Absorption Spectra of Coordination Compounds. V. The Hyperchromic Series of Ligands

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Introduction

Although an extensive literature is available about the nature of absorption bands of metallic complexes and as to the relations among the wave-lengths of their absorption maxima, investigations on the effects of substitution of ligands on the intensity of absorption have seldom been carried out.(1)(2) One of the present authors has reported that the magnitude of extinction coefficients of a "specific absorption band" is approximately proportional to the number of the ligands concerned in the complex.(3) Mathieu(4) has found that extinction coefficients for an absorption band of a cobaltic complex increase as molecules of ammonia are substituted by heavier ligands such as ethylenediamine and propylenediamine, the effect being attributed mainly to the change of mass. Sueda(5) attempted to express intensities of absorption bands of several complexes by the addition of component absorptions, each of which was assigned over the regions of an absorption band for a pair of respective ligands in *trans*-positions.

The present paper deals with the effect of substitution of ligands on the maximal extinction coefficients of coordination compounds.

Hyperchromic Series of Ligands

If one ligand in a complex is substituted for by another, the absorption bands of the complex are subjected to a hypsochromic or bathochromic effect respectively according as the immigrant ligand precedes or stands behind the emigrant in the spectrochemical

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(1) R. Tsuchida and M. Kobayashi, *J. Chem. Soc. Japan*, **59**, 591 (1938).

(2) R. Tsuchida and H. Kuroya, ibid., **59**, 1142 (1938).

(3) R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 476 (1938).

(4) J. P. Mathieu, *Bull. Soc. Chim. France*, **3**, 463 (1936).

(5) H. Sueda, *J. Chem. Soc. Japan*, **57**, 406, 542 (1936); ibid., **59**, 47 (1938).

series.(6) At the same time the bands suffer a hyperchromic or hypochromic change according to the nature of the ligands concerned. Thus NO_2 is more hyperchromic than NH_3 and the latter in its turn is hyperchromic to H_2O, as is shown in Table 1.

Table 1

Comparison of Hyperchromic Effects of Ligands for the First Absorption Band

Compound	ν 10^{13}/sec.	log ε	Ref.
NO_2 and NH_3			
$[Co(NH_3)_6]Cl_3$	63.6	1.66	(7)
$[Co(NH_3)_5NO_2]Cl_2$	65.8	1.95	(7)
$[Co(NH_3)_4(NO_2)_2{}^{(1}_{(2)}]Cl$	65.5	1.99	(7)
$[Co(NH_3)_3(NO_2)_3]$	68.7	2.21	(7)
$[Co(NH_3)_2(NO_2)_4]NH_4$	69.0	2.56	(7)
NH_3 and H_2O			
$[Co(NH_3)_6]Cl_3$	63.6	1.66	(7)
$[Co(NH_3)_5H_2O]Cl_3$	61.6	1.62	(7)
$[Co(NH_3)_4(H_2O)_2]Cl_3$	60.0	1.40	(7)

The extinction coefficients of nitroammine complexes increase with the number of NO_2-ions in coordination.

Further examples of substitution are shown in Table 2, in which oxalate ion (ox) is the most hyperchromic and NH_3 the most hypochromic, ethylenediamine (en) being intermediate.

Table 2

Comparison of Hyperchromic Effects of Ligands for the First and the Second Absorption Bands

Compound	1st Band		2nd Band		Ref.
	ν 10^{13}/sec.	log ε	ν	log ε	
en and NH_3					
$[Co(NH_3)_6]Cl_3$	63.6	1.66	88.8	1.57	(7)
$[Co(NH_3)_2en_2]Cl_3$	64.8	1.72	89.2	1.62	(9)
$[Co\ en_3]Br_3$	65.2	1.88	89.2	1.81	(9)
ox and en					
$[Co\ en_3]Br_3$	65.2	1.88	89.2	1.81	(9)
$[Co\ en_2ox]Br$	60.0	1.96	84.2	2.10	(9)
$[Co\ ox_3]K_3$	49.6	2.09	71.0	2.19	(9)

From the above considerations, it is expected that there should be a series concerning the hyperchromic effects of ligands. On the basis of experimental data with pentammine cobaltic complexes (Table 3) was obtained the following series as the descending order of the hyperchromic effect of ligands on the first absorption band(7):

$$NCS^- \quad CrO_4^= \quad SO_3^= \quad NO_2^- \quad CO_3^= \quad C_2O_4^= \quad \text{en}$$
$$OH^- \quad NO_3^- \quad SO_4^= \quad Br^- \quad NH_3Cl^- \quad H_2O$$

Table 3

Hyperchromic Series with Pentammine Complexes for the First Absorption Band

Ligand	Compound	ν 10^{13}/sec.	log ε	Ref.
NCS^-	$[Co(NH_3)_5NCS]Cl_2$	60.2	2.16	(6), (7)
$CrO_4^=$	$[Co(NH_3)_5CrO_4]NO_3$	55.6	2.16	(6), (7)
$SO_3^=$	$[Co(NH_3)_5SO_3]Cl$	63.6	2.15	(8)
NO_2^-	$[Co(NH_3)_5NO_2]Cl_2$	65.8	1.95	(6), (7)
$CO_3^=$	$[Co(NH_3)_5CO_3]NO_3$	59.0	1.90	(6), (7)
$ox^=$	$[Co(NH_3)_5ox]Br$	59.2	1.87	(6), (7)
OH^-	$[Co(NH_3)_5OH](NO_3)_2$	59.8	1.82	(6), (7)
NO_3^-	$[Co(NH_3)_5NO_3](NO_3)_2$	60.0	1.74	(6), (7)
$SO_4^=$	$[Co(NH_3)_5SO_4]I$	60.0	1.70	(6), (7)
Br^-	$[Co(NH_3)_5Br]Br_2$	55.4	1.68	(6), (7)
NH_3	$[Co(NH_3)_5NH_3]Cl_3$	63.6	1.66	(6), (7)
Cl^-	$[Co(NH_3)_5Cl]Cl_2$	57.5	1.64	(6), (7)
H_2O	$[Co(NH_3)_5H_2O]Cl_3$	61.6	1.62	(6), (7)

It is seen that the above series hold also for the tetrammine series (Table 4), and for complexes containing only one kind of ligand (Table 5).

Table 4

Hyperchromic Series with Cobaltic Tetrammine Complexes

Ligand	Compound	1st Band		2nd Band		Ref.
		ν 10^{13}/sec.	log ε	ν 10^{13}/sec.	log ε	
NO_2^-	$[Co(NH_3)_4(NO_2)_2]Cl$					
	trans.	67.9	2.32			(7)
	cis.	65.5	1.99			(7)
$CO_3^=$	$[Co(NH_3)_4CO_3]Cl$	57.2	2.02	82.6	2.03	(7)
$C_2O_4^=$	$[Co(NH_3)_4ox]Cl$	58.8	1.78	84.0	1.88	(7)
NH_3	$[Co(NH_3)_4(NH_3)_2]Cl_3$	63.6	1.66	88.8	1.57	(7)
H_2O	$[Co(NH_3)_4(H_2O)_2]Cl_3$	60.0	1.40	84.0	1.48	(7)

Table 5

Hyperchromic Series with Cobaltic Hexa-coordinated Complexes

Ligand	Compound	1st Band		2nd Band		Ref.
		ν 10^{13}/sec.	log ε	ν 10^{13}/sec.	log ε	
$ox^=$	$[Co\ ox_3]K_3$	49.6	2.09	71.0	2.19	(7)
en	$[Co\ en_3]Br_3$	65.2	1.88	89.2	1.81	(10)
NH_3	$[Co(NH_3)_6]Cl_3$	63.6	1.66	88.8	1.57	(7)

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(6) R. Tsuchida, *J. Chem. Soc. Japan*, **59**, 586, 731, 819 (1938).

(7) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938), etc.

The above series, which has been deduced for simpler cases, would be considered to hold for more general cases unless mutual relations among ligands are highly complicated. The series holds also for chromic complexes, so far without the slightest alteration, though experimental data are less numerous (Table 6 and 7) in comparison with cobaltic complexes.

Table 6

Comparison of Hyperchromic Effects of Ligands for Chromic Complexes

Compound	1st Band ν 10^{13}/sec.	1st Band log ε	2nd Band ν 10^{13}/sec.	2nd Band log ε	Ref.
NCS and NH_3					
$[Cr(NH_3)_6]Cl_3$	65.0	1.48	86.0	1.44	(7)
$[Cr(NH_3)_5NCS](NCS)_2$	61.6	1.82	(83)	1.67	(7)
$[Cr(NH_3)_2(NCS)_4]NH_4$	57.5	1.95	(75)	1.75	(7)
$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00	(7)
ox and H_2O					
$[Cr(H_2O)_6]Cl_3$	52.5	1.02	73.6	1.20	(7)
$[Cr(H_2O)_2ox_2]K$ *cis.*	53.1	1.80	72.3	1.83	(10)
$[Cr(H_2O)_2ox_2]K$ *trans.*	53.1	1.71	71.4	1.63	(10)
$[Cr\ ox_3]K_3$	52.6	1.87	71.4	1.91	(10)

Table 7

Hyperchromic Series with Chromic Complexes

Ligand	Compound	1st Band ν 10^{13}/sec.	1st Band log ε	2nd Band ν 10^{13}/sec.	2nd Band log ε	Ref.
NCS^-	$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00	(7)
$ox^=$	$[Cr\ ox_3]K_3$	52.6	1.87	71.4	1.91	(11)
en	$[Cr\ en_3]Cl_3$	65.9	1.84	85.7	1.72	(11)
NH_3	$[Cr(NH_3)_6]Cl_3$	65.0	1.48	86.0	1.44	(7)
H_2O	$[Cr(H_2O)_6]Cl_3$	52.2	1.02	73.6	1.20	(7)

Relation between ν_{max} and $\mathcal{E}_{max}$

It is of interest to compare the hyperchromic and the spectrochemical series.

The hyperchromic series:

$$NCS^-\ CrO_4^=\ SO_3^=\ NO_2^-\ CO_3^=\ C_2O_4^=\ en$$
$$OH^-\ NO_3^-\ SO_4^=\ Br^-\ NH_3Cl^-\ H_2O$$

The spectrochemical series(6), (12):

$$CN^-\ NO_2^-\ SO_3^=\ en\ NH_3ONO^-\ H_2O\ NCS^-$$
$$SO_4^=\ NO_3^-\ OH^-\ C_2O_4^=\ CO_3^=\ Cl^-\ CrO_4^=\ Br^-$$

It appears to be difficult at first sight to find any relation between the series, for ligands preceding in one of the series do not always take precedence in the other. For examples, NCS^- at the head of the hyperchromic series stands in the middle part of the spectrochemical series and $CrO_4^=$, one of the most hyperchromic ligands, is nearly at the tail end of the latter series, while NO_2^- is situated among the highest positions in both the series.

One of the principal factors which determine the nature of absorption of a complex is the kind of atom coordinated directly to the central ion. From this viewpoint the ligands are classified into the following groups: viz. (A) those coordinated with an atom of inert-gas structure, such as Cl^-, NH_3, OH_2 and their derivatives including oxygen-acid anions, (B) those coordinated with an atom of incomplete-shell structure, such as NO_2^-, and (C) those coordinated with an atom having one or more π-electrons, such as NCS^-, CN^-, N_3^-, NC_5H_5, NO, CO, etc. Among the similar ligands of the group A, there exists a regularity with respect to the hyperchromic and the hypsochromic property. For example, in Fig. 1 are plotted $\mathcal{E}_{max}$'s against ν_{max}'s of the first bands of pentammine-cobaltic complexes containing various oxygen-acid anions. It is seen in the figure that an approximately linear relation holds between ν_{max} and $\mathcal{E}_{max}$.

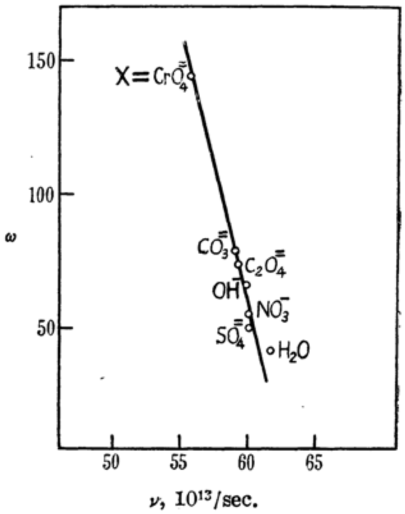

Fig. 1.—ν versus ε for the first band of pentammine cobaltic complexes containing various oxygen-acid anions, $[Co(NH_3)_5X]^{(3-n)+}$.

A similar relation exists between ν_{max} and $\mathcal{E}_{max}$ of the first band of halogenopentammine

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(8) A. v. Kiss and D. v. Czegledy, *Z. Anorg. Chem.*, **235**, 407 (1938).

(9) R. Tsuchida and H. Kuroya, This Bulletin, **15**, 427 (1940).

(10) K. Sone, *J. Chem. Soc. Japan*, **71**, 270 (1950).

(11) A. Mead, *Trans. Faraday Soc.*, **30**, 1052 (1934).

(12) Y. Shimura, This Bulletin, **25**, 49 (1952).

Table 8

Compound	1st Band ν 10^{13}/sec.	1st Band log ε	2nd Band ν 10^{13}/sec.	2nd Band log ε	3rd Band ν 10^{13}/sec.	3rd Band log ε
$K_3[Fe(CN)_6]$	72.5	2.97	100.0	3.29	115.5	3.24
$K_3[Cr(CN)_6]$	78.9	1.81	96.6	1.66	114.7	3.87
$K_3[Co(CN)_6]$	(72.0)	(−0.28)	97.2	2.37	117.0	2.08

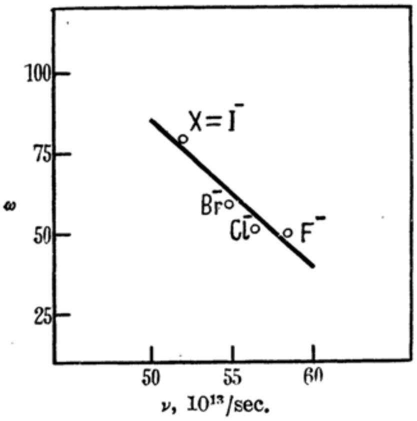

Fig. 2.—ν versus ε for the first band of halogeno-pentammine cobaltic complexes, $[Co(NH_3)_5X]^{2+}$.

cobaltic complexes, as is shown in Fig. 2⁽¹³⁾.

For similar ligands of the group A, therefore, the order in the hyperchromic series is completely reverse to that in the spectrochemical series, showing that the stronger the coordinate linkage the less the chances of transitions of d-electrons.

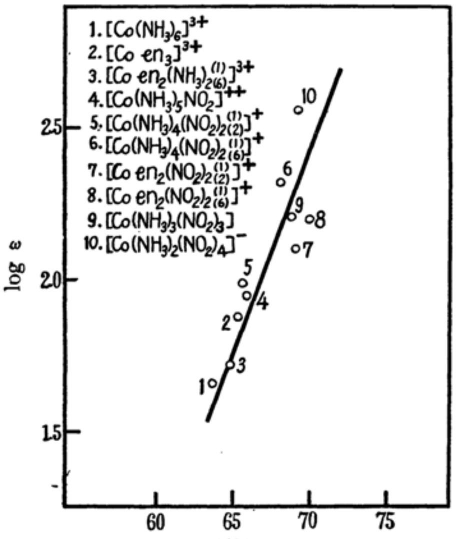

Fig. 3.—ν versus log ε for the first band of nitroammine cobaltic complexes.

In Fig. 3 are plotted log $\mathcal{E}_{max}$'s against the corresponding ν_{max}'s of the first bands of complexes containing NO_2^- of the group B.

It is found that there exists a quite different relation from that for the ligands of group A. Namely, NO_2^- stands almost at the head of both the hyperchromic and the hypsochromic series, making a remarkable contrast to the ligands of group A, among which the more hyperchromic are the more bathochromic.

This difference between the groups A and B suggests that the modes of coordination of the ligands are quite different from each other. The incomplete shell of the nitrogen atom in NO_2^- favours the transitions of d-electrons, which reinforce the coordinate linkage, resulting in the strong absorption and the stable coordination.

The absorption of complexes containing ligands of the group C seems rather complicated. The high extinction coefficients of rhodanato-complexes may be explained as due to the interaction of the π-electron of the ligand with d-electrons of the central cation, which facilitates transitions of the latter electrons. To this category belongs CN^-, which is usually hypsochromic and hyperchromic. For examples, the first bands of $K_3[Fe(CN)_6]$ and $K_3[Cr(CN)_6]$ are fairly strong as is shown in Table 8.⁽¹⁴⁾

But CN^- is sometimes hypsochromic and hypochromic, e.g., the first band of $K_3[Co(CN)_6]$ is extremely weak.⁽¹⁴⁾ This fact may be understood as due to a sort of anti-parallel bonding between the d- and π-electron, which suppresses transitions of the d-electron. As an evidence for such a bonding, may be cited the planar configuration of $[Au(dipyridyl)(CN)_2]^-$ and $[Au(phenarthrolin)(CN)_2]^-$, in spite of the pseudo-inert-gas structure of the central ion.

The position of CN^- in the hyperchromic series, therefore, varies according to the nature of the central ion in such a way that it is hypochromic or hyperchromic according as the central ion has the same number of

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(13) Experimental data are taken from the work by M. Linhard and M. Weigel, *Z. Anorg. Chem.*, **266**, 4 (1951).

(14) H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan*, **61**, 597 (1940).

d-electrons as the number of the ligands or not.

The Hyperchromic Effects of Ligands in Geometrical Isomers

It has been recognized by investigations on chemical behaviour and absorption spectra of complexes that there is greater interaction between negative ligands coordinated in *trans*-positions to each other than between those in *cis*-positions. Thus Shibata(15) has explained the third absorption bands of nitroammine cobaltic complexes by his *trans*-dinitro-hypothesis. And extending the Shibata hypothesis, one of the present authors(16) explained the third bands of many other complexes as due to a pair or pairs of negative ligands in *trans*-positions to each other. Basolo(17) reported that complexes with a pair of negative ligands in *cis*-positions also showed the third bands, which, however, were always located in regions of shorter wave-lengths than those of the *trans*-isomers. Recently, Shimura(12) has found on investigating wave-lengths of absorption maxima of the first bands of geometrical isomers that a pair of ligands in *trans*-positions has a greater effect on the first band than a pair in *cis*-positions, whether it is bathochromic or hypsochromic. The trans-effect has been recognized also on reactions of complex compounds. Thus Chernyaev(18) reported that ligands trans to negative groups are more mobile than those opposite to neutral groups, and the idea of the trans-effect has been extended in explanation of reactions of coordination compounds.(19) All these results imply that there should be a larger pairing interaction between ligands, especially anions, in *trans*-positions than between those in *cis*-positions. Experimental results with tetrammine cobaltic complexes are shown in Table 9.

Table 9

Comparison between *cis*- and *trans*-Isomers

Compound		1st Band		Ref.
		ν 10^{13}/sec.	log ε	
$[Co\ en_2(NCS)_2]Cl$	*trans*-	59.0	2.42	(21)
	cis-	59.3	2.40	(21)
$[Co(NH_3)_4(SO_3)_2]Na$	*trans*-	66.6	2.32	(12)
	cis-	65.9	2.26	(12)
$[Co(NH_3)_4(NO_2)_2]Cl$	*trans*-	67.9	2.32	(7)
	cis-	65.5	1.99	(7)
$[Co\ en_2(NO_2)_2]NO_3$	*trans*-	69.9	2.20	(10)
	cis-	69.0	2.10	(10)
$[Co\ en_2Cl_2]Cl$	*trans*-	48.0	1.54	(20)
	cis-	56.6	1.88	(20)
$[Co\ en_2(H_2O)_2]Br_3$	*trans*-	60.4	1.65	(20)
	cis-	60.6	1.85	(20)

From the experimental data the following rule may be induced: of geometrical isomers of a hexa-coordinated complex containing ligands of two kinds, in which a pair of ligands of one kind has larger hyperchromic and trans-pairing effects than the remaining four of the other kind, the *trans*-isomer has larger ε_{max} than the *cis*-isomer.

Thus, since NO_2 stands much higher in the hyperchromic series than en or NH_3, the *trans*-isomers of dinitro-complexes have larger extinction coefficients than the corresponding *cis*-isomers. The same is true for dirhodanato- and disulphono-complexes, which contain respectively NCS^- and $SO_3^{=}$, the most hyperchromic ligands. On the contrary, in regard to geometrical isomers of tetrammine-cobaltic complexes which coordinate H_2O or Cl^-, the least hyperchromic ligands, the *trans*-isomers have smaller extinction coefficients than the corresponding *cis*-isomers.

Summary

The relation between the kind of ligands and extinction coefficients of the first absorption bands of cobaltic complexes has been discussed. The order of ligands as to the magnitude of the effect which they exert on extinction coefficients of the first bands has been determined empirically, thus

$$NCS^- \; CrO_4^{=} \; SO_3^{=} \; NO_2^- \; CO_3^{=} \; C_2O_4^{=} \; \text{en}$$
$$OH^- \; NO_3^- \; SO_4^{=} \; Br^- \; NH_3Cl^- \; H_2O.$$

For pentammine cobaltic complexes with the sixth ligands, each of which is coordinated with an oxygen atom, a linear relation has been found to hold between ν_{max}'s and ε_{max}'s of the first bands. For complexes of the type $[CoA_4X_2]$, the *trans*-isomer has larger ε_{max} if X has more hyperchromic and trans-pairing effects than A. This investigation was supported by a grant from the Ministry of Education.

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(15) Y. Shibata, *J. Chem. Soc. Japan*, **36**, 1243 (1915).

(16) R. Tsuchida, This Bulletin, **13**, 436 (1938).

(17) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2643 (1948); **72**, 4393 (1950).

(18) I. I. Chernyaev, *Ann. Inst. Platine*, **4**, 243 (1926).

(19) H. D. K. Drew, et al, *J. Chem. Soc.*, 1004 (1932); D. I. Ribchikov, *Compt. rend. U. R. S. S.*, **28**, 231 (1940); J. C. Bailar and D. F. Peppard, *J. Am. Chem. Soc.*, **70**, 2634 (1948), etc.

(20) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950); data in methanolwater solvent.

(21) Y. Shimura, *J. Am. Chem. Soc.*, **73**, 5079 (1951).