The Absorption Spectra of Cobalt(III) Complexes. III.[1] *The Spin-forbidden Bands*

By Junnosuke FUJITA and Yoichi SHIMURA

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In marked contrast to the extensive work on the first and the second absorption bands of cobalt(III) complexes, relatively few investigations have been made of the weak absorption bands observed on the longer wavelength side adjacent to the first band. According to the ligand field theory,[2] the former two can be assigned to the spin-allowed transitions and the weak latter to the spin-forbidden transitions, although all these bands between the d levels of the cobalt(III) ion split because of the field perturbations of ligands.

Previously, Yoneda et al.[3] have reported on the existence of some weak absorption bands in the near infrared spectra ($0.8\sim1.3\,\mu$) of $[Co(CO_3)(NH_3)_4]NO_3$ and $K_3[Co\,ox_3]$. Inamura and Kondo[4] have also found weak bands in this region for some polynuclear cobalt(III) complexes. Later, Jørgensen[5] studied the nature of these weak bands and assigned them to the spin-forbidden transitions. More recently, Linhard and Weigel[6] have carefully measured the near infrared spectra of $[Co\,en_3]^{3+}$, $[Co(NH_3)_6]^{3+}$ and $[Co(X)(NH_3)_5]^{2+}$ ($X=F^-, Cl^-, Br^-, I^-$) and shown that each complex has two absorption bands due to the spin-forbidden transitions which correspond well with the theoretical assignment.[2] These two bands were named the A and the B bands, beginning from the longer wavelength side.

In order to investigate the nature of these A and B bands in more detail, as has been done for the first and the second bands,[1] we have measured the absorption spectra of about fifty complexes of cobalt(III). By combining these findings with those on the first and the second bands, it will be possible to discuss the experimental relationships among them in this paper.

Experimental

A Beckman DU spectrophotometer was used to obtain the absorption spectra in the range between 25 and 120 ($\times10^{13}$/sec.). Aqueous solutions almost saturated were used to measure the near infrared spectra. All measurements were made at room temperature.

The complexes used in this work were prepared according to the methods described in the available literature, except for several new compounds which will be described below. All the compounds were recrystallized carefully before measuring the weak absorption bands.

***trans*-Chloro-nitro-bis(ethylenediamine)-cobalt(III) Perchlorate, *trans*-$[Co(Cl)NO_2\,en_2]ClO_4$.**—A finely powdered *trans*-$[Co(NO_2)_2\,en_2]NO_3$ was dissolved in hydrochloric acid (1 : 1). The crude product was precipitated from this clear solution by the addition of solid sodium perchlorate. The red precipitate which was filtered off was dissolved again in hydrochloric acid (1 : 1). The addition of perchloric acid (60%) to this solution resulted in the formation of orange red crystals, which were then filtered, washed with alcohol and dried in air. This complex was anhydrous.

Found: ClO_4^-, 27.1. Calcd. for $[Co(Cl)NO_2en_2]ClO_4$: 27.6%.*

***trans*-Bromo-nitro-bis(ethylenediamine)-cobalt(III) Perchlolate, *trans*-$[Co(Br)NO_2\,en_2]ClO_4$.**—The mixture of 4 g. *trans*-$[Co(NO_2)_2\,en_2]Br\cdot2H_2O$ and 6 ml. concentrated hydrobromic acid ($d=1.48$) was warmed on a water bath while being stirred. After the evolution of gas ceased, the resulting materials were kept in a cool place for a while. Then the precipitate was separated; it was the crude product of *trans*-$[Co(Br)NO_2\,en_2]Br$ and could be recrystallized from concentrated hydrobromic acid by the addition of acetone. The pure perchlorate was prepared by the addition of perchloric acid (60%) to the solution of this precipitate in concentrated hydrobromic acid. The complex was separated as anhydrous, brownish red crystals.

Found: ClO_4^-, 23.8. Calcd. for $[Co(Br)NO_2en_2]ClO_4$: 24.6%

Tetrammine-mono(ethylenediamine)-cobalt(III) Bromide Monohydrate, $[Co(NH_3)_4\,en]Br_3\cdot H_2O$.—This complex was prepared by the method described previously.[8]

Potassium Pentacyano-nitro-cobaltate(III), $K_3[Co(CN)_5NO_2]$.—The mixture containing 8 g. of $[Co(NO_2)(NH_3)_5]Cl_2$ and 10 g. of potassium cyanide

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[1] Parts I and II of this series: Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955); **29**, 311 (1956).

[2] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

[3] H. Yoneda, S. Kida and M. Kobayashi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **73**, 518 (1952).

[4] Y. Inamura and Y. Kondo, ibid., **74**, 627 (1953).

[5] C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 152 (1953).

[6] M. Linhard and M. Weigel, *Z. physik. Chem. N. F.*, **11**, 308 (1957).

* For the analysis of the perchlorate ion, the method of Linhard and Stirn[7] was employed.

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[8] Y. Shimura, This Bulletin, **31**, 311 (1958).

TABLE I. SUMMARY OF THE MEASUREMENT

The frequencies are given in 10^{13}/sec., and the intensities by log ε in parentheses

Complex	A Band	B Band	I Band	II Band	B–A	II–I	I–A	Ref.
$[Co(NH_3)_6]Cl_3$	40.1($\bar{1}$.42)	ca. 51($\bar{1}$.8)	62.9(1.76)	88.3(1.68)	10.9	25.4	22.8	
$[Co\ en_3]Cl_3 \cdot 3H_2O$	41.5($\bar{1}$.52)	ca. 52($\bar{1}$.8)	63.9(1.94)	88.4(1.90)	10.5	24.5	22.4	
$[Co(NH_3)_4\ en]Br_3 \cdot H_2O$	40.8($\bar{1}$.47)	ca. 51($\bar{1}$.9)	63.6(1.83)	88.4(1.76)	10.2	24.8	22.8	
$[Co\ dip_3](ClO_4)_3 \cdot 3H_2O$	43.5(0.04)	—	66.6(1.84)	—	—	—	23.1	9
$[Co\ en_2\ phen]SO_4Cl \cdot 2H_2O$	42.2($\bar{1}$.88)	—	64.6(2.01)	—	—	—	22.4	9
$[Co(l\text{-}leu)\ en_2]Cl_2$	38.0($\bar{1}$.72)	ca. 49(0.1)	61.5(2.02)	86.1(2.06)	11.0	24.6	23.5	
$[Co\ ox(NH_3)_4]Cl$	35.8($\bar{1}$.81)	ca. 46(0.0)	58.7(1.91)	84.0(2.11)	10.2	25.3	22.9	
$[Co\ CO_3en_2]Cl \cdot H_2O$	34.7(0.05)	ca. 45(0.3)	58.4(2.13)	83.0(2.09)	10.3	24.6	23.7	
$[Co(phthal)en_2]Br \cdot 3H_2O$	ca. 33 ($\bar{1}$.91)	ca. 43(0.1)	55.6(1.92)	ca. 85 (2.07)	10.0	19.4	22.6	9
$[Co(salic)(NH_3)_4]Cl \cdot H_2O$	35.0(0.18)	—	56.6(2.20)	ca. 78 (2.5)	—	21.4	21.0	9
$[Co(salic)en_2]Cl \cdot 2H_2O$	37.0(0.08)	—	58.2(2.36)	ca. 79 (2.6)	—	20.8	21.2	9
fac-$[Co(gly)_3] \cdot H_2O$	33.0(0.02)	ca. 46(0.3)	57.7(2.20)	80.2(2.15)	13.0	22.5	24.7	
mer-$[Co(gly)_3] \cdot 2H_2O$	29.8($\bar{1}$.82)	ca. 42($\bar{1}$.9)	55.7(2.00)	80.6(2.18)	12.2	24.9	25.9	
fac-$[Co(dl\text{-}ala)_3]$	33.2(0.12)	ca. 45(0.3)	57.9(2.27)	80.3(2.21)	11.8	22.4	24.7	
mer-$[Co(dl\text{-}ala)_3]$	30.3($\bar{1}$.96)	ca. 43(0.1)	55.6(2.00)	80.9(2.18)	12.7	25.3	25.3	
fac-$[Co(picol)_3]$	34.6(0.22)	ca. 46(0.3)	58.3(2.17)	79.6(2.24)	11.4	21.3	23.7	9
mer-$[Co(picol)_3]$	ca. 34 (0.08)	—	57.8(2.02)	80.0(2.34)	—	22.2	23.8	9
cis-$NH_4[Co\ ox_2(NH_3)_2] \cdot H_2O$	31.2(0.02)	ca. 42(0.3)	54.0(2.04)	78.2(2.30)	10.8	24.2	22.8	
cis-$K[Co(CO_3)_2(NH_3)_2] \cdot 3H_2O$	27.3(0.64)	ca. 40(0.9)	52.2(2.24)	76.0(2.41)	12.7	23.8	24.9	10
$Na[Co\ ox_2en] \cdot H_2O$	33.3($\bar{1}$.91)	ca. 44(0.2)	55.6(1.93)	77.9(2.12)	10.7	22.3	22.3	10
$K[Co\ malo_2en] \cdot H_2O$	33.3(0.02)	ca. 43(0.2)	55.6(1.96)	77.9(2.08)	9.7	22.3	22.3	10
$Na[Co\ edta] \cdot 4H_2O$	30.8($\bar{1}$.96)	ca. 43(0.4)	55.9(2.51)	78.1(2.36)	12.2	22.2	25.1	
cis-(N)-$K[Co(ada)_2] \cdot 3/2H_2O$	28.4(0.00)	ca. 41(0.2)	53.4(2.18)	79.0(2.13)	12.6	25.6	25.0	10
cis-(N)-$K[Co(ata)gly] \cdot 2H_2O$	27.3(0.07)	ca. 40(0.3)	53.0(2.35)	78.2(2.23)	12.7	25.2	25.7	10
$K_3[Co\ ox_3] \cdot 3H_2O$	25.0(0.25)	ca. 38(0.5)	49.7(2.17)	70.9(2.30)	13.0	21.2	24.7	
cis-$[Co(Cl)NH_3en_2]Cl_2 \cdot 2H_2O$	35.8($\bar{1}$.64)	ca. 47(0.1)	56.9(1.86) 65.6(1.36)	82.2(1.87)	11.2	25.3	21.1	14
cis-$[Co(NO_2)_2en_2]Cl$	ca. 45 ($\bar{1}$.8)	—	68.8(2.27)	—	—	—	23.8	
trans-$[Co(NO_2)_2en_2]Cl$	ca. 48 ($\bar{1}$.5)	—	70.0(2.30)	—	—	—	22.0	
trans-$[Co(Cl)NO_2en_2]ClO_4$	ca. 41 ($\bar{1}$.6)	—	62.5(1.97)	—	—	—	21.5	
trans-$[Co(Br)NO_2en_2]ClO_4$	ca. 42 (0.7)	—	60.0(2.12)	—	—	—	18.0	
cis-$[Co(N_3)_2(NH_3)_4]ClO_4$	33.0(0.12)	—	55.8(2.42)	—	—	—	22.8	
trans-$[Co(N_3)_2(NH_3)_4]N_3$	31.8($\bar{1}$.86)	—	53.0(2.49)	—	—	—	21.2	
$Na_2[Co(NO_2)edta] \cdot 3H_2O$	26.4($\bar{1}$.81)	ca. 38($\bar{1}$.9)	51.4(1.97) 60.4(2.32)	—	11.6	—	25.0	
$K_2[Co(Cl)edta] \cdot 3H_2O$	27.2($\bar{1}$.89)	ca. 39(0.3)	51.6(2.38)	74.5(2.43)	11.8	22.9	24.4	
$Na[Co(Br)edtaH] \cdot 3H_2O$	30.0(0.25)	ca. 39(0.6)	51.0(2.34)	—	9.0	—	21.0	
$K_3[Co(CN)_6]$	ca. 75 ($\bar{1}$.9)	—	96.8(2.29)	116.8(2.12)	—	20.0	21.8	
$K_4[Co(CN)_5SO_3] \cdot 3H_2O$	ca. 70 (0.7)	—	89.6(2.59)	—	—	—	19.6	
$K_3[Co(CN)_5NO_2]$	ca. 66 (0.9)	—	ca. 86 (2.5)	—	—	—	20	
$K_3[Co(CN)_5N_3] \cdot 2H_2O$	ca. 57 ($\bar{1}$.9)	—	78.9(2.86)	—	—	—	21.9	
$K_3[Co(CN)_5Cl]$	59.6(0.04)	—	76.9(2.31)	ca. 99 (2.1)	—	22.1	17.3	11
$K_3[Co(CN)_5Br]$	58.4(0.95)	—	75.6(2.21)	—	—	—	17.2	11
$K_3[Co(CN)_5I]$	60.7(1.98)	—	ca. 73 (2.3)	—	—	—	13.7	11
$[Co(CN)_2en_2](SO_4)_{1/2} \cdot 3/2H_2O$	49.6($\bar{1}$.71)	—	74.4(1.95)	97.3(1.94)	—	22.9	24.8	

dissolved in 100 ml. of water was warmed on a water-bath while being stirred. After the evolution of gaseous ammonia, the orange yellow solution obtained was filtered and kept at room temperature for a while. The addition of methanol to the solution gave a pale yellow precipitate, which was then filtered off, washed with alcohol and ether, and dried in air. Recrystallization from the aqueous solution to obtain well-formed pale yellow crystals was effected by the slow addition of methanol and by leaving it to stand in a refrigerator.

Found: Co, 16.5; C, 16.40; N, 23.51. Calcd. for $K_3[Co(CN)_5NO_2]$: Co, 16.73; C, 17.05; N, 23.85%.

Potassium Pentacyano-azido-cobaltate(III) Dihydrate, $K_3[Co(CN)_5N_3]\cdot 2H_2O$.—The recrystallized yellow crystals of this complex were obtained by almost the same method as the nitro-complex, described above, using 8.4 g. of $[Co(N_3)(NH_3)_5]Cl_2$ and 10 g. of potassium cyanide. The only difference was that the reaction took place at room temperature, without the complex being warmed on a water-bath.

Found: Co, 15.8; C, 15.77; N, 30.15; H_2O, 9.53. Calcd. for $K_3[Co(CN)_5N_3]\cdot 2H_2O$: Co, 15.33; C, 15.75; N, 29.15; H_2O, 9.37%.

Potassium Pentacyano-sulfono-cobaltate(III) Trihydrate, $K_4[Co(CN)_5SO_3]\cdot 3H_2O$.—To 50 ml. of an aqueous solution containing 10 g. of $K_3[Co(CN)_5Br]$, 5 g. of $K_2SO_3\cdot 2H_2O$ dissolved in 50 ml. of water was added. The resulting solution was heated on a water-bath until the initial reddish color turned pale yellow. After the solution had cooled, the addition of methanol to the filtered solution gave pale-yellow crystals, which were then filtered off, washed with alcohol and ether, and dried in air. These were recrystallized from the aqueous solution by the addition of methanol.

Found: Co, 12.5; C, 12.26; N, 15.08; H_2O, 11.52. Calcd. for $K_4[Co(CN)_5SO_3]\cdot 3H_2O$: Co, 12.29; C, 12.52; N, 14.60; H_2O, 11.27%.

Results and Discussion

In Table I are listed the numerical data for the A, the B, the first, and the second absorption bands. Some typical absorption curves of all the spectra measured are shown in Figs. 1—6.

From these data, the following conclusions may be obtained.

1) The spectrochemical series[1,12] determined experimentally for the first and the second bands is also valid for the A and the B bands. This indicates that the lower the frequencies of the first and the second bands, the lower the corresponding A and B bands. In Fig. 1, the spectra of the cobalt(III) complexes of the ammine-oxalato series are shown to illustrate how the successive substitutions of ammonia by oxalate ions cause shifts in all these bands and how the magnitude of the shifts is proportional to the degree of substitution.[1]

2) As may be seen in Fig. 7, there is a linear relationship between the frequencies of the A band and those of the first band. A similar relation is seen between the first and the second bands[13] (Fig. 8), and also between the A and the B bands (Fig. 9). This indicates that these bands are closely related to

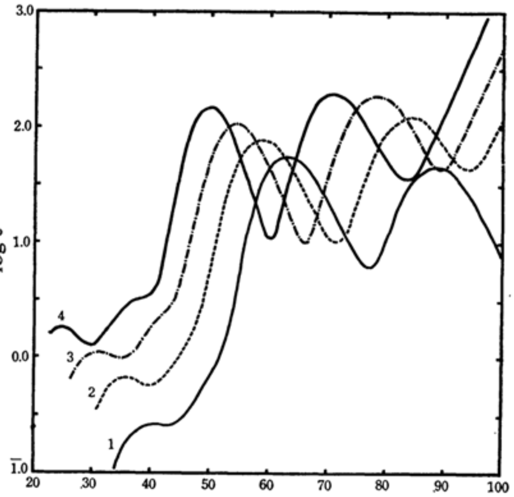

Fig. 1. Absorption spectra of: 1, $[Co(NH_3)_6]^{3+}$; 2, $[Co\,ox(NH_3)_4]^+$; 3, $[Co\,ox_2(NH_3)_2]^-$; 4, $[Co\,ox_3]^{3-}$.

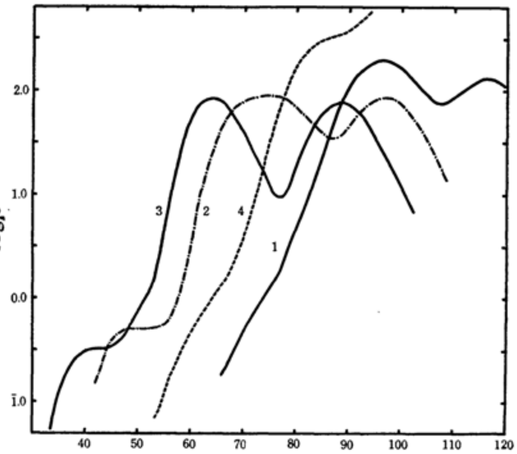

Fig. 2. Absorption spectra of: 1, $[Co(CN)_6]^{3-}$; 2, $[Co(CN)_2en_2]^+$; 3, $[Co\,en_3]^{3+}$; 4, $[Co(CN)_5SO_3]^{4-}$.

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[9] N. Matsuoka, Y. Shimura and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1637 (1961).

[10] J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, 35, 567 (1962).

[11] J. Fujita, will be reported in detail later.

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[13] K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 71, 270, 316 (1950).

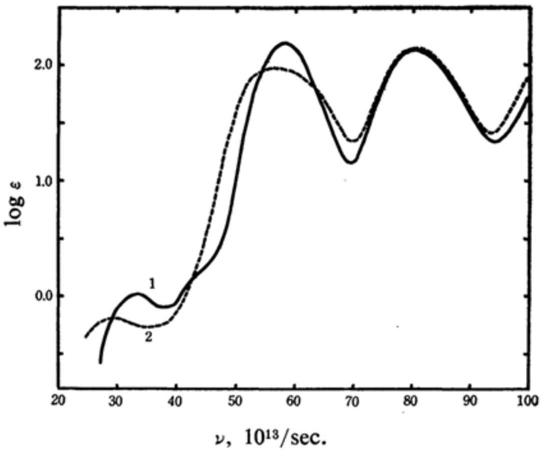

Fig. 3. Absorption spectra of: 1, fac-[Co(gly)$_3$]; 2, mer-[Co(gly)$_3$].

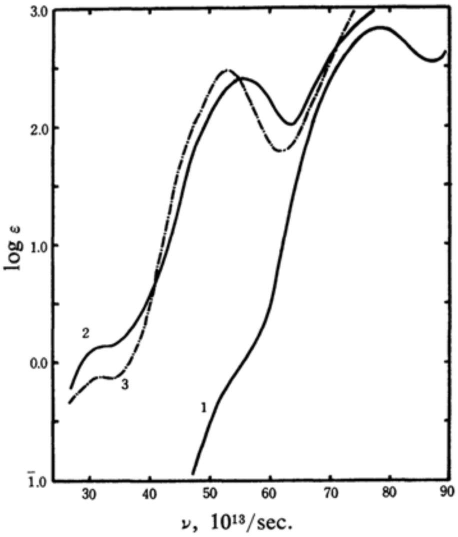

Fig. 4. Absorption spectra of: 1, $[Co(CN)_5N_3]^{3-}$; 2, *cis*-$[Co(N_3)_2(NH_3)_4]^+$; 3, *trans*-$[Co(N_3)_2(NH_3)_4]^+$.

each other in origin, in agreement with the theoretical assignment.

3) The slope of the straight line for the relation between the A band and the first band (Fig. 7) indicates that the frequency separation between these bands becomes smaller as the first band shifts to a shorter wavelength. For this reason, the spin-forbidden bands, especially the B band, of a complex, the first band of which appears in the shorter wavelength region, are often hidden by the strong first band. For the ion $[Co(CN)_6]^{3-}$, for example, only the band is observed as a shoulder on the foot of the first band, as may be seen in Fig. 2.

4) The absorption intensities of the A and the B bands are usually about 1/100 as weak as those of the first and the second bands. For most complexes, as the intensity of the first band increases, the intensity of the A band increases also. A parallel relationship exists, therefore, between the first and the A bands in both the frequencies of absorption maxima and the intensities. Figures 1 and 3 show such relationships clearly.

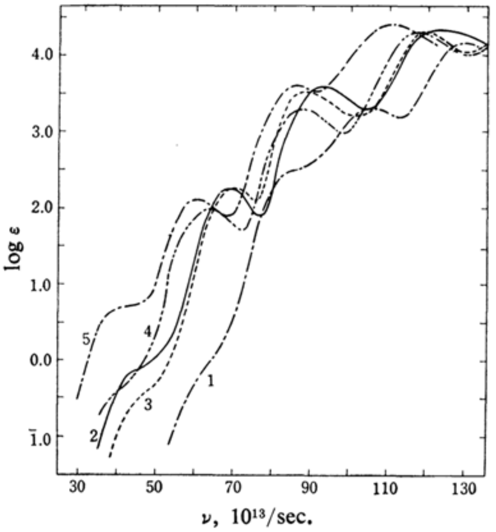

Fig. 5. Absorption spectra of: 1, $[Co(CN)_5NO_2]^{3-}$; 2, *cis*-$[Co(NO_2)_2 en_2]^+$; 3, *trans*-$[Co(NO_2)_2 en_2]^+$; 4, *trans*-$[Co(Cl)NO_2 en_2]^+$; 5, *trans*-$[Co(Br)NO_2 en_2]^+$.

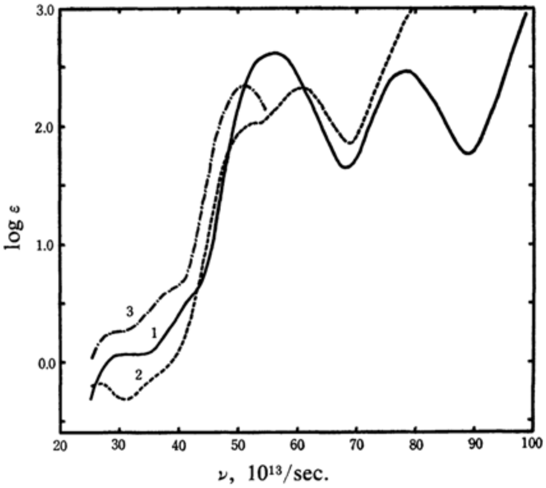

Fig. 6. Absorption spectra of: 1, $[Co\,edta]^-$; 2, $[Co(NO_2)\,edta]^{2-}$; 3, $[Co(Br)\,edtaH]^-$.

5) The absorption curves shown in Figs. 4 and 5 indicate that the absorption intensity of the A band in a cis-complex is higher than that in the corresponding trans-complex. This may be due to the lower molecular symmetry in a cis-complex as compared with that in a trans-complex.

6) The absorption intensities of the A bands

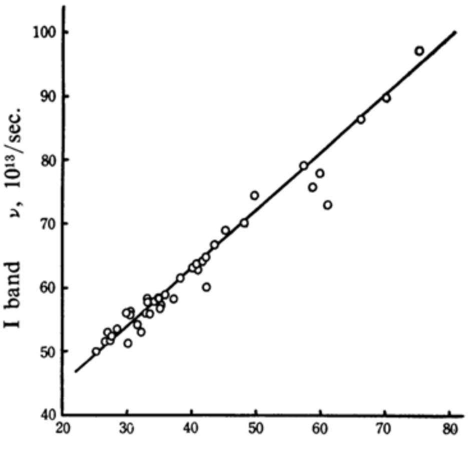

Fig. 7. The linear relation between the A and the I bands.

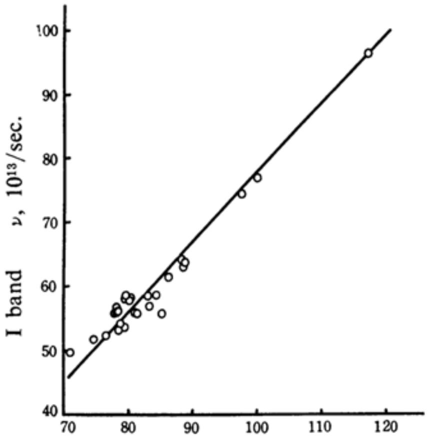

Fig. 8. The linear relation between the I and the II bands.

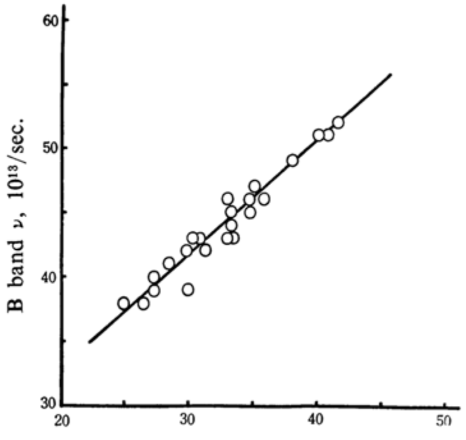

Fig. 9. The linear relation between the A and the B bands.

in bromo-complexes are quite high compared with those of the other complexes (Figs. 5 and 6). The same observation has been made on the spectrum of $[Co(Br)(NH_3)_5]^{2+}$ by Linhard and Weigel.(6) Furthermore, the linear relationship mentioned above between the maximum positions of the first band and those of the A band does not hold for these bromo-complexes. If the data for the bromo-complexes are plotted, as in Fig. 7, these points deviate considerably from a straight line. In other halogeno-complexes such as $[Co(I)(NH_3)_5]^{2+}$,(6) *cis-* and *trans-*$[Co(X)NH_3\,en_2]^{2+}$ ($X=Br^-$, I^-)(14) or a series of halogeno-pentacyanocobalt(III) complexes, $[Co(CN)_5X]^{3-}$ ($X=Cl^-$, Br^-, I^-),(11) the same anomalies have been observed.

7) As may be seen in Figs. 3 and 6, in a complex the first band of which splits, the A band is broad. This indicates that the band splittings may also occur in the A bands. In the case of $[Co(NO_2)edta]^{2-}$, a linear relationship for the A and the first bands shown in Fig. 7 exists, if the observed A band is plotted against the low frequency component (Ia) of the first band. If the mean frequency of the two components of the first band is taken, however, the linear relationship breaks down. This suggests that the other component of the A band which corresponds to the high frequency component of the first band (Ib) may be hidden under or may be overlapped by the B band.

All the conclusions 1)—7) mentioned above coincide well with the theoretical assignments of the weak bands A and B to the spin-forbidden transitions, $^1A_{1g}\rightarrow{}^3T_{1g}$ and $^1A_{1g}\rightarrow{}^3T_{2g}$ respectively, in the expression of an O_h-symmetry approximation. The numerical data listed in Table I may be useful in determining the "nephelauxetic series"(15) of these low-spin d^6 complexes.

Summary

The near infrared, visible and near ultraviolet absorption spectra of about fifty complexes of cobalt(III) have been measured and the data discussed mainly in order to find the relationships existing among the two weak spin-forbidden bands and the two well-known spin-allowed bands.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

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