199°. This did not depress the melting point of the tri-*p*-biphenylylsilanol reported above.

Attempted Preparation of Tri-*p*-biphenylylchlorosilane.—Three grams (0.006 mole) of tri-*p*-biphenylylsilanol was dissolved in 100 ml. of dry benzene, and dry hydrogen chloride was passed into the solution for 5 hours. There was no heat evolved and no precipitate formed. On distillation of the solvent, a quantitative recovery of tri-*p*-biphenylylsilanol (mixed melting point) was obtained. This method has been very successful for preparing triphenylchlorosilane from triphenylsilanol.[18]

In a second attempt, 2.5 g. (0.005 mole) of tri-*p*-biphenylylsilanol was suspended in 25 ml. of acetyl chloride, and dry hydrogen chloride was passed into the suspension for 12 hours. The solid was then filtered off, washed with petroleum ether (b.p. 28–38°), and found to weigh 2.5 g. (100% recovery) and melt at 200–201°. A mixed melting point with starting material was not depressed. In case the failure of this reaction was due to the insolubility of the silanol in acetyl chloride, the recovered tri-*p*-biphenylylsilanol was dissolved in a slight excess of benzene, and an equal volume of acetyl chloride was added. Dry hydrogen chloride was passed into this solution for 5 hours. Evaporation of the solvent left 2.5 g. of tri-*p*-biphenylsilanol, melting at 197–198°, identified by mixed melting point.

Hexa-*p*-biphenylyldisilane.—Since tri-*p*-biphenylylchlorosilane was not readily available, hexa-*p*-biphenylyldisilane was prepared from hexachlorodisilane and *p*-biphenylyllithium. To 2.69 g. (0.01 mole) of hexachlorodisilane in 100 ml. of ether was added 0.068 mole of *p*-biphenylyllithium in ether. The mixture was refluxed until Color Test I became negative (20 hours), then hydrolyzed with water. The material insoluble in both ether and water was filtered off and dried. It weighed 7.5 g., and melted at 320–370°. This solid was digested with benzene for 4 hours, then filtered and washed with benzene. The benzene, on cooling, deposited 1.5 g. of white solid melting at 260–263°. Recrystallization from benzene gave 1.2 g. (23%) of tetra-*p*-biphenylylsilane melting at 270–272°. The melting point reported in the literature is 274°.[19] The benzene-insoluble residue weighed 3 g. and melted at 400–415°. This material was insoluble in all the organic solvents available with the exception of nitrobenzene. Recrystallization from nitrobenzene gave a product with a lighter color (tan) but the same melting range. It was then discovered that the material was partly soluble in pyridine. After four hours of digestion with hot pyridine, the hot suspension was filtered to give a colorless residue weighing 1.3 g. and melting at 432–434°. The yield is 14%.

Anal. Calcd. for $C_{72}H_{54}Si_2$: Si, 5.75. Found: Si, 5.73, 5.77.

Attempted Reaction of Hexa-*p*-biphenylyldisilane with Oxygen and Iodine.—A suspension of 0.30 g. of hexa-*p*-biphenylyldisilane in 50 ml. of dry xylene was heated to reflux for 48 hours while passing a stream of dry air through the mixture. The xylene was then removed under vacuum. The residue weighed 0.294 g. (98% recovery) and melted at 432–434° alone, or mixed with starting material.

Two 0.30-g. samples of hexa-*p*-biphenylyldisilane were weighed out and suspended, one in 50 ml. of xylene, and the other in 50 ml. of chloroform. To the xylene suspension was added 0.10 g. of iodine and 3 drops of quinoline, and to the chloroform solution was added 1 drop of 0.001 *M* iodine in chloroform. Both solutions were refluxed for 10 hours, then filtered hot. The residue from the xylene suspension weighed 0.252 g. (84%) and that from the chloroform suspension weighed 0.260 g. (87%). Both melted at 432–434° alone or mixed with starting material. The iodine color had not disappeared from either solution, even though it had been very faint in the chloroform solution from the beginning.

Cleavage of Tri-*p*-biphenylylsilanol by Phenyllithium.—Several triarylsilanols have been cleaved to diaryl-*n*-butylsilanols and phenyllithium by treatment with *n*-butyllithium in ether, but up to the present no triarylsilanol has been cleaved by another aryllithium reagent.[15,20] Since the tri-*p*-biphenylylsilanol which was at hand seemed to offer good possibilities of cleavage, it was treated with phenyllithium. Three grams (0.006 mole) of tri-*p*-biphenylylsilanol was refluxed for 48 hours with 0.060 mole of phenyllithium in 175 ml. of dry ether. The mixture was carbonated and worked up as previously described,[15] to give an acid melting at 104–108°. This was extracted with hot water. The material which did not dissolve in hot water melted at 175–190° and, after several crystallizations from aqueous ethanol, it yielded 0.14 g. (12%) of *p*-phenylbenzoic acid, m.p. 227–228°, identified by mixed melting point with an authentic specimen.

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(18) C. A. Kraus and R. Rosen, THIS JOURNAL, **47**, 2739 (1925); H. Gilman, B. Hofferth and H. W. Melvin, *ibid.*, **72**, 3045 (1950).

(19) W. C. Schumb, J. Ackerman, Jr., and C. M. Saffer, Jr., *ibid.*, **60**, 2486 (1938).

(20) See H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949), for cleavages of organosilicon compounds by acids.

AMES, IOWA RECEIVED MARCH 12, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, OSAKA UNIVERSITY]

The Relation between the Geometrical Configurations of Inorganic Complexes and their Absorption Bands. I. The Third Absorption Band of *trans*-Dirhodanato-bis-ethylenediamine-cobalt(III) Chloride

BY YOICHI SHIMURA

The absorption spectra of *cis*- and *trans*-$[Co\,en_2(NCS)_2]Cl\cdot H_2O$, and $[Co\,(NH_3)_5NCS]SO_4$ have been measured. It is concluded that the rhodanato- or nitro-specific absorption bands of *trans*-forms of Co(III) complexes have longer wave lengths than those of the *cis*-forms, and that the *trans*-$[Co\,en_2(NCS)_2]Cl\cdot H_2O$ has the third absorption band at about 108 × 10^{13} sec.$^{-1}$. It had not been found in this complex ion because it is entirely obscured by the larger rhodanato-specific absorption band. The *cis*-form of this salt has no such band. This detection of the third absorption band of *trans*-$[Co\,en_2(NCS)_2]^+$ is in good accord with the Shibata–Tsuchida's hypothesis of the *trans*-pairing of negative groups.

Introduction

There are few relationships of recognized validity concerning the absorption spectra of geometrical isomers of metallic complexes, except the *trans*-anions hypothesis dealing with the occurrence of a third absorption band proposed by Shibata[1] and Tsuchida.[2,3] According to this hypothesis, complex radicals with a pair or pairs of negative groups in *trans*-positions are expected to have these third absorption bands, which are situated almost always in the spectral region 110–120 × 10^{13} sec.$^{-1}$ for Co(III) or Cr(III) complexes. Recently Basolo[4,5] reported that a few Co(III) complexes with two negative ions in *cis*-positions have also the third bands in the region of shorter wave lengths than those of the *trans*-isomers, and that this fact can be

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(1) Y. Shibata, *J. Chem. Soc. Japan*, **36**, 1243 (1915); *J. College Sci., Imp. Univ. Tokyo*, **37**, Art. 2 (1915).

(2) R. Tsuchida, *Bull. Chem. Soc. Japan*, **11**, 721 (1936).

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

(4) F. Basolo, THIS JOURNAL, **70**, 2634 (1948).

(5) F. Basolo, *ibid.*, **72**, 4393 (1950).

applied to establish the configurations of geometrical isomers.

At the same time, Basolo[5] reported the absorption spectra of *trans*-[Co $en_2(NCS)_2$]NCS and *trans*-[Co en_2NCS·Cl]NCS in methanol–water solutions, and stated that these two salts have no third bands in the near ultraviolet even though there are anions coördinated in *trans*-positions of each complex radical. The absorption spectrum of *trans*-[Co en_2NCS·Cl]$^+$, however, had been observed with its bromide in aqueous solution by Kuroya and Tsuchida,[6] and it was shown that this complex has clearly the third absorption band at 110.4 × 10^{13} sec.$^{-1}$. The discrepancies between Basolo and Kuroya–Tsuchida may result from the difference of solvents, but this third band due to the Cl^-–NCS^- couple lies in the region of longer wave length than the third bands due to the pairs of NO_2^-–NO_2^- or NO_2^-–Cl^- in *trans*-[Co $en_2(NO_2)_2$]$^+$, *trans*-[Co en_2-NO_2·Cl]$^+$, etc. The formal extinction coefficient at the absorption maximum of the former is considerably smaller than those of the latter. This band was overlapped by a larger absorption band of the coördinated NCS^- radical which extends from 80 × 10^{13} sec.$^{-1}$ to 110 × 10^{13} sec.$^{-1}$, and hence this may be the reason why Basolo could not find the third band in this salt. As for the third band of *trans*-[Co $en_2(NCS)_2$]$^+$, which has two coördinated NCS^- groups, it is probable that greater difficulties than in the case of [Co en_2NCS.Cl]$^+$ would be encountered in detecting it.

The present paper deals with this third absorption band of *trans*-[Co $en_2(NCS)_2$]$^+$ and discusses the analysis of the rhodanato-specific absorption band. The relationships of the specific absorption bands of Co(III) complex salts with their geometrical structures are discussed.

Experimental

The three rhodanato-Co(III) complexes were prepared and the absorption spectra of their aqueous solutions were observed in the spectral region from 50 × 10^{13} sec.$^{-1}$ to 125 × 10^{13} sec.$^{-1}$. The formal extinction coefficient ε is given by the equation: $I = I_0 \times 10^{-\epsilon c d}$, where c is the concentration of complex ion in gram-ion per liter and d the thickness of the layer in cm.

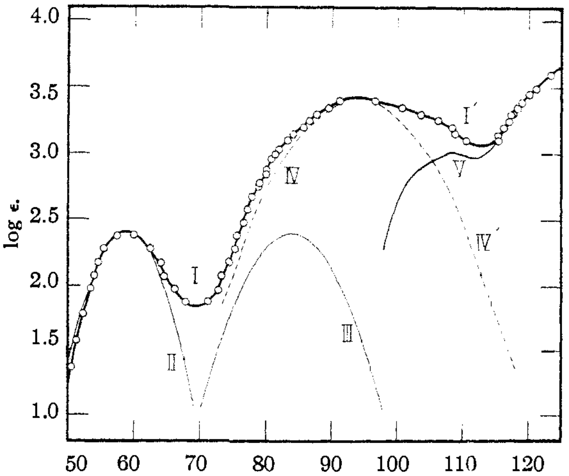

Fig. 1.—Absorption spectrum of *trans*-[Co $en_2(NCS)_2$]-Cl·H_2O: I-I′, experimental curve; II, first absorption band calculated from equation (3); III, second absorption band calculated from equation (4); IV-IV′, rhodanato-specific band; V, third absorption band.

trans-[Co $en_2(NCS)_2$]Cl·H_2O was prepared by the method of Werner and Bräunlich.[7] Spectrographic measurements: c = $^1/_{100}$ and $^1/_{500}$ gram-ion/l., d = 5 to 0.1 cm.

cis-[Co $en_2(NCS)_2$]Cl·H_2O was prepared by the method of Werner and Bräunlich.[8] Spectrographic measurements: c = $^1/_{100}$ and $^1/_{1000}$ gram-ion/l., d = 5 to 0.1 cm.

[Co$(NH_3)_5$NCS]SO_4 was prepared by the method of Werner and Müller.[9] Spectrographic measurements: c = $^1/_{300}$ gram-ion/l., d = 5 to 0.1 cm.

Results

The results are given in Figs. 1–3 and in Table I.

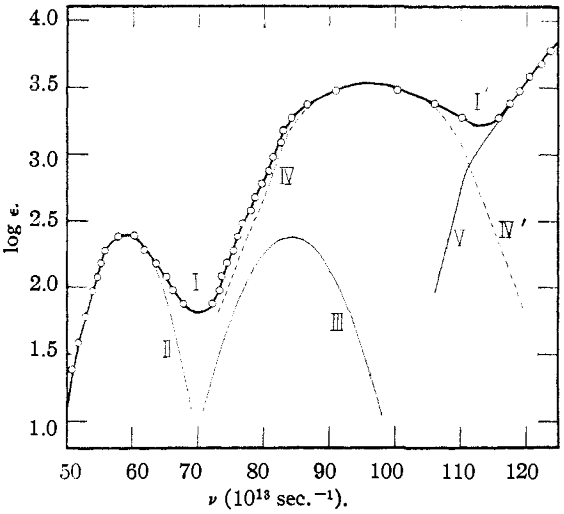

Fig. 2.—Absorption spectrum of *cis*-[Co $en_2(NCS)_2$]-Cl·H_2O: I-I′, experimental curve; II, first absorption band calculated from equation (5); III, second absorption band calculated from equation (6); IV-IV′, rhodanato-specific band; V, "end absorption."

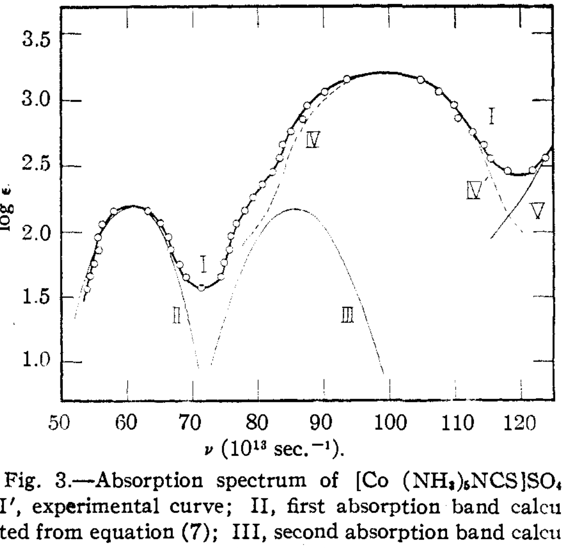

Fig. 3.—Absorption spectrum of [Co $(NH_3)_5$NCS]SO_4: I-I′, experimental curve; II, first absorption band calculated from equation (7); III, second absorption band calculated from equation (8); IV-I′-IV′, rhodanato-specific band; V, "end absorption."

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[6] H. Kuroya and R. Tsuchida, *Bull. Chem. Soc. Japan*, **15**, 427 (1940).

[7] A. Werner and F. Bräunlich, *Z. anorg. Chem.*, **22**, 130 (1899).

[8] *Ibid.*, **22**, 141 (1899).

[9] A. Werner and H. Müller, *ibid.*, **22**, 101 (1899).

TABLE I

ABSORPTION RESULTS

Complex salt	1st absorption band ν_1 (max.), 10^{13} sec.$^{-1}$	 log ϵ_1 (max.)	 ν_1'	Rhodanato-specific band ν_{NCS} (max.), 10^{13} sec.$^{-1}$	 log ϵ_{NCS} (max.)	 ϵ_{NCS} (max.)	Ratio of ϵ_{NCS} (max.)
cis-[Co $en_2(NCS)_2$]Cl.H_2O	59.3	2.40	4.6 × 2	96.6	3.53	3390	2.1
trans-[Co $en_2(NCS)_2$]Cl.H_2O	59.0	2.42	4.7 × 2	94.0	3.44	2750	1.7
[Co$(NH_3)_5$NCS]SO_4	60.8	2.20	5.1 × 2	99.6	3.20	1590	1.0

According to Tsuchida and his co-workers,[3,10] the absorption bands, which complex salts show in the near infrared, the visible, and the near ultraviolet regions, are classified by their origins into the first, the second, the third and the specific absorption bands. Each of the absorption curves in Figs. 1–3 has two absorption maxima, one of which, the first band, is found in the visible, and the other in the ultraviolet. From the fact that the values of ϵ_{NCS}(max.) in Table I are approximately proportional to the number of coördinated NCS^- groups, it can be concluded that these ultraviolet absorption bands are the rhodanato-specific bands.[3]

The inflection at about 80 × 10^{13} sec.$^{-1}$ in the curve for [Co $(NH_3)_5$NCS]SO_4 can be attributed to the second absorption band, which is hidden under a large rhodanato-specific band. The second bands of the other two salts are also entirely covered by the larger specific bands. As stated in the introduction, the third band of *trans*-[Co $en_2(NCS)_2$]Cl·H_2O is not explicitly detected.

Analyses of Absorption Curves and Discussion

The first and second bands of the observed three complexes were analyzed by the method of Kuroya.[11] According to Kuroya, the first and the hidden second bands of a Co(III) complex are, respectively, represented by the formulas: for the 1st band

$$\log \epsilon_1 = \log \epsilon_1 \text{ (max.)} - 0.434 \left(\frac{\nu_1 \text{ (max.)} - \nu}{\frac{\nu_1'}{1.665}} \right)^2 \quad (1)$$

and for the hidden 2nd band

$$\log \epsilon_2 = 0.99 \log \epsilon_1 \text{ (max.)} - 0.434 \left(\frac{\nu_1 \text{ (max.)} + 25.0 - \nu}{7.81} \right)^2 \quad (2)$$

where ϵ and ϵ(max.) are the formal extinction coefficients at frequencies $\nu \times 10^{13}$ sec.$^{-1}$ and ν(max.) × 10^{13} sec.$^{-1}$, respectively. $\nu_1^s \times 10^{13}$ sec.$^{-1}$ implies the so-called half-value width of the first band, *i.e.*, the frequency difference between the two points, where the extinction coefficients are equal to $\frac{1}{2}\, \epsilon_1$(max.). But, practically, the difference between ν_1(max) × 10^{13} sec.$^{-1}$ and the frequency at the point on the long wave length side of the first band where $\epsilon = \epsilon_1$(max.)/2 was taken and the twice of this value was assumed to be equal to the half-value width. The values for each complex are presented in Table I.

The Third Absorption Band of *trans*-[Co $en_2(NCS)_2$]$^+$.—For *trans*-[Co $en_2(NCS)_2$]Cl, equations (1) and (2) can be written as

$$\log \epsilon_1 = 2.42 - 0.434 \left(\frac{59.0 - \nu}{5.65} \right)^2 \quad (3)$$

$$\log \epsilon_2 = 2.40 - 0.434 \left(\frac{84.0 - \nu}{7.81} \right)^2 \quad (4)$$

The values of the ϵ's calculated from these equations are plotted in Fig. 1 (curves II and III). Then the ϵ's of the first and second bands (curves II and III) were successively subtracted from those of the experimental curve I. After this operation, there remains curve IV, which is the rhodanato-specific absorption band. If the symmetrical nature of rhodanato-specific bands of Co(III) complexes is assumed (the validity of this assumption will be verified in the latter part of this paper) the whole rhodanato-specific band will be curve IV–IV′. The curve IV–IV′ was subtracted from the experimental curve I′. The resultant curve V has a maximum (log ϵ(max.) = 3.02) at about 108 × 10^{13} sec.$^{-1}$. This absorption maximum is in the region similar to that of the third band of *trans*-[Co en_2NCS·Cl]$^+$ which has been mentioned above. Thus this maximum is to be identified as the third absorption band of this salt, which is due to the *trans*-pairing of NCS^- radicals through the central Co(III) ion. This conclusion is in good agreement with Shibata and Tsuchida's theory.

In a similar manner, the analysis of the curve of *cis*-[Co $en_2(NCS)_2$]Cl was performed: *i.e.*, for the 1st band

$$\log \epsilon_1 = 2.40 - 0.434 \left(\frac{59.3 - \nu}{5.53} \right)^2 \quad (5)$$

and for the 2nd band

$$\log \epsilon_2 = 2.38 - 0.434 \left(\frac{84.3 - \nu}{7.81} \right)^2 \quad (6)$$

Thus the symmetrical rhodanato-specific band, curve IV–IV′ in Fig. 2, was obtained. After subtracting the curve IV–IV′ from the experimental curve I′, the curve V of the *cis*-form has no maximum and is very different from the curve V of the *trans*-form. Consequently we have found that the *cis*-form has no third band in this region, in agreement with the observations of Basolo.

Symmetrical Rhodanato-specific Band.—The preceding analyses have been based on the symmetrical nature of the rhodanato-specific band. To test the characteristics of Co(III) complexes, the absorption curve of [Co$(NH_3)_5$NCS]SO_4 was analyzed by separation of the first and the second bands: for the 1st band

$$\log \epsilon_1 = 2.20 - 0.434 \left(\frac{60.8 - \nu}{6.13} \right)^2 \quad (7)$$

and for the 2nd band

$$\log \epsilon_2 = 2.18 - 0.434 \left(\frac{85.8 - \nu}{7.81} \right)^2 \quad (8)$$

In consequence the very symmetrical rhodanato-specific band IV–I′–IV′ in Fig. 3 was obtained.

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(10) R. Tsuchida, "Colours and Structures of Metallic Compounds," Zoshindo Co., Osaka, Japan, 1944, (in Japanese).

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

The rhodanato-specific band of *cis*-[Co en$_2$NCS·Cl]Cl[6] has no definite maximum since its short wave length part is superimposed by the so-called end absorption (Fig. 4). In order to find the maximum point of this band, the following approximation was made: the extrapolated line V of a tangent of the observed curve I′ at about 125 × 10^{13} sec.$^{-1}$ was subtracted from the curve I′. We obtained thus the curve IV′ as the short wave length part of this specific band. The long wave length side of this band has been analyzed by Kuroya[12] (curve IV). Curve IV–IV′ is also symmetrical, and its absorption maximum is found at about 98.5 × 10^{13} sec.$^{-1}$ (log ϵ_{NCS}(max.) = 3.34).

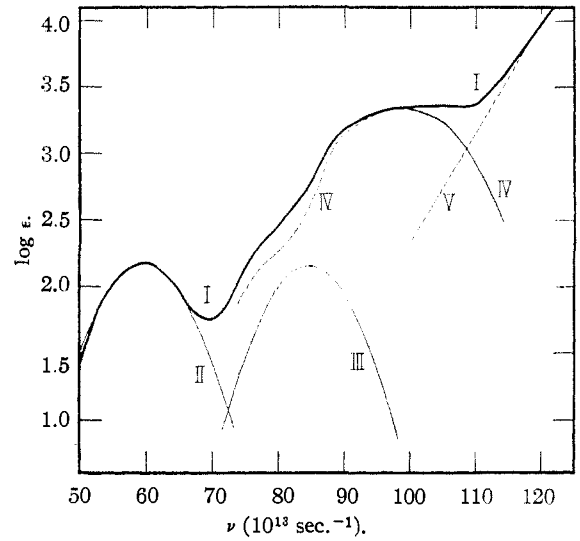

Fig. 4.—Absorption spectrum of *cis*-[Co en$_2$NCS·Cl]Cl: I-I′, observed curve according to Kuroya; II and III, first and second absorption bands calculated by Kuroya; IV-IV′, analyzed rhodanato-specific band; V, assumed "end absorption."

Relation of *cis–trans* Isomerism to Specific Absorption Band.—The rodanato-specific bands of several *cis*- and *trans*-Co(III) complexes are summarized in Table II.

The nitro-specific bands[11,12] are also given in Table III.

TABLE II

RHODANATO-SPECIFIC BAND

Complex ion	Configuration	ν_{NCS} (max.), 10^{13} sec.$^{-1}$	log ϵ_{NCS} (max.)	Ref.
[Co en$_2$(NCS)$_2$]$^+$	*cis*	96.6	3.53	Author
	trans	94.0	3.44	Author
[Co en$_2$NCS·Cl]$^+$	*cis*	98.5	3.34	6 and author
	trans	92.5	3.36	6
[Co en$_2$NCS·NH$_3$]$^{2+}$	*cis*	92.9	3.30	5
	trans	90.4	3.55	5

TABLE III

NITRO-SPECIFIC BAND

Complex ion	Configuration	ν_{NO_2} (max.), 10^{13} sec.$^{-1}$	log ϵ_{NO_2} (max.)	Ref.
[Co en$_2$(NO$_2$)$_2$]$^+$	*cis*	92.8	3.68	6
	trans	88.6	3.44	6
[Co(NH$_3$)$_4$(NO$_2$)$_2$]$^+$	*cis*	91.5	3.90	11
	trans	86.8	3.90	11
[Co en$_2$NO$_2$·Cl]$^+$	*cis*	89.0	3.26	5
	trans	88.2	3.14	5
[Co(NH$_3$)$_3$(NO$_2$)$_3$]	*cis*	92.3	3.65	13
	trans	88.2	3.65	14

From these tables, it has been shown that the specific band of the *trans*-form is always more bathochromic than the band of the *cis*-form. This is valid not only for the complex salts which contain two NCS$^-$ or NO_2^s groups, but also for those containing only one NCS$^-$ or NO$_2^-$ radical. So it can be pointed out that the groups such as Cl$^-$ or NH$_3$ which have nothing to do with the existence of these specific bands, produce also some delicate effects on the positions of the specific bands, and that the *cis–trans* isomerism of complex radical has an appreciable influence upon the specific absorption band. It is suggested that the relation demonstrated in Table II or III may be used for the configurational determinations of Co(III) complex salts.

Acknowledgment.—The author wishes to express sincere thanks to Professor R. Tsuchida and Mr. S. Yamada for their kind interests and helpful suggestions during the course of this research.

OSAKA, JAPAN RECEIVED MARCH 6, 1951

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(12) Ref. 10, p. 155.

(13) H. Sueda, *Bull. Chem. Soc. Japan*, **13**, 450 (1938).

(14) H. Sueda, *ibid.*, **12**, 188 (1937).