The Relation between the Geometrical Configurations of Inorganic Complexes and their Absorption Bands. II.⑴

The Configurations of Two Isomers of Sodium Disulfono-tetrammine-cobaltiate

By Yoichi SHIMURA

(Received October 9, 1951)

The two isomers of $Na[Co(NH_3)_4(SO_3)_2]$ were first prepared by Hofmann and Jenny,⑵ who designated a brown, more insoluble dihydrate as *cis*-form and another golden yellow, more soluble tetrahydrate as *trans*-form. But this assignment was unreliable, since it was deduced from an uncertain analogy with two isomers of dinitro-tetrammine-cobalt(III) salt.

As will be shown in this report, however, the spectral data prove that the brown salt is *trans*-isomer and the golden yellow salt *cis*-isomer. There is, of course, a possibility of other isomerism, *i. e.*, sulfono-sulfito isomerism, which corresponds to nitro-nitrito isomerism of the complexes containing some NO_2^--radicals. In such case, the difference between both isomers consists in the difference of the atom which combines directly with the central cobalt (III) ion: in sulfono-isomer the S-atom of $SO_3^=$-radical is bound to the cobalt and in sulfito-isomer the O-atom is bound to it. But the spectral data exclude this possibility as will be seen later.

Results and Discussion

The absorption spectra of the two salts were measured at the spectral region from 55 to 125×10^{13}/sec. in 3 % aqueous solutions of NH_3. The absorption curves are shown in Fig. 1.

The brown salt has three absorption maxima in this region and the yellow salt only two maxima. It has been well known⑶ that the complex ions with a pair or pairs of negative ligands in *trans*-positions have the third absorption bands, which are situated almost always in the region $110–120 \times 10^{13}$/sec. for Co (III) or Cr (III) complex salts. Accordingly, the brown salt which has a third band at 113.6×10^{13}/sec. is *trans*-isomer concerning the positions of $SO_3^=$-radicals, and the yellow salt which has no absorption band in the region of $110–120 \times 10^{13}$/sec. is *cis*-isomer.

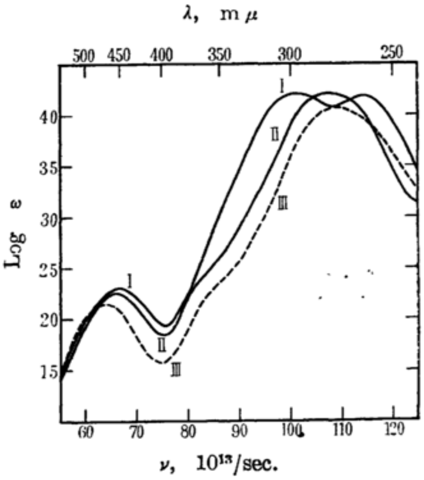


Fig. 1.—Absorption spectra of: I, brown salt, $Na[Co(NH_3)_4(SO_3)_2]\cdot 2H_2O$ (*trans*) in 3 % NH_3 aq.; II, golden yellow salt, $Na[Co(NH_3)_4(SO_3)_2]\cdot 4H_2O$ (*cis*) in 3 % NH_3 aq.; III, $[Co(NH_3)_5SO_3]Cl$ (Kiss and Czeglédy).

The larger absorption bands, which are distributed at 101.0×10^{13} / sec. for *trans*-compound and at 107.8×10^{13}/sec. for *cis*-compound, are the "$SO_3^=$-specific absorption bands" due to the coördinated $SO_3^=$-radicals. The absorption spectra of $[Co(NH_3)_5SO_3]Cl$ (Fig. 1, Curve III) and $Na_5[Co(CN)_4(SO_3)_2]$, which have been reported by Kiss and his co-workers,⑷,⑸ have also the similar $SO_3^=$-specific bands.

The $SO_3^=$-specific band of the *trans*-salt is more bathochromic than that of the *cis*-salt. In a previous paper,⑴ the author has pointed out that the rhodanato- or nitro-specific bands

---

⑴ Part I of this report: Y. Shimura, *J. Am. Chem. Soc.*, **73**, 5079 (1951).

⑵ K. A. Hofmann and A. Jenny, *Ber.*, **34**, 3855(1901).

⑶ R. Tsuchida, This Bulletin, **13**, 388, 433 (1938).

⑷ Á. v. Kiss and D. v. Czeglédy, *Z. anorg. Chem.*, **235**, 407 (1938).

⑸ Á. v. Kiss, G. Auer and E. Major, *ibid.*, **246**, 28 (1941).

Table 1

First Band of $[Co(NH_3)_4A_2]$

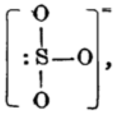
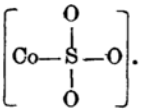
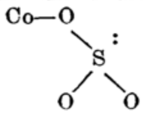
Spectrochemical series of ligands	Complex ion	Position of first band, 10^{13}/sec.	Ref.
NO_2^-	*trans*-$[Co(NH_3)_4(NO_2)_2]^+$	68.2,[(a)] 68.9	(6), (7)
	cis-$[Co(NH_3)_4(NO_2)_2]^+$	67.0,[(a)] 69.0	(6), (7)
$SO_3^=$	*trans*-$[Co(NH_3)_4(SO_3)_2]^-$	66.6 [(b)]	
	cis-$[Co(NH_3)_4(SO_3)_2]^-$	65.9 [(b)]	
NH_3	$[Co(NH_3)_4(NH_3)_2]^{3+}$	63.4	(7)
H_2O	$[Co(NH_3)_4(H_2O)_2]^{3+}$	60.0	(8)
$C_2O_4^=$	$[Co(NH_3)_4\,C_2O_4]^+$	58.8	(7)
$CO_3^=$	$[Co(NH_3)_4\,CO_3]^+$	58.4	(7)
Cl^-	*trans*-$[Co(NH_3)_4\,Cl_2]^+$	<50	(8)

(a) in methanol-water solution.   (b) in 3% NH_3 aq.

of *trans*-forms of Co(III) complexes have the longer wave-lengths than those of the *cis*-forms. Now it is recognized that such regularity is also true for the $SO_3^=$-specific absorption bands.

It has been shown by Tsuchida[(3)] that the near infra-red, the visible and the ultra-violet absorption bands of the complex salts are classified by their origins into the first, second, third and specific absorption bands. As is clear from Fig. 1, each of the isomers has the first band, but the second bands are inexplicit, since those are hidden under the larger $SO_3^=$-specific bands. The first band of the *trans*-salt is slightly shifted to the shorter wave-length than that of the *cis*-salt. In this connection, the relationship of the first band to the *cis-trans* isomerism will be discussed in the third report of this series. A small inflexion of the absorption curve of the *cis*-form at about 82×10^{13}/sec. is attributed to the second band. A similar hump is found in the absorption curve of the pentammine salt.

To determine the position of $SO_3^=$-radical on the spectrochemical series,[(3)] $[Co(NH_3)_4A_2]$ type complex ions (A = a molecule or a negative ion) were arranged in Table 1 in the order of frequencies of their first bands. From the table, $SO_3^=$-radical is located between NO_2^- and NH_3 on the series. This fact indicates that $SO_3^=$-radical coördinates around the central Co(III) ion by the lone pair of electrons of its S-atom, since it is expected that if $SO_3^=$-radical is bound to cobalt by O-atom, its position on the series should be behind NH_3. For instance, NO_2^--radical is ahead of NH_3 on the series when it coördinates by its lone pair electrons of N-atom, while it is behind NH_3 when it coördinates by O-atom forming the nitrito-complexes. The *cis-* and *trans*-salts studied in this paper, therefore, should be named sodium disulfono-tetrammine-cobaltiate, instead of disulfito-tetrammine-cobaltiate.

Moreover, the above discussion is confirmed from the following consideration. The absorption spectrum of a free $SO_3^=$-ion has a maximum at 100×10^{13}/sec.[(4)] All of the $SO_3^=$-specific bands of the complexes given in Fig. 1, are distributed in the more hypsochromic region than the absorption maximum of the free $SO_3^=$-ion. This shows that the coördinated $SO_3^=$-radical is more stable than a free $SO_3^=$-ion. $SO_3^=$-ion has a pyramidal structure, in which 3 $O^=$-ions and a lone pair of electrons are bound tetrahedrally around the central sulfur ion as  $\left[\begin{array}{c} O \\ | \\ :S-O \\ | \\ O \end{array}\right]^=$, whilst this lone pair of S-atom is utilized in sulfono-Co (III) complexes, by which the structure should be compared to a sulfate type, *i. e.*,  $\left[\begin{array}{c} O \\ | \\ Co-S-O \\ | \\ O \end{array}\right]$. In this manner, the sulfono-radical in coördination is more symmetrical and more stable than a free $SO_3^=$-radical. Thus the hypsochromic shift of the absorption band of $SO_3^=$ is observed. If the radical is coördinated by O-atom as , this sulfito-radical in coördination becomes more unstable than a single $SO_3^=$-ion and in consequence the "sulfito-specific band" should appear in the long wave-length side as compared with the absorption maximum of a free $SO_3^=$-ion. Therefore, the specific bands given in Table

---

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

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

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

2a, are undoubtedly the "sulfono-specific bands", and these salts are the disulfono-tetrammine- or sulfono-pentammine-cobaltiate. This is also clear from comparing the Table 2a with Table 2b.

Table 2

a: Position of Sulfono- or Sulfitoo-specific Absorption Band

	$\times 10^{13}$/sec.	Ref.
Sulfito-specific band	(smaller than 100)	
Absorption maximum of a free $SO_3^{=}$-ion	100(log ε=1.0)	(4)
Sulfon-specific band:		
trans-$Na[Co(NH_3)_4(SO_3)_2]$	101.0(log ε=4.22)	
cis-$Na[Co(NH_3)_4(SO_3)_2]$	107.8(log ε=4.21)	
$[Co(NH_3)_5SO_3]Cl$	109.5(log ε=4.08)	(4)

b: Position of Nitro- or Nitrito-specific Absorption Band

	$\times 10^{13}$/sec.	Ref.
Nitrito-specific band	83–84	(7)
Absorption maximum of a free NO_2^--ion	84.5(log ε=1.3)	(9)
Nitro-specific band:		
trans-$[Co(NH_3)_4(NO_2)_2]Cl$	86.8(log ε=3.90)	(7)
cis-$[Co(NH_3)_4(NO_2)_2]NO_3$	91.5(log ε=3.90)	(7)
$[Co(NH_3)_5NO_2]SO_4$	91.3(log ε=3.57)	(7)

Structure of $NH_4[Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$—Two isomers of $NH_4[Co(NH_3)_4(SO_3)_2]$ have also been known, *i. e.*, a dark brown trihydrate and other reddish brown tetrahydrate. According to Hofmann and Jenny,⁽²⁾ the dark brown isomer corresponds to the brown sodium salt and the reddish brown isomer to the golden yellow sodium salt. From the data of the photochemical decompositions of the salts, Schwarz and Tede⁽¹⁰⁾ supported the theory that the dark brown salt is *cis*-isomer and the reddish brown salt is *trans*-isomer. Klement,⁽¹¹⁾ and Bailar and Peppard⁽¹²⁾ also concluded, from the studies of reactions starting from the dark brown trihydrate, that the salt has two $SO_3^{=}$-groups in *cis*-positions. But the conclusions are not very reliable, since some rearrangements of ligands might have taken place in the course of such reactions.

The absorption spectrum of the dark brown isomer, however, is almost identical to that of the brown sodium salt (Table 3). This suggests that the salt is ammonium *trans*-disulfono-tetrammine-cobaltiate, although it is contrary to the several investigators' assignments of *cis*-configuration, and to solve this contradiction, it is hoped that the detailed reaction mechanism of the salt will be studied.

Experimental

Materials—*trans*-$Na[Co(NH_3)_4(SO_3)_2]\cdot 2H_2O$(brown salt) and *cis*-$Na[Co(NH_3)_4(SO_3)_2]\cdot 4H_2O$ (golden yellow salt) were partly prepared by the method of Hofmann and Jenny,⁽²⁾ and partly by a modification of that as follows: 21 grams of anhydrous cobaltous carbonate were dissolved in 250 ml. of *ca.* 30% acetic acid and mixed with 250 ml. of 28% NH_3 aq. A vigorous stream of air was drawn through the solution for 24 hours. Through the resultant solution gaseous sulfur dioxide was passed until a considerable amount of brownish orange precipitates appeared. After removal of the precipitates, a mixture of 38 grams sodium bisulfite dissolved in 100 ml. of water and 100 ml. of 28% NH_3 aq. was added to the filtrate. Leaving the mixture for 4 hours at room temperature, the precipitated dark yellow powder was removed by filtration. The filtrate, on cooling in water for 6 hours, precipitated the brown crystals of *trans*-$Na[Co(NH_3)_4(SO_3)_2]\cdot 2H_2O$. Then it precipitated, by cooling in ice for 10 hours, first a little amount of *cis-trans* mixtures and then the almost pure golden yellow crystals of *cis*-$Na[Co(NH_3)_4(SO_3)_2]\cdot 4H_2O$. The rough products of both the isomers were recrystallized from concentrated aqueous solutions by addition of 95% methanol. These were washed by methanol and dried in air. The absorption spectra of the two salts which were obtained by the above method com-

Table 3

Absorption Maxima of Three Disulfono-complexes

Complex salt	First band		Second band		Third band		Sulfono-specific band	
	ν_1, 10^{13}/sec.	log ε_1	ν_2, 10^{13}/sec.	log ε_2	ν_3, 10^{13}/sec.	log ε_3	ν_s, 10^{13}/sec.	log ε_s
trans-$Na[Co(NH_3)_4(SO_3)_2]\cdot 2H_2O$ (brown salt)	66.6	2.32	?		113.6	4.19	101.0	4.22
cis-$Na[Co(NH_3)_4(SO_3)_2]\cdot 4H_2O$ (golden yellow salt)	65.9	2.26	?		—	—	107.8	4.21
$NH_4[Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$ (dark brown form)	66.6	2.35	?		114.2	4.20	101.2	4.22

---

(9) H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan*, **59**, 1142 (1938).

(10) R. Schwarz and K. Tede, *Ber.*, **60**, 63 (1927).

(11) R. Klement, *Z. anorg. Chem.*, **150**, 117 (1926).

(12) J. C. Bailar, Jr. and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

pletely accord with those of the salts obtained by the original direction of Hofmann and Jenny.

The dark brown form of ammonium disulfonotetrammine-cobaltiate, $NH_4[Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$, was prepared by the method of 'Bailar and Peppard.(12)

Spectrographic Measurements—The formal extinction coefficient ε was calculated from the equation: $I=I_0\times 10^{-\varepsilon cd}$, where c is the concentration of the complex ion in gram-ion per liter and d the thickness of the layer in cm. The measurements were made in 3% aqueous solutions of NH_3, because aqueous solutions of the disulfono-complexes because turbid when allowed to stand for about 30 minutes in an open place, while in 3% NH_3 aq. the clearness could be kept almost perfectly for a long time. The comparison cell was also filled with 3% NH_3 aq. Measurements were done at room temperature, with concentrations of 2.5×10^{-3} and 1.0×10^{-4} gram-ion per liter and with varying thickness from 5 to 1 cm.

Summary

The visible and ultra-violet absorption spectra of $Na[Co(NH_3)_4(SO_3)_2]\cdot 2H_2O$ (brown salt) and $Na[Co(NH_3)_4(SO_3)_2]\cdot 4H_2O$ (yellow salt) have been measured. The results have proved that the $SO_3^{=}$-radical coördinates around the central cobalt (III) ion by the lone pair electrons of its sulfur atom, and that the brown salt has *trans*-configuration concerning the positions of the $SO_3^{=}$-radicals and the yellow salt *cis*-configuration.

The absorption spectrum of $NH_4[Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$ (dark brown form) has also been studied and it has been assumed that the salt is *trans*-isomer contrary to several investigators' assignments of *cis*-structure.

The author expresses sincere thanks to Professor R. Tsuchida for his kind advice and encouragement.

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