Absorption Spectra of Co(III) Complexes. I. Curve Analyses of the First and Second Absorption Bands[1)]

By Yoichi SHIMURA and Ryutaro TSUCHIDA

(Received April 25, 1955)

Introduction

There have been offered two experimental equations of some applicability for the broad absorption band such as the first or second absorption band[2)] of metallic complexes. The one is the equation of Kuhn and Braun[3)], and the other, Lowry and Hudson's[4)]:

Kuhn and Braun's equation

$$\varepsilon=\varepsilon_{\max}\exp\left(-\left[\frac{\nu_{\max}-\nu}{\theta}\right]^2\right), \qquad (1)$$

Lowry and Hudson's equation

$$\varepsilon=\varepsilon_{\max}\exp\left(-\left[\frac{\nu_{\max}}{\nu}\cdot\frac{\nu_{\max}-\nu}{\theta}\right]^2\right), \qquad (2)$$

1) Presented at the Symposium on Co-ordination Compounds, Tokyo, November 14, 1954.

2) For general discussion of the first and second bands of co-ordination compound the reader is requested to refer to the following literature. a) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938). b) R. Tsuchida, "The Colours and Structures of Metallic Compounds", (in Japanese), Osaka, 1944. c) Y. Inamura and Y. Kondo, *J. Chem. Soc. Japan*, **72**, 843 (1951).

3) W. Kuhn and E. Braun, *Z. phys. Chem.*, **B 8**, 281 (1930).

4) T.M. Lowry and H. Hudson, *Phil. Trans.*, **A 232** 117 (1933).

where ε and ε_{max} are the formal extinction coefficients at frequencies ν and ν_{max}, ν_{max} being the frequency of maximum absorption. The value of θ is determined by the relation

$$\theta=\frac{l}{2\sqrt{\ln 2}}=\frac{l}{1.665}, \quad (3)$$

where l is the half-value width of the band, i.e., the difference between the two frequencies, ν_k and ν_l, where the formal extinction coefficients are equal to the half of ε_{max}:

$$l=\nu_l-\nu_k \ (\nu_l>\nu_k). \quad (4)$$

The equation (1) is based upon the assumption of a symmetrical distribution in frequencies, while the equation (2) postulates a symmetrical distribution in wave-lengths.

Kuroya[5] and Shimura[6] employed the equation of Kuhn and Braun in the analyses of the spectra of Co(III) nitro- or isothiocyanato-complexes, and the Lowry and Hudson's equation was used by Mead[7] and Mathieu[8] in studying Cr(III) and Co(III) complexes. All these authors, however, adopted the equations with some modifications of the values of θ's in order to get agreement with experimental curves.

As will be seen in this paper, in fact, the first and second bands of the Co(III) complex compounds are not symmetrical either on the scale of frequency or of wave-length. An unsymmetrical equation of absorption band had been offered by Bielecki and Henri[9], but this was not superior to the equation (1) or (2). In this report, a new unsymmetrical equation has been developed and the general applicability has been substantiated by the analyses of absorption curves of the typical Co(III) complexes.

Experimental

The visible and ultraviolet absorption spectra of about fifteen typical Co(III) complexes were measured in aqueous solutions. The numerical data for the first and second bands of the complexes are collected in Table I, and typical absorption curves are shown in Figs. 1–4. The

TABLE I

ABSORPTION DATA OF THE FIRST AND SECOND BANDS OF Co(III) COMPLEXES

Type	Complex Salt	First Band				Second Band				$\Delta(\nu_{max})$	$\Delta(\log\varepsilon_{max})$
		ν_{max} (10^{13}/sec.)	$\log\varepsilon_{max}$	l (10^{13}/sec.)	δ (10^{13}/sec.)	ν_{max} (10^{13}/sec.)	$\log\varepsilon_{max}$	l (10^{13}/sec.)	δ (10^{13}/sec.)	(10^{13}/sec.)	
6N	$[Co(NH_3)_6](ClO_4)_3$	62.9	1.68	10.3	0.45	88.3	1.60	12.5	0.35	25.4	−0.08
	$[Co\ en_3](ClO_4)_3$	63.9	1.94	10.4	0.55	88.4	1.90	12.0	0.4	24.5	−0.04
	trans-$[Co\ en_2(NH_3)_2](ClO_4)_3\cdot H_2O$	64.2	1.77	10.8	0.8	89.2	1.73	12.3	0.55	25.0	−0.04
	cis-$[Co\ en_2(NH_3)_2](ClO_4)_3\cdot H_2O$	64.4	1.79	10.7	0.65	89.4	1.74	12.6	0.5	25.0	−0.05
5N1O	$[Co\ en_2$ glycine'$](ClO_4)_2$	61.3	2.00	11.2	0.7	86.4	2.04	12.5	0.3	25.1	+0.04
	$[Co\ en_2$ leucine'$](ClO_4)_2$	61.5	2.02	11.3	0.65	86.1	2.06	12.4	0.5	24.6	+0.04
4N2O	$[Co(NH_3)_4\ ox]ClO_4\cdot H_2O$	58.7	1.91	10.4	0.5	84.0	2.11	12.3	0.35	25.3	+0.20
	$[Co\ en_2\ ox]Cl\cdot 3H_2O$	60.1	2.05	10.1	0.45	84.3	2.16	12.7	0.45	24.2	+0.11
	$[Co(NH_3)_4CO_3]ClO_4$	57.4	2.01	9.8	0.35	82.6	2.02	—*	—*	25.2	+0.01
	$[Co\ en_2\ CO_3]ClO_4$	58.4	2.13	9.4	0.3	83.0	2.09	13.3	0.0	24.6	−0.04
3N3O	α-[Co glycine'$_3$]**	—	—	—	—	80.4	2.16	12.1	0.35	—	—
	β-[Co glycine'$_3$]***	57.7	2.20	9.1	0.55	80.2	2.14	12.7	0.6	22.5	−0.06
2N4O	$[Co\ ox_2(NH_3)_2]NH_4\cdot H_2O$	54.0	2.04	9.6	0.6	78.2	2.30	11.4	0.3	24.2	+0.26
	[Co edta] $Na\cdot 4H_2O$****	55.9	2.51	10.4	0.2	78.1	2.36	10.6	0.5	22.2	−0.15
1N5O	No example.										
6O	$[Co\ ox_3]K_3\cdot 3H_2O$	49.7	2.17	8.0	0.35	70.9	2.30	10.8	0.65	21.2	+0.18
	$[Co(O_6Mo_6O_{18}H_6)](NH_4)_3\cdot 7H_2O$	49.2	1.29	9.0	0.3	72.8	1.30	12.3	0.2	23.6	+0.01
	Mean.....			10.0	0.5			12.2	0.4		

* Omitted because of uncertainty. For the details, see the next paper of this series.
** The first absorption of this complex is split into two bands. The details will be reported separately.
*** Measured in 60% perchloric acid.
**** edta represents a ethylenediaminetetraacetate ion (quadrivalent).

5) H. Kuroya, *J. Inst. Polytech., Osaka City Univ.* C 1, No. 1, 29 (1950).
6) Y. Shimura, *J. Am. Chem. Soc.*, 73, 5079 (1951).
7) A. Mead, *Trans. Farad. Soc.*, 30, 1052 (1934).
8) J.-P. Mathieu, *Bull. soc. chim.*, [5] 3, 463 (1936).
9) J. Bielecki and V. Henri, *Phys. Z.*, 14, 516 (1913).

experimental details will appear in the next paper of this series.

In Fig. 5, the spectrum of [Co en_2 Cl_2] Cl is given. This was determined in methyl alcoholic solution with concentration of 3.3×10^{-3} F. A Beckman DU spectrophotometer was used.

Inclination of Absorption Band

Lowry and Hudson[4] previously stated that absorption spectra of most organic compounds are not symmetrical but steeper on the side of longer wave-lengths. As will be seen in Figs. 1–5, this is also true of the first and second bands of Co(III) complexes.

In order to obtain precise information about the unsymmetrical nature of these absorption bands, a new parameter, δ, was introduced (see, Fig. 1):

$$\delta=\frac{\nu_k+\nu_l}{2}-\nu_{max.} \tag{5}$$

This is a measure of the inclination of the absorption band. The values of the parameters determined are given in Table I. The following conclusions were drawn from these data: (a) the values of the inclination parameters vary from 0.0 to $+0.8(\times10^{13}/\text{sec.})$. Thus the first or second bands of these complexes are almost always steeper on the side of longer wave-lengths. (b) Among the values of δ's no apparent regularities were recognized. (c) In summary, these bands are not symmetrical either on the scale of frequency or wave-length.

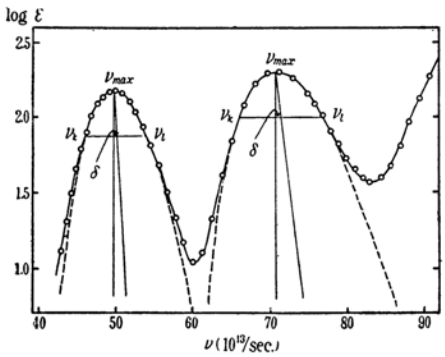

Fig. 1. [Co ox_3]$^{3-}$:
-o-o-o-, experimental curve;
-----, first and second bands calculated by the new equation.

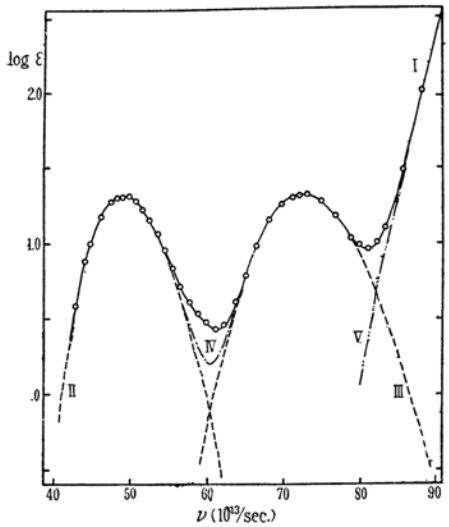

Fig. 2. [$Co(O_6Mo_6O_{18}H_6)$]$^{3-}$:
I, experimental curve; II, calculated first band; III, calculated second band; IV, II+III; V, I−III.

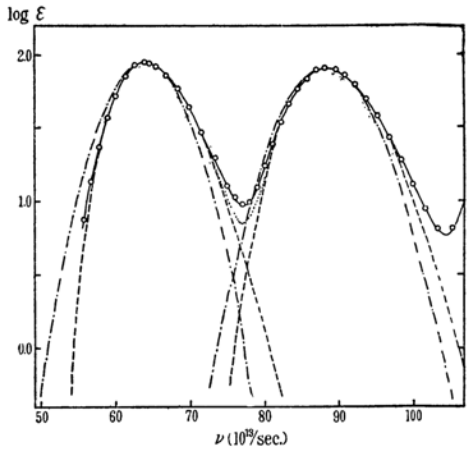

Fig. 3. [Co en_3]$^{3+}$:
-o-o-o-, experimental curve;
-----, calculated by the new equation;
———, calculated by Kuhn and Braun's equation.

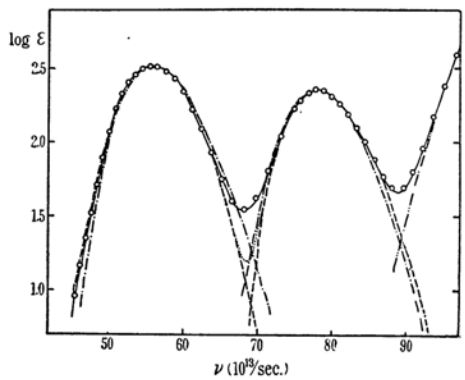

Fig. 4. [Co edta]$^{-}$:
-o-o-o-, experimental curve;
-----, calculated by the new equation;
———, calculated by Lowry and Hudson's equation.

Experimental Equation

To fit the unsymmetrical absorption bands, a new absorption equation (6) was developed:

$$\varepsilon=\varepsilon_{max}\exp\left(-\left[\frac{\theta-\sqrt{\theta^2-2\delta'(\nu_{max}-\nu)}}{\delta'}\right]^2\right) \quad (6)$$

where

$$\delta'=2\times0.434\times\frac{\delta}{0.3} \quad (7)$$

As in equation (1) and (2), θ is defined by the relation (3).

The principal feature of the new equation is that it is a modification of Kuhn and Braun's equation by the addition of a correction term, which contains the inclination parameter δ. Thus the equation (6) becomes

$$\nu=\nu_{max}\pm\theta'\sqrt{\log\varepsilon_{max}-\log\varepsilon}+\frac{\delta}{0.3}(\log\varepsilon_{max}-\log\varepsilon), \quad (8)^*$$

where $\theta'=\dfrac{\theta}{\sqrt{0.434}}$. If the third term is neglected, the equation (8) is reduced to the equation (1). The expression (8) has practical conveniences because it is applicable to either symmetrical or unsymmetrical bands ($\delta=0$ for symmetrical and $\delta\neq0$ for unsymmetrical).

The curve of equation (8) passes the three points (ν_{max}, ε_{max}), (ν_k, $\frac{1}{2}\varepsilon_{max}$) and ($\nu_l$, $\frac{1}{2}\varepsilon_{max}$), and adequately represents the essential characteristics of the experimental curve. Both the calculated and experimental curves for some of the Co(III) complexes are shown in Figs. 1–4. The agreement is now so close as to approach the limits of experimental error throughout the first and the second bands except where there is serious overlapping of the two bands. The values calculated by the equations (1) or (2) are also plotted for comparison (Figs. 3 and 4). From these figures, it is clear that the new equation shows a closer resemblance to the observed curves than the equation (1) or (2), especially on the side of shorter wavelengths.

The new equations are also applied successfully to the analyses of the specific absorption bands, for example, the isothiocyanato specific bands of Co(III) complexes, which will be the subject of a later paper of this series.

It should be added that integration of the equation (6) gives for the total intensity F of a broad absorption band:

$$F=\int\varepsilon d\nu=\int\varepsilon_{max}\exp\left(-\left[\frac{\theta-\sqrt{\theta^2-2\delta'(\nu_{max}-\nu)}}{\delta'}\right]^2\right)d\nu \fallingdotseq\varepsilon_{max}\theta\int_{-\infty}^{\infty}e^{-t^2}dt=\varepsilon_{max}\cdot\theta\cdot\sqrt{\pi}=1.06\,\varepsilon_{max}\cdot l \quad (9)$$

This formula is useful for determining experimentally the oscillator strengths of broad absorption bands.

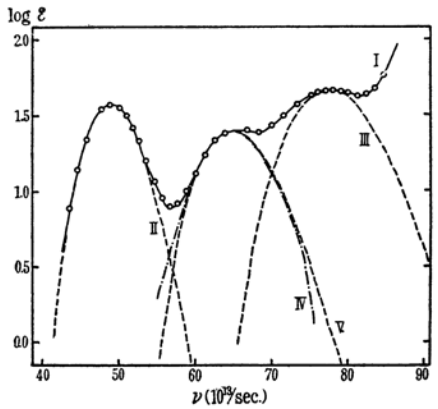

Fig. 5. *trans*-[Co en_2Cl_2]$^+$:
I, experimental curve; II, calculated first component of first bands; III, calculated second band; IV, I−(II+III); V, calculated second component of first bands.

Application to the spectra of trans-[Co en₂ Cl₂]⁺

Recently[10,11] it was confirmed that the first absorption of *trans*-[Co en_2 Cl_2]$^+$ was spilit into two peaks, overlapping the second component on the second absorption band. The analyses of these bands using equation (8) are shown in Fig. 5. As with the first peak of the first bands, the curve II was calculated by the use of the parameters determined experimentally. For the second band, by using the mean values of the half-value widths and inclination parameters for the second bands ($l=12.2$, $\delta=0.4\times10^{13}$/sec., as listed in Table I), curve III has resulted. After subtracting curves II and III from the experimental curve I, a peak appeared at 64.9 ($\times10^{13}$/sec.) with intensity of $\log\varepsilon=1.41$. The resultant band IV was exactly reproduced by the curve V, which was calculated using the values, $l=10.5$ and $\delta=0.45$. The parameters of these bands are given in Table II.

* $\varepsilon>\varepsilon_{max}e^{-(\theta/\delta')^2}$, for $\nu<\nu_0$ if $\delta>0$ and for $\nu>\nu_0$ if $\delta<0$.

10) M. Linhard and M. Weigel, *Z. anorg. allg. Chem.*, **271**, 101 (1952).
11) S. Yamada, A. Nakahara, Y. Shimura and R. Tsuchida, This Bulletin, **28**, 222 (1955).

TABLE II
FIRST AND SECOND BANDS OF *trans*-$[Co\ en_2\ Cl_2]^+$

Band	ν_{max} (10^{13}/sec.)	log ε_{max}	l (10^{13}/sec.)	δ (10^{13}/sec.)
First Bands				
First component	48.8	1.58	7.8	0.3
Second component	64.9	1.41	10.5	0.45
Second Band	77.5	1.68	(12.2)	(0.4)

Relation between the First and the Second Bands

i) Frequency of Maximum Absorption.— Some close relationships have been recognized between the first and the second bands of metallic complexes[12]. As regards the Co(III) complexes, Kuroya[5] and Sone[12] derived each an experimental formula for the positions of the first and the second bands:

Kuroya's formula $\nu_2=\nu_1+25.0$ (10)

Sone's formula $\nu_2=1.189\,\nu_1+13.31$, (11)

where ν_1 and ν_2 are the frequencies in 10^{13}/sec. of absorption maxima of the first and the second bands.

In Fig. 6, both the formulae are plotted

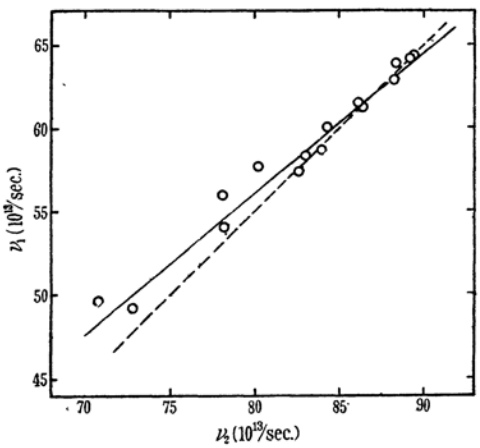

Fig. 6. Frequency of absorption maximum of the first band vs. that of the second band:
○ , experimental data;
-----, plot of Kuroya's formula;
———, plot of Some's formula.

with the new data listed in Table I. It is seen that Sone's formula shows excellent agreement with the experimental data. From the values of $\Delta(\nu_{max})$ listed in Table I, which is the frequency difference between the maxima of the second and the first bands, it is also shown that Kuroya's formula is useful for the complexes of hexammine-, pentammine- and tetrammine-types. But the values of $\Delta(\nu_{max})$ for complexes of triammine-, diammine- and hexacido-types deviate considerably from 25.0. Such a condition is also clearly observed in Fig. 7, on the left

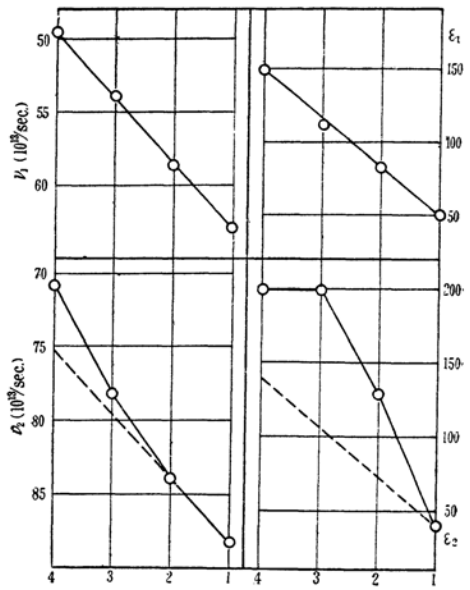

Fig. 7. Frequency positions and formal extinction coefficients of the ammine-oxalato Co(III) complexes:
1, $[Co(NH_3)_6]^{3+}$;
2, $[Co(NH_3)_4\ ox]^+$;
3, $[Co(NH_3)_2ox_2]^-$;
4, $[Co\ ox_3]^{3-}$.

part of which are plotted the frequency values for the first and second bands of Co(III) complexes belonging to an ammine-oxalato series. From the diagrams it has been confirmed that the successive substitutions of ammonia molecules by oxalate ions cause the shifts in the first absorption bands which are directly proportional to the degree of the substitution. On the other hand, the shifts in the second bands are not proportional to the degree of substitution; the greater shifts were observed for the second bands as compared with the first bands.

It is interesting to note that a similar relation exists among the absorption intensities of these complexes (See right part of Fig. 7). In view of these relations it should be suggested that the first and the second bands arise from some what different origins.

ii) Intensity.—Many previous authors recognized that the intensities of the first and the second bands are nearly of the same order. This is also supported by the values of $\Delta(\log \varepsilon_{max})$ listed in Table I ($\Delta(\log \varepsilon_{max})$ denotes the difference between $\log \varepsilon_{max}$'s of

12) K. Sone, *J. Chem. Soc. Japan*, 71, 270, 316 (1950).

the second and the first bands. It should be added, however, that all oxalato-complexes studied are stronger in the second bands than in the first bands.

iii) Half-value Width. — The half-value widths of the first bands are always smaller than those of the second bands (see Table I).

iv) Inclination Parameter.—The inclination parameters of the first bands are almost always greater than those of the second bands (see Table I).

Summary

The measurements of the visible and ultraviolet absorption spectra of about fifteen Co(III) complex compounds have revealed that the first and second bands of these complexes are not symmetrical either on the scale of frequency or wave-length, and that these bands cannot be represented by the equation of Kuhn and Braun, nor of Lowry and Hudson.

To fit the unsymmetrical absorption bands, a new experimental absorption equation has been developed and its adequacy substantiated.

Some relationships between the first and the second bands of Co(III) complexes are also investigated.

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