J. Coll. Sci., Tokyo Imp. Univ.*, **41** (1917), Art. 2.
(18) *J. Chem. Soc.*, **123** (1923), 617.

given a cis-configuration to the compound, while E. H. Riesenfeld and R. Klement(19), a trans-configuration.

As shown in the comparison (4), the absorption intensity due to the complex $K[Co(NH_3)_2(NO_2)_4]$ is nearly twice that of the *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$. According to the above-mentioned idea, this is easily understood by assuming that $K[Co(NH_3)_2(NO_2)_4]$ may contain two (NO_2-Co-NO_2) in its complex radical. The author wishes to give a trans-configuration (see Fig. 2) to this Erdemann's salt.

Application of the above-mentioned assumption to aquo-chloro-ammine salts of cobalt and chromium. In the case of the already described nitro-ammine complex salts, as their absorption capacity is so remarkably increased by the nitro-radical that the influence due to (NH_3-Co-NH_3) can be neglected, the discussion becomes comparatively simple. But to give more weight to the assumption, the author has tried to apply it to the cases where the absorptions are little influenced by the substitution which occurs in a complex radical.

According to the author's assumption, when two or three absorption curves are known for some compounds in a series, a characteristic absorption can be deduced, and an absorption of an other salt can be assumed by a suitable combination of those characteristic absorptions. To verify this assumption, observed curves were compared with those which are assumed from the characteristic curves.

(1) *Absorption curves given by cobalti-ammine complex salts in visible region.* Absorption curves of $[Co(NH_3)_6]Cl_3$(20), $[Co(NH_3)_5(H_2O)]Cl_3$(20), $[Co(NH_3)_4(H_2O)_2]Cl_3$(20), $[Co(NH_3)_5Cl]Cl_2$(20), $[Co(NH_3)_4Cl(H_2O)]Cl_2$(21) and *cis*-$[Co(NH_3)_4Cl_2]Cl$(21) were used for calculation.

According to my assumption, the absorption of $[Co(NH_3)_6]Cl_3$ should be three times the characteristic absorption (NH_3-Co-NH_3). The absorption of $[Co(NH_3)_4(H_2O)_2]Cl_3$ should be represented by the sum of (NH_3-Co-NH_3) and 2(NH_3-Co-H_2O), as this complex salt is supposed to take cis-configuration. Therefore, (NH_3-Co-H_2O) can be calculated by deducting (NH_3-Co-NH_3), which is given as 1/3 of the absorption $[Co(NH_3)_6]Cl_3$, from the absorption of $[Co(NH_3)_4(H_2O)_2]Cl_3$ and

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(19) *Z. anorg. allgem. Chem.*, **124** (1922), 1.

(20) The absorption data of these salts were transferred from Colmar and Schwartz's work (*loc. cit.*).

(21) The absorption data of these salts were obtained from the curves published in the paper by Luther and Nikolopulos (*loc. cit.*).

dividing the difference in two. By combining (NH_3-Co-NH_3) and (NH_3-Co-H_2O), the value of "2(NH_3-Co-NH_3) + (NH_3-Co-H_2O)" can easily be deduced as the calculated value corresponding to the absorption shown by $[Co(NH_3)_5(H_2O)]Cl_3$. This calculation gives a good coincidence with the observation as seen in Table 1.

Table 1(22).

λ (mμ)	$[Co(NH_3)_6]Cl_3$	(NH_3-Co-NH_3)	$\left[\begin{matrix}Co(NH_3)_4\\(H_2O)_2\end{matrix}\right]Cl_3$	(NH_3-Co-H_2O)	$[Co(NH_3)_5(H_2O)]Cl_3$	
					obs.	calc.
450	46.1	15.4	22.4	3.5	34.9	34.3
460	53.8	17.9	30.4	6.3	40.8	42.1
470	56.1	18.7	36.4	8.9	45.5	46.3
480	55.5	18.5	44.9	13.2	46.5	50.2
490	49.1	16.4	49.5	16.6	47.9	49.4
500	33.6	11.2	52.9	20.9	45.5	43.3
520	18.9	6.3	49.1	21.4	39.2	34.0
540	5.7	1.9	39.3	18.7	25.9	22.5
560	0.4	0.1	26.2	13.4	13.6	13.6

The value of (NH_3-Co-Cl) can be obtained from (NH_3-Co-NH_3) and the absorption data shown by $[Co(NH_3)_5Cl]Cl_2$ which should be represented as "2(NH_3-Co-NH_3) + (NH_3-Co-Cl)". As $[Co(NH_3)_4(H_2O)Cl]Cl_2$ takes a cis-configuration, its absorption should be given by "(NH_3-Co-NH_3) + (NH_3-Co-H_2O) + (NH_3-Co-Cl)". As Table 2 indicates, the sum of these characteristic absorptions obtained from calculation are somewhat greater than the observed values, but the position of the maximum absorption band is nearly matched.

The absorption of *cis*-$[Co(NH_3)_4Cl_2]Cl$ can be resolved into "(NH_3-Co-NH_3) + 2(NH_3-Co-Cl)", and the calculated values are also much greater than the observed data, although a coincidence for the position of the absorption band can be recognized. A part of the discordance of calculated and observed values in extinction coefficients comes perhaps

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(22) The numerical data in the tables used in this paper are shown in extinction coefficient (ε), 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 mol; d, layer length of solution in cm.

from the difficulty of accurate measurement which is due to the instability of the salt in aqueous solution.

Table 2.

λ (mμ)	$[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$	($\mathrm{NH_3}$-Co-Cl)	$[\mathrm{Co(NH_3)_4(H_2O)Cl}]\mathrm{Cl_2}$		*cis*-$[\mathrm{Co(NH_3)_4Cl_2}]\mathrm{Cl}$	
			obs.	calc.	obs.	calc.
450	24.2	-6.6	16	12.3	15.5	2.2
460	30.4	-5.4	20	18.8	20	7.1
470	33.4	-4.0	25	23.6	25	10.7
480	37.5	0.5	29.5	32.2	29.5	19.5
490	40.9	8.1	35	41.1	35	32.6
500	43.1	20.7	40	52.8	41	52.6
520	47.5	34.9	46.5	62.6	48	76.1
540	44.0	40.2	48	60.8	48	82.3
560	34.6	34.4	33	47.8	41	68.9

(2) *Absorption curves given by chromi-ammine complex salts in visible and ultraviolet regions.* $[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}$(23), $[\mathrm{Cr(NH_3)_5(H_2O)}]\mathrm{Cl_3}$(23), $[\mathrm{Cr(NH_3)_4(H_2O)_2}]\mathrm{Cl_3}$(23), $[\mathrm{Cr(NH_3)_3(H_2O)_3}]\mathrm{Cl_3}$(23), $[\mathrm{Cr(NH_3)_2(H_2O)_4}]\mathrm{Cl_3}$(20) and $[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$(20) were taken for calculation. Analysis and synthesis of the absorption curves can be performed in the same manner when applied to the cobalt-ammines. The value of ($\mathrm{NH_3}$-Cr-$\mathrm{H_2O}$) was obtained from the absorption of $[\mathrm{Cr(NH_3)_3(H_2O)_3}]\mathrm{Cl_3}$, and that of ($\mathrm{NH_3}$-Cr-$\mathrm{NH_3}$), from the absorption given by $[\mathrm{Cr(NH_3)_5(H_2O)}]\mathrm{Cl_3}$ and ($\mathrm{NH_3}$-Cr-$\mathrm{H_2O}$). By combining these characteristic absorptions, the calculated values of $[\mathrm{Cr(NH_3)_4(H_2O)_2}]\mathrm{Cl_3}$ and $[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}$ were deduced. These are compared with the observed data in Table 3. Next, the absorption of $[\mathrm{Cr(NH_3)_2(H_2O)_4}]\mathrm{Cl_3}$ was calculated from the value of ($\mathrm{H_2O}$-Cr-$\mathrm{H_2O}$) which is given from $[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$, and that of ($\mathrm{NH_3}$-Cr-$\mathrm{H_2O}$) for comparing with the observed data. These observed and calculated values are considered as showing a passable coincidence in Table 3.

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(23) The absorption data in the visible region of these salts were taken from Colmar and Schwartz's publication (*loc. cit.*), and those in ultraviolet from the curves measured by Uemura and Sueda (*loc. cit.*).

Table 3.

λ(mμ)	$[Cr(NH_3)_3(H_2O)_3]Cl_3$	(NH_3-Cr-H_2O)	$[Cr(NH_3)_5(H_2O)]Cl_3$	(NH_3-Cr-NH_3	$[Cr(NH_3)_4(H_2O)_2]Cl_3$		$[Cr(NH_3)_6]Cl_3$	
					obs.	calc.	obs.	calc.
320	6	2	8	3	7	7	8	9
330	9	3	15	6	10	12	18	18
340	11	4	19	8	14	16	22	24
350	15	5	24	9	18	19	28	27
360	19	6	29	12	23	24	29	36
370	23	8	30	11	26	27	21	33
380	26	9	26	9	28	27	16	27
390	29	10	23	7	25	27	10	21
400	29	10	20	5	22	25	7	15
410	26	9	20	6	19	24	7	16
420	23	8	21	7	—	—	14	21
450	12.2	4.1	26.7	11.3	19.7	19.5	36.1	33.9
460	16.5	5.5	31.9	13.2	22.8	24.2	40.8	39.6
470	18.7	6.2	34.1	14.0	26.6	26.4	39.2	42.0
480	22.0	7.3	35.4	14.0	30.5	28.6	33.8	42.0
490	25.6	8.5	34.4	13.0	30.9	30.0	27.5	39.0
500	26.1	8.7	31.5	11.4	30.6	28.8	19.7	34.2
510	25.4	8.5	27.8	9.7	28.1	26.7	12.6	29.1
520	24.8	8.3	21.9	6.8	24.0	23.4	8.4	20.4
530	22.0	7.3	17 2	5.0	19.8	19.6		
540	19.7	6.6	12.1	2.8	14.4	16.0		
550	16.7	5.6	9.4	1.9	10.0	13.1		

λ (mμ)	$[Cr(H_2O)_6]Cl_3$	(H_2O-Cr-H_2O)	$[Cr(NH_3)_2(H_2O)_4]Cl_3$	
			obs.	calc.
500	3.6	1.2	19.1	18.6
510	4.3	1.4	20.1	18.4
520	5.0	1.7	20.6	18.3
530	5.8	1.9	20.2	16.5
540	6.7	2.2	19.3	15.4
550	7.4	2.5	16.7	13.7

Consideration on results. Some discordances between the calculated and observed values were found in the above comparison. I think that the causes of this difference come first from the weakness of the assumption itself and secondly from the experimental error produced by the quantitative measurement of absorption.

The weakness of the assumption is due to the complete neglect of the influence given by the groups situated in cis-position. If the oscillations of the co-ordinated groups for central ion may be supposed to have an effect upon an absorption, some influences, produced by the groups in cis-position, would be naturally taken into account, though they might be slight. So, it is sure that one of the causes has appeared in adopting the data which are neglected for the corrections due to the cis-groups.

The second cause can of course be considered as nearly inevitable. For the purpose of ascertaining the number of experimental errors produced by an absorption measurement, I have taken an example of results given by R. I. Colmar, F. W. Schwartz⁽⁴⁾ and F. W. Beyer⁽²⁴⁾ for the absorption of $[Co(NH_3)_6]Cl_3$. The mean difference in the extinction coefficients measured by these authors was found to be about 8% between 450 mμ and 500 mμ of wave length.

Strictly speaking, the assumption that I have proposed, needs some corrections. But the author believes his assumption can afford a means to determine the configurations of complex salts within a limit of the present accuracy of absorption measurement. It may also suggest some physical meanings on light absorption of complex salts.

Summary.

(1) From the comparison of absorption curves given by nitro-ammine-cobaltic complex salts near 360 mμ of wave length, the following assumption was deduced: the absorption band presented by complex salt solutions can be resolved into the elements (characteristic absorption) which are due to the pairs of co-ordinated groups situated in trans-position in a complex radical, and these elements show an additive property in the same complex ion.

(2) By taking into account of the above-mentioned point of view, $K[Co(NH_3)_2(NO_2)_4]$ (Erdemann's salt) should have a trans-configuration.

(3) This assumption may also be applied to the absorptions given by aquo-chloro-ammine salts of cobalt and chromium, in visible and ultra-violet regions.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Shibata of the Imperial University of Tokyo, and also to Assist. Prof. T. Uemura of the Tokyo University of Engineering for their kind encouragements.

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(24) *Z. Physik*, **83** (1933), 806.