The Relation between the Geometrical Configurations of Inorganic Complexes and their Absorption Bands. III.⁽¹⁾

A General Rule for the First and Second Bands of Co (III) Complexes

By Yoichi SHIMURA

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Introduction

Many data have been reported in scientific literature about the absorption spectra of the geometrical isomers of Co(III) complex salts, but the relation between the *cis-trans* isomerism of the complexes and their absorption bands has not been completely clarified. It is well known that the visible and ultra-violet absorption bands of Co(III) complexes consist of the first, second, third and some other specific bands. The relations of these bands to the geometrical configurations, which have already been offered by some authors, are summarized as follows.

(1) **Third band.**—According to Shibata-Tsuchida's *trans*-anions hypothesis,(2) the Co(III) complexes which contain a pair or pairs of negative ligands in *trans*-positions are expected to have a third band at the region of 110-120 $\times 10^{13}$/sec. More recently, Basolo(3) reported the third bands of some *cis*-anions complexes in the shorter wave-lengths than the corresponding *trans*-isomers. These facts are applicable to the configurational determination of the complex salt.

(2) **Specific bands.**—The bands are due to the special ligands in the coördination sphere. In the previous reports,(4),(1) the author has shown that the nitro-, rhodanato- and sulfono-

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(1) Part II of this report, Y. Shimura, This Bulletin, **25**, 46 (1952).

(2) R. Tsuchida, *ibid.*, **13**, 388, 436 (1938).

(3) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

(4) Y. Shimura, *ibid.*, **73**, 5079 (1951).

specific bands of the *trans*-isomers of Co(III) complexes have always the longer wave-lengths than those of the *cis*-forms. This relationship is also useful for the configurational determination of complex salt.

(3) **First band.**—The band is always in the visible region for Co(III) complexes and the color of the complex salt is due to the band. It has frequently been stated that the *cis*-isomers are more highly colored than the *trans*-isomers, but this rule is not reliable since many exceptions are known.

(4) **Second band.**—According to Tsuchida,(2) this band, which appears in the near ultra-violet region for Co(III) complexes, gives a measure of stability of the complex. Basolo(3) stated that the second band of *cis*-form is shifted towards the shorter wave-length as compared with that of *trans*-form, even though his "second band" is confused with the nitro- or rhodanato-specific band.

At the same time, Basolo assumed that whenever the stability differences of stereoisomers are sufficiently large to cause a shift in the absorption band positions, then the one that absorbs at the shorter wave-length is the *cis*-isomer. But it must be noticed here that in fact the first bands of *trans*-compounds containing some nitro- or sulfon-radicals are almost always shifted slightly more towards the shorter wave-lengths than the corresponding *cis*-compounds.

Thus, the relation of the third and some

Table 1

First Band of [Co en_2 A_2] or [$Co(NH_3)_4A_2$] Type Complex Ion

No.	Spectrochemical series of ligand A	Complex ion	First band (10^{13}/sec.) of: *cis*-isomer, ν_c	First band (10^{13}/sec.) of: *trans*-isomer, ν_t	$\nu_c-\nu_t$	Solvent	Ref.
1	NO_2^-	$[Co(NH_3)_4(NO_2)_2]^+$	67.0	68.2	−1.2	methanol-water	Basolo(3)
1a	NO_2^-	$[Co(NH_3)_4(NO_2)_2]^+$	65.5	67.9	−2.4	water	Kuroya and Tsuchida(5)
1b	NO_2^-	$[Co(NH_3)_4(NO_2)_2]^+$	69.0	68.9	+0.1	water	Kuroya(6)
2	NO_2^-	$[Co\ en_2\ (NO_2)_2]^+$	69.0	69.9	−0.9	water	Kuroya and Tsuchida(5)
2a	NO_2^-	$[Co\ en_2\ (NO_2)_2]^+$	68.5	69.3	−0.8	methanol-water	Basolo(3)
3	$SO_3^{=}$	$[Co(NH_3)_4(SO_3)_2]^-$	65.9	66.6	−0.7	3%-NH_3 aq.	Shimura(1)
4	NH_3	$[Co\ en_2\ (NH_3)_2]^{3+}$	63.8	63.8	0.0	water	Basolo(3)
5	H_2O	$[Co\ en_2\ (H_2O)_2]^{3+}$	60.6	60.4	+0.2	water *p*H 0.7	Basolo(3)
6	NCS^-	$[Co\ en_2\ (NCS)_2]^+$	59.3	59.0	+0.3	water	Shimura(4)
6a	NCS^-	$[Co\ en_2(NCS)_2]^+$	57.7	58.3	−0.6	methanol-water	Basolo(3)
7	Cl^-	$[Co(NH_3)_4Cl_2]^+$	(57.3)(a)	<50.0	>+7.3	water	Tsuchida(8)
8	Cl^-	$[Co\ en_2\ Cl_2]^+$	56.6	48.0	+8.6	methanol-water	Basolo(3)
8a	Cl^-	$[Co\ en_2\ Cl_2]^+$	55.8	48.4	+7.4	alcohol-water	Ernsberger and Brode(7)
9	Br^-	$[Co\ en_2\ Br_2]^+$	54.5	45.6	+8.9	alcohol-water	Ernsberger and Brode(7)

(a) datum of the crystal.(9)

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

(6) H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 1, Ser. C, 29 (1950).

(7) M. L. Ernsberger and W. R. Brode, *J. Am. Chem. Soc.*, **56**, 1842 (1934).

(8) R. Tsuchida, This Bulletin, **11**, 721 (1936).

(9) R. Tsuchida and M. Kobayashi, *ibid.*, **13**, 619 (1938).

Table 2

First Band of [Co en_2 A·B] or [$Co(NH_3)_4$ A·B] Type Complex Ion(a)

No.	Spectrochemical series of ligand B	Complex ion	First band (10^{13}/sec.) of: cis-isomer, ν_c	trans-isomer, ν_t	$\nu_c-\nu_t$	Solvent	Ref.
(a)	Monochloro-bisethylenediamine or -tetrammine series ($A=Cl^-$)						
1	NO_2^-	[Co en_2 Cl·NO_2]$^+$	64·5	64.4	+0.1	methanol-water	Basolo(3)
2	NCS^-	[Co en_2 Cl·NCS]$^+$	59.6	54.0	+5.6	water	Kuroya and Tsuchida(5)
2a	NCS^-	[Co en_2 Cl·NCS]$^+$	58.8	57.7	+1.1	methanol-water	Basolo(3)
3	H_2O	[$Co(NH_3)_4Cl·H_2O$]$^{2+}$	58.5	50.0	+8.5	water	Tsuchida(6)
4	Cl^-	[Co en_2 Cl·Cl]$^+$	56.6	48.0	+8.6	methanol-water	Basolo(3),(b)
5	Br^-	[Co en_2 Cl·Br]$^+$	55.1	47.0	+8.1	alcohol-water	Ernsberger and Brode(7)
(b)	Mononitro-bisethylenediamine or -tetrammine series ($A=NO_2^-$)						
1	NO_2^-	[$Co(NH_3)_4NO_2·NO_2$]$^+$	67.0	68.2	−1.2	methanol-water	Basolo(3),(b)
2	NO_2^-	[Co en_2 NO_2·NO_2]$^+$	69.0	69.9	−0.9	water	Kuroya and Tsuchida(5),(c)
3	NCS^-	[$Co(NH_3)_4NO_2$·NCS]$^+$	62.6	64.0	−1.4	water	Shimura (present paper)
4	NCS^-	[Co en_2 NO_2·NCS]$^+$	64.8	65.3	−0.5	water	Kuroya and Tsuchida(5)
5	Cl^-	[Co en_2 NO_2·Cl]$^+$	64.5	64.4	+0.1	methanol-water	Basolo(3)
(c)	Monorhodanato-bisethylenediamine or -tetrammine series ($A=NCS^-$)						
1	NO_2^-	[$Co(NH_3)_4$NCS·NO_2]$^+$	62.2	64.0	−1.4	water	Shimura (present paper)
2	NO_2^-	[Co en_2 NCS·NO_2]$^+$	64.8	65.3	−0.5	water	Kuroya and Tsuchida(5)
3	NH_3	[Co en_2 NCS·NH_3]$^{2+}$	60.0	58.8	+1.2	methanol-water	Basolo(3)
4	NCS^-	[Co en_2 NCS·NCS]$^+$	59.3	59.0	+0.3	water	Shimura(4),(b)
5	Cl^-	[Co en_2 NCS·Cl]$^+$	59.6	54.0	+5.6	water	Kuroya and Tsuhcida(5),(c)
(d)	Monoammine-bisethylenediamine series ($A=NH_3$)						
1	NH_3	[Co en_2 NH_3·NH_3]$^{3+}$	63.8	63.8	0.0	water	Basolo(3)
2	H_2O	[Co en_2 NH_3H_2O]$^{3+}$	61.9	61.9	0.0	water pH 0.7	Basolo(3)
3	NCS^-	[Co en_2 NH_3·NCS]$^{2+}$	60.0	58.8	+1.2	methanol-water	Basolo(3)
4	OH^-	[Co en_2 NH_3·OH]$^{2+}$	60.6	60.6	0.0	water	Basolo(3)

(a) [Co en_2NH_3·Cl]$^{2+}$ is excluded, because the absorption data(3) of its *trans*-isomer are very queer and not agree with its color.

(b) for the other investigator's data, see Table 1.

(c) for the other investigator's data, see Table 2 a.

specific bands to the *cis-trans* isomerism have thoroughly been clarified, but those of the first and second bands are yet in confusion. It is the purpose of the present paper to report on a new regularity about the first or second band and the geometrical isomerism.

Results and Discussion

First Band.—The first bands of the geometrical isomers of Co(III) complexes available in previous reports as well as in the author's measurements are presented in Tables 1 and 2.

In Table 1, the bands of [Co en_2A_2] and [$Co(NH_3)_4A_2$] type complex ions (A = a molecule or a negative ion) are arranged in the order of the spectrochemical series of the ligand A, *i.e.*,

CN^-, NO_2^-, $SO_3^=$, en, NH_3, ONO^-, H_2O, NCS^-, $SO_4^=$, NO_3^-, OH^-, $C_2O_4^=$, $CO_3^=$, $S_2O_3^=$, Cl^-, $CrO_4^=$, Br^-, I^-.

This represents a decreasing order of the frequencies at the maximum absorption of the first bands of the complexes having such ligands.(2),(1) It is readily recognized from Table 1, that the frequency of the first band of [Co en_2A_2] or [$Co(NH_3)_4A_2$] type ion decreases in the order of the spectrochemical series of the ligand A. From the table, if the data 1b and 6a are omitted, the frequency difference of the first bands of *cis*- and *trans*-isomers, $\nu_c-\nu_t$, is minus for the ligand NO_2^- or $SO_3^=$, zero for NH_3, and plus for H_2O, NCS^- and Cl^-. Considering the very close distribution of NH_3 and en on the spectrochemical series, the fact is generalized as follows. The values $\nu_c-\nu_t$ of [Co X_4A_2] type ions are respectively minus or plus according as the position of the ligand A in the spectrochemical series is ahead of or behind the ligand X. This is interpreted as the result of a *trans*-influence of the ligands, that is, the substitution of two A, which is ahead of X on spectrochemical series, for the two X of [Co X_6], has a greater hypsochromic effect in the case of *trans*-[Co X_4A_2] as compared with the case of the *cis*-[Co X_4A_2], while when A is behind X, such substitution has a greater bathochromic effect in the case of *trans*-substitution than the case of *cis*. In summary, it seems that a *trans*-substitution causes a greater shift of the first band than corresponding *cis*-substitution and the direction of this shift is ruled by the relative positions of the ligands on the spectrochemical series. Thus the first bands of *trans*-isomers of dinitro-complexes are at the shorter wave-lengths than the *cis*-isomers, and the reverse relation is observed in the dichloro-complexes.

About [Co $X_4A{\cdot}B$] type complexes, the similar regularities are substantiated from the Table 2. As for monochloro-bisethylenediamine or -tetrammine series, $\nu_c-\nu_t$ is always plus, because Cl^- is far behind en or NH_3 on spectrochemical series. In the mononitro-bisethylenediamine or -tetrammine series, $\nu_c-\nu_t$ is for the most part minus according as the higher position of NO_2^- than that of NH_3 or en. In the mono-rhodanato-bisethylenediamine or -tetrammine series, the value starts from -1.4 for [$Co(NH_3)_4NCS{\cdot}NO_2$]$^+$ and comes to $+5.6$ for [Co $en_2NCS{\cdot}Cl$]$^+$. From the data of these three series, it is also shown that the farther separations occur between the ligand B and en or NH_3 on the spectrochemical series, the greater absolute value of $\nu_c-\nu_t$ is attained.

Finally in the monoammine-bisethylenediamine series (Table 2 d), $\nu_c-\nu_t$ is almost zero. This is distinctly due to the condition that the position of NH_3 on the spectrochemical series is very close to that of en and that these complexes are compared to a pentammine type, in which the *cis-trans* isomerism can not be taken place.

Second Band.—The data of the second are summarized in Table 3. Since the second bands of the complexes having NO_2^-, $SO_3^=$ and NCS^-, are generally covered by the large specific bands, the bands of such complexes could not be confirmed. From the table, it is clear that the tendency of $\nu_c-\nu_t$ is the same as that of the first band, though the example of minus,

Table 3

Second Band of Geometrical Isomer of Co(III) Complex Ion

Complex ion	Second band (10^{13}/sec.)			
	cis-isomer, ν_c	*trans*-isomer, ν_t	$\nu_c-\nu_t$	Ref.
[Co en_2 $NH_3{\cdot}NH_3$]$^{3+}$	88.8	88.8	0.0	(3)
[Co en_2 $NH_3{\cdot}H_2O$]$^{3+}$	88.2	87.0	+1.2	(3)
[Co en_2 $H_2O{\cdot}H_2O$]$^{3+}$	84.5	*ca.* 84.5	*ca.* 0	(3)
[Co en_2 $NH_3{\cdot}OH$]$^{2+}$	83.3	82.2	+1.1	(3)
[$Co(NH_3)_4H_2O{\cdot}Cl$]$^{2+}$	82.5	74.5	+8.0	(8)
[Co en_2 $Cl{\cdot}Cl$]$^+$	*ca.* 76.9	66.7	*ca.* +10.2	(3)

value of $\nu_c - \nu_t$ is unknown.

Moreover, it must be noticed here that some difference values are observed in the case of $[\mathrm{Co\ en_2\ NH_3 \cdot H_2O}]^{3+}$ and $[\mathrm{Co\ en_2\ NH_3 \cdot OH}]^{2+}$, in which $\nu_c - \nu_t$ of the first band was zero. This indicates that the second band is more sensitive to the geometrical configurations as compared to the first band. Tsuchida⁽²⁾ has offered a theory concerning the origins of the absorption bands, that the first band is due to the electron transitions in the unsaturated transition shell of the central ion and that the second band is attributed to the transitions of the coördination electrons. The above fact is smoothly explained by this theory of Tsuchida, since the coördination electrons are presumably more sensitive to the geometrical configurations than the electrons in the transition shell of the central ion.

Absorption Spectra and Configurations of Two Isomers of $[\mathrm{Co(NH_3)_4NO_2 \cdot NCS}]^+$

The configurations of two stereoisomers of $[\mathrm{Co(NH_3)_4NO_2 \cdot NCS}]^+$ have not been studied. The chloride of an isomer was prepared by Werner and Klien⁽¹⁰⁾ from $[\mathrm{Co(NH_3)_4HO_2 \cdot Cl}]\mathrm{Cl}$, whose structure has been determined as *trans* from its method of preparation⁽¹¹⁾ and the spectral data.⁽¹²⁾ The monohydrated bromide of another isomer was prepared by Werner⁽¹³⁾ as the following process.

$$[\mathrm{Co[NH_3)_4(H_2O)_2]_2(SO_4)_3} \xrightarrow{\mathrm{NH_4NCS,\ KBr}}$$

$$[\mathrm{Co(NH_3)_4H_2O \cdot NCS]Br_2} \xrightarrow{\mathrm{NaNO_2}}$$

$$[\mathrm{Co(NH_3)_4H_2O \cdot NCS](NO_2)_2} \xrightarrow[\mathrm{KBr}]{\text{heat}}$$

$$[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Br \cdot N_2O}$$

From their preparations, it can be expected that $[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Cl}$ is *trans*-isomer and $[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Br \cdot H_2O}$ is *cis*-isomer. For the purpose of confirming this point of view, the author has prepared the two salts and investigated their absorption spectra, comparing them with those of the corresponding bisethylenediamine salts, which have already been measured by Kuroya and Tsuchida.⁽⁵⁾

The spectrographic measurements were done at room temperature, in the aqueous solutions slightly acidified with acetic acid in order to avoid the decomposition of the salts. The results are shown in Fig. 1 with those of the corresponding bisethylenediamine salts.

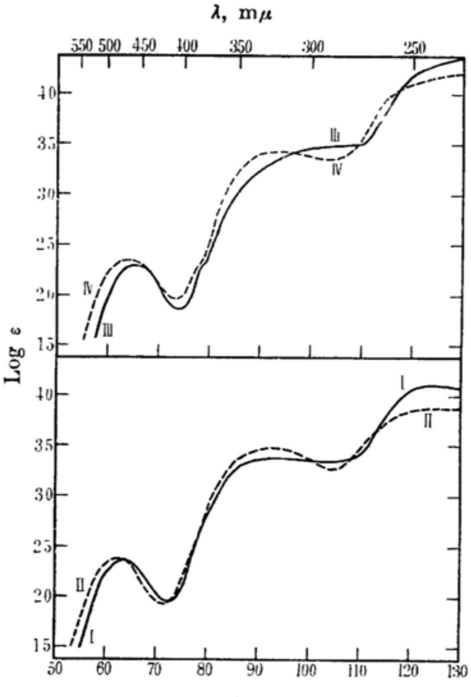

Fig. 1.—Absorption spectra of: I, *trans*-$[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Cl}$; II, *cis*-$[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Br \cdot H_2O}$; III, *trans*-$[\mathrm{Co\ en_2\ NO_2 \cdot NCS]NCS}$ (Kuroya and Tsuchida); IV, *cis*-$[\mathrm{Co\ en_2\ NO_2 \cdot NCS]Cl}$ (Kuroya and Tsuchida).

As is clear from the shapes of the curves and from the positions of the first bands, $[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]\ Cl}$ is analogous to *trans*-$[\mathrm{CO\ en_2\ NO_2 \cdot NCS]NCS}$ and $[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Br \cdot H_2O}$ to *cis*-$[\mathrm{Co\ en_2\ NO_2 \cdot NCS]Cl}$. Thus the former is *trans*-salt and the latter *cis*-salt. This conclusion coincides with the above presumption from the method of preparations.

As for the first bands of both salts, the band positions and the logarithms of maximum formal extinction coefficients are as follows;

trans-$[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Cl}$
64.0×10^{13}/sec. ($\log \varepsilon = 2.34$)

cis-$[\mathrm{Co(NH_3)_4NO_2 \cdot NCS]Br \cdot H_2O}$
62.6×10^{13}/sec. ($\log \varepsilon = 2.36$).

With regard to the second or third band as well as the nitro- or rhodanato-specific band, it is impossible to explain the detail because of the intricated superposition of these bands.

Summary

A survey of the absorption data of the tetrammine- or bisethylenediamine-Co(III) complexes available in previous literature as well as in the author's measurements has shown that the frequency differences of the first bands

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(10) A. Werner and R. Klien, *Z. anorg. Chem.*, **22**, 111 (1900).

(11) S. M. Jörgensen, *ibid.*, **7**, 290 (1894).

(12) R. Tsuchida and S. Kashimoto, This Bulletin, **11**, 785 (1936).

(13) A. Werner, *Ber.*, **40**, 776 (1907).

(or second bands) of the *cis*- and *trans*-isomers are closely related to the spectrochemical series of the ligands which coördinated in *cis*- or *trans*-positions. This correlation has been interpreted as the result of a *trans*-influence of the ligands, *i. e.*, a *trans*-substitution causes a greater shift of the first band (or second band) than corresponding *cis*- substitution. The visible and ultraviolet absorption spectra of two isomers of $[Co(NH_3)_4NO_2 \cdot NCS]^+$ have been measured and the steric configurations of both ions have been determined.

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Department of Chemistry, Faculty of Science,
Osaka University, Osaka