# Splitting Parameters in Ligand Field Absorption Bands of Cobalt(III) Ammine Complexes with Chloro or Aqua Ligands

Yoshihiro MITSUTSUKA,* Ichiji KONDO, and Masayoshi NAKAHARA†
Department of Chemistry, Faculty of Science and Engineering, Meisei University,
Hodokubo, Hino 191
†Department of Chemistry, Faculty of Science, Rikkyo University,
Nishiikebukuro, Toshima-ku, Tokyo 171

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The splitting parameters of ligand field absorption bands for cobalt(III) ammine complexes containing aqua or chloro ligands were investigated by microspectrophotometry. The polarized absorption spectra were measured for these crystals. The spectra obtained were separated into Gaussian components according to a nonlinear least-squares method. The splitting parameters were determined from the locations of the components for the first absorption band.

The splitting pattern of the ligand field absorption band for cobalt(III) complexes with different ligands was predicted according to a semiempirical procedure proposed by Yamatera,[1)] the so-called Yamatera's rule. Further, the rule was applied to the ligand field bands of cobalt(III) chelate complexes by Matsuoka et al.[2)]; it is well-known that the rule does hold in the splitting pattern of the band.

The present work was carried out in order to establish the splitting parameters of some ligands in cobalt(III) complexes. In an aqueous solution it should be possible to determine the parameters of shifting and splitting in spectral patterns, but some complexes are more or less subject to hydrolysis in an aqueous solution and an exact spectrum cannot be obtained. Therefore, a spectral measurement in a crystalline solid is preferable.

In this study, polarized spectra were measured for a single crystal in order to intensify particular components of the absorption band of the complex and to increase the reliability of the spectral analyses. The microspectrophotometric technique was used for the spectral measurement since it is very difficult to grow a single crystal large enough to measure the absorption spectra by a common technique.

## Experimental

**Microspectrophotometer.** The electronic spectra were recorded on a Shimadzu D40R-w spectrophotometer. A part of the optical construction in the microphotometer is illustrated in Fig. 1. Two photomultipliers (R928, Hamamatsu TV) were used for the measurement. Polarized light was obtained by using a Glan Thompson prism in front of a mirror chopper. A sample beam was focused on a crystal of the complex salt with a reflecting objective (MO30X, Olympus) and collected on a photomultiplier with another objective. Since the intensity of the sample beam decreased by approximately 60%, the reference beam was balanced by adjusting an attenuator. The size of the focused beam was 0.03 mm in width and 0.06 mm in length; the width could be reduced by narrowing the slit of the spectrophotometer.

**Sample.** A large single crystal of the complex salt was required for this experiment. Cobalt(III) ammine complexes, containing chloro and aqua as ligands, were used because these complexes form large single crystals. Since these ligands differ regarding ligand field strength from each other, the components of the absorption band could be distinctly observed. As a result it was easy to analyze the spectrum. The complexes prepared by conventional means were identified by chemical analyses as well as IR and UV spectrophotometry. When the absorbance of the crystal was too high, the crystal was sliced[3)] in the desired direction and was then polished smooth and flat.

**Measurement.** To ensure the best alignment of the electric vector of the incident beam with the axis of maximum absorbance, a Glan Thompson prism was turned until the absorbance reached a maximum. The spectrum of a single crystal was then recorded. After the optical axis of the prism was rotated 90°, another polarized spectrum was also measured. After the crystal was removed from the light beam, a base line was recorded. A net spectrum was obtained by subtracting the base-line absorbance from the observed spectrum.

**Curve Analysis.** It was proposed by Mead[4)] that the absorption curve of the complex was empirically represented by the sum of Gaussian error functions. The absorption

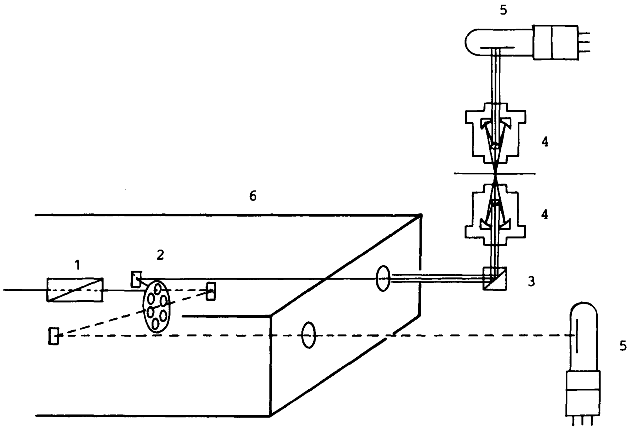


Fig. 1. Apparatus for microspectrophotometry.
1: Glan Thompson prism, 2: chopper, 3: total reflection prism, 4: reflecting objectives, 5: photomultipliers, 6: spectrophotometer.

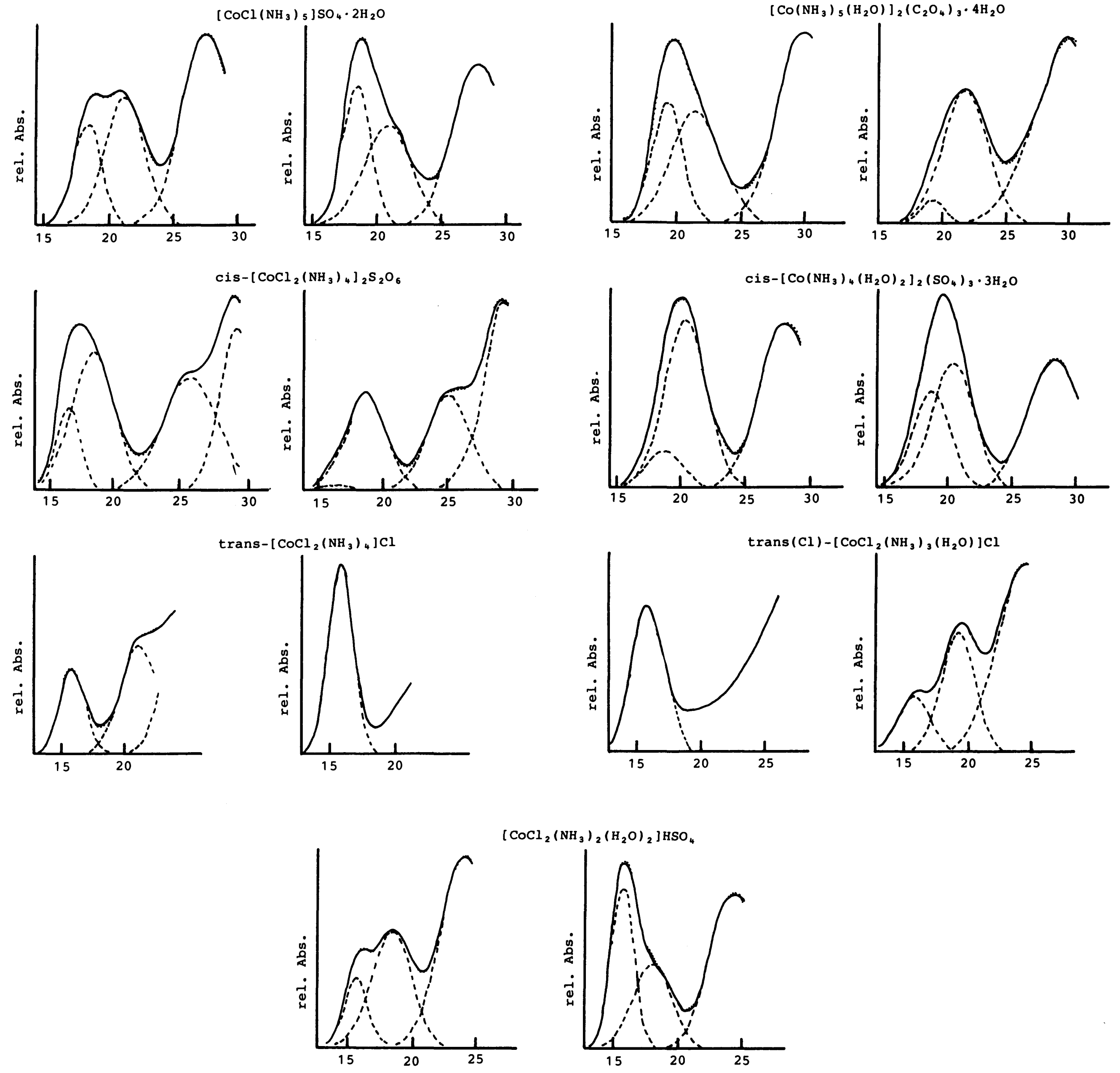


Fig. 2. Polarized crystal spectra of the complexes: solid line, observed spectra; dashed line, calculated Gaussian component; dotted line, sum of the Gaussian components. The numbers on the abscissa indicate wave number ($\times 10^3$ cm$^{-1}$).

curve obtained was statistically separated into its band components by using the nonlinear least-squares method (SSVM method[5]).

## Results and Discussion

Figure 2 shows the electronic spectra of the complexes studied and the calculated curves. The peak positions of the calculated Gaussian components are summarized in Table 1. The splitting components can be clearly distinguished for the so-called first absorption band ($^1T_{1g} \leftarrow {}^1A_{1g}$ in $O_h$ complexes and the corresponding transitions in the complexes of lower symmetries). In this case, no explicit splitting was observed in the so-called second absorption band, ($^1T_{2g} \leftarrow {}^1A_{1g}$ in $O_h$ complexes and the corresponding transitions in the complexes of lower symmetries); the rule of average environment was followed. Furthermore, the second band in some cases somewhat overlapped the charge-transfer band. Thus, the average position of the band is listed in Table 1.

The splitting pattern of the absorption band for octahedral and pseudooctahedral complexes having various ligands has been qualitatively explained according to Yamatera's rule. The rule was applied to

Table 1. Positions of the Absorption Bands of Amminecobalt(III) Complexes

| Complex | Analyzed component positions of the first absorption band/ × $10^3$ cm$^{-1}$ | | Average value of the second absorption band/ × $10^3$ cm$^{-1}$ |
|---|---|---|---|
| $[CoCl(NH_3)_5]SO_4 \cdot 2H_2O$ | 18.28 | 21.27 | 27.55 |
| *cis*-$[CoCl_2(NH_3)_4]_2S_2O_6$ | 16.41 | 18.66 | 25.53 |
| *trans*-$[CoCl_2(NH_3)_4]Cl$ | 15.87 | 21.05 | — |
| $[Co(NH_3)_5(H_2O)]_2(C_2O_4)_3 \cdot 4H_2O$ | 19.34 | 21.61 | 29.95 |
| *cis*-$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$ | 18.69 | 20.32 | 28.34 |
| *trans(Cl)*-$[CoCl_2(NH_3)_3(H_2O)]Cl$ | 15.75 | 19.21 | 24.15 |
| $[CoCl_2(NH_3)_2(H_2O)_2]HSO_4$ | 15.63 | 18.48 | 24.10 |

Table 2. Band Positions and Expressions Corresponding to the Skeleton

| Complex | Skeleton | Components of the first band | Observed position × $10^3$ cm$^{-1}$ |
|---|---|---|---|
| $[Co(NH_3)_6](ClO_4)_3$ | N<br>N+N<br>N | $\delta(NH_3)$ | 21.30 |
| $[CoCl(NH_3)_5]SO_4 \cdot 2H_2O$ | Cl<br>N+N<br>N | $\frac{1}{4}\delta(Cl^-) + \frac{3}{4}\delta(NH_3)$ | 18.28 |
| | N<br>N+N<br>N | $\delta(NH_3)$ | 21.27 |
| *cis*-$[CoCl_2(NH_3)_4]_2S_2O_6$ | Cl<br>N+Cl<br>N | $\frac{1}{2}\delta(Cl^-) + \frac{1}{2}\delta(NH_3)$ | 16.41 |
| | Cl<br>N+N<br>N | $\frac{1}{4}\delta(Cl^-) + \frac{3}{4}\delta(NH_3)$ | 18.66 |
| *trans*-$[CoCl_2(NH_3)_4]Cl$ | Cl<br>N+N<br>Cl | $\frac{1}{2}\delta(Cl^-) + \frac{1}{2}\delta(NH_3)$ | 15.87 |
| | N<br>N+N<br>N | $\delta(NH_3)$ | 21.05 |
| $[Co(NH_3)_5(H_2O)]_2(C_2O_4)_3 \cdot 4H_2O$ | O<br>N+N<br>N | $\frac{1}{4}\delta(H_2O) + \frac{3}{4}\delta(NH_3)$ | 19.34 |
| | N<br>N+N<br>N | $\delta(NH_3)$ | 21.61 |
| *cis*-$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$ | O<br>N+O<br>N | $\frac{1}{2}\delta(H_2O) + \frac{1}{2}\delta(NH_3)$ | 18.69 |
| | O<br>N+N<br>N | $\frac{1}{4}\delta(H_2O) + \frac{3}{4}\delta(NH_3)$ | 20.32 |

the spectra of the complete series of $[Co(ox)_x(gly)_y(en)_z]$ chelate complexes as reported by Matsuoka et al.[2] They suggested that the rule describes the band location and shape for these chelate complexes. In the present work, complexes including only unidentate ligands were employed in order to eliminate the chelate effect.

According to Yamatera's rule, the first band of octahedral and pseudooctahedral complexes consists of three components corresponding to the transitions $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{yz} \rightarrow d_{y^2-z^2}$, and $d_{zx} \rightarrow d_{z^2-x^2}$. When a complex has the same six ligands, the three transition energies should be the same; therefore, it appears that the first absorption band shows no splitting. However, the presence of two or more kinds of ligands in a complex gives rise to band splitting. In this study Yamatera's parameter was somewhat modified and used as follows. For example, when a $d_{xy} \rightarrow d_{x^2-y^2}$ transition takes place in a plane including the four ligands of L1, L2, L3, and L4 (located on the X and Y axes), the

Table 3. δ Values of Amminecobalt(III) Complexes

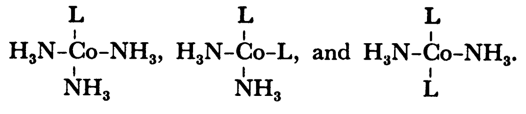
| Complex | δ($NH_3$) $\times 10^3$ cm$^{-1}$ | δ(L) $\times 10^3$ cm$^{-1}$ | |
|---|---|---|---|
| $[Co(NH_3)_6](ClO_4)_3$ | 21.30[6] | — | |
| $[CoCl(NH_3)_5]SO_4\cdot 2H_2O$ | 21.27 | δ($Cl^-$) | 9.30 |
| *cis*-$[CoCl_2(NH_3)_4]_2S_2O_6$ | 20.91 | δ($Cl^-$) | 11.91 |
| *trans*-$[CoCl_2(NH_3)_4]Cl$ | 21.05 | δ($Cl^-$) | 10.69 |
| $[Co(NH_3)_5(H_2O)]_2(C_2O_4)_3\cdot 4H_2O$ | 21.61 | δ($H_2O$) | 12.53 |
| *cis*-$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3\cdot 3H_2O$ | 21.95 | δ($H_2O$) | 15.43 |

energy of the transition can be represented by the sum of the (1/4)δ(L) contributions to the ligand field strength from individual ligands:

$$\frac{1}{4}[\delta(L1)+\delta(L2)+\delta(L3)+\delta(L4)].$$

Expressions corresponding to the other transitions can be similarly represented. The skeletons and expressions of their band positions are shown in Table 2. The δ(L) for each ligand in an individual complex is readily calculated from their expressions in the respective complex. Yamatera's parameters δ(L), thus obtained, are also listed in Table 3.

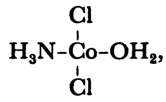
It is known[6] that the positions of the absorption maxima of various complexes in a crystal vary with the kind of counter ion; for example, the maximal degree in band shifts due to counter ions is about 300 cm$^{-1}$ in $[Co(NH_3)_6]X_3$ crystals, except for the occurrence of strong association absorption bands or charge-transfer bands. Therefore, the δ($NH_3$) values of these complexes are in fair agreement with each other (Table 3). Then, it can be assumed that the usable value of δ($NH_3$) is 21.3×10$^3$ cm$^{-1}$. However, the treatment of a δ(L) other than δ($NH_3$) is not so simple. The order of δ(L) (L=$H_2O$, $Cl^-$) obtained from $[CoL(NH_3)_5]$ and also from *cis*-$[CoL_2(NH_3)_4]$ agrees with that of the spectrochemical series.[7,8] The values of δ($Cl^-$) obtained from $[CoCl(NH_3)_5]$, *cis*-$[CoCl_2(NH_3)_4]$, and *trans*-$[CoCl_2(NH_3)_4]$ are 9.31, 11.91, and 10.69×10$^3$ cm$^{-1}$, respectively. These values differ from one another depending on their coordination states. The difference of (1/4) δ(L) values is considered here for the following skeletons:



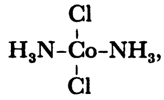
$$H_3N\text{-}\underset{NH_3}{\overset{L}{Co}}\text{-}NH_3,\quad H_3N\text{-}\underset{NH_3}{\overset{L}{Co}}\text{-}L,\quad \text{and}\quad H_3N\text{-}\underset{L}{\overset{L}{Co}}\text{-}NH_3.$$

The δ value of ligand L is variable, depending on the other ligands at the cis or trans position. Therefore, particular consideration is necessary for these results. Since the ligand field splitting, 10 Dq, essentially corresponds to the energy difference between $e_g^*(\sigma)$ and $t_{2g}^*(\pi)$, or between σ and π antibonding levels, the difference stated above in the δ(L)'s in chloro and aquacomplexes also arises from the differences in their splitting effects. $NH_3$ is a fairly strong σ donor but a poor π donor. On the other hand, $H_2O$ and $Cl^-$ with one or two π donor electron pairs will have a much larger ligand-to-metal π interaction than that of $NH_3$. While the values of δ($NH_3$), 21.30×10$^3$ cm$^{-1}$, are nearly the same for any complex, the values of δ($Cl^-$) and δ($H_2O$) vary according to their coordination structure, as described above. Thus δ(L) values of such ligands should be adopted according to the respective coordination structure.

Here, the δ values determined above are applied to a complex whose structure is known. The first absorption band in *trans*(Cl)-$[CoCl_2(NH_3)_3(H_2O)]Cl$, dichro salt,[10] should split into three components corresponding to the skeletons of

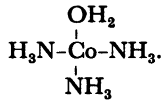


$$H_3N\text{-}\underset{Cl}{\overset{Cl}{Co}}\text{-}OH_2, \tag{I}$$



$$H_3N\text{-}\underset{Cl}{\overset{Cl}{Co}}\text{-}NH_3, \tag{II}$$

and



$$H_3N\text{-}\underset{NH_3}{\overset{OH_2}{Co}}\text{-}NH_3. \tag{III}$$

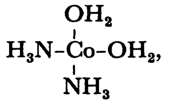
Since the δ($H_2O$) for the skeleton (**I**) was not obtained, the δ value is taken to be the same as that for (**III**); then, the calculated positions corresponding to three skeletons are:

$$\frac{1}{2}\delta(Cl^-) + \frac{1}{4}\delta(H_2O) + \frac{1}{4}\delta(NH_3) = 13.80, \tag{1}$$

$$\frac{1}{2}\delta(Cl^-) + \frac{1}{2}\delta(NH_3) = 15.99, \tag{2}$$

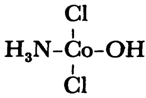
$$\frac{1}{4}\delta(H_2O) + \frac{3}{4}\delta(NH_3) = 19.11. \tag{3}$$

The values of (2) and (3) agree well with the observed band positions, 15.75 and 19.21×10$^3$ cm$^{-1}$ (Table 1). In spite of careful experiments extending as far as ca. 1100 nm (9000 cm$^{-1}$), the band corresponding to (**I**) could not be found. The question arises as to why the band splits into only two components. A possible explanation is that the predicted δ($H_2O$) value for (**I**) is different from that for (**III**). The presence of two $Cl^-$ ligands at the cis positions for $H_2O$ would increase the δ($H_2O$) value for (**I**). To make this more clear, the spectra of $[CoCl_2(NH_3)_2(H_2O)_2]HSO_4$ were measured (Table 1). Although the crystal structure of this complex has not been clarified, Kyuno[11] has given a coordination structure which was presumed from its UV and IR spectra; two chloro ligands coordinate in the trans positions, as well as two ammine and two aqua ligands in the cis positions. Therefore, the first band should consist of two components corresponding to



$$\begin{array}{c} OH_2 \\ | \\ H_3N\text{-}Co\text{-}OH_2, \\ | \\ NH_3 \end{array} \qquad (\mathbf{IV})$$

and



$$\begin{array}{c} Cl \\ | \\ H_3N\text{-}Co\text{-}OH_2. \\ | \\ Cl \end{array} \qquad (\mathbf{V})$$

The position corresponding to skeleton (**IV**) can then be calculated from the values in Table 3:

$$\frac{1}{2}\delta(H_2O) + \frac{1}{2}\delta(NH_3) = 18.37 \qquad (4)$$

The value is in good agreement with the observed value, $18.48\times10^3\,cm^{-1}$ (Table 1). Therefore, skeleton (**V**) should correspond to the value observed at $15.63\times10^3\,cm^{-1}$; thus

$$\frac{1}{2}\delta(Cl^-) + \frac{1}{4}\delta(H_2O) + \frac{1}{4}\delta(NH_3) = 15.63. \qquad (5)$$

From the resuls described above, the component corresponding to (1) should appear at about $15.63\times10^3\,cm^{-1}$. Thus, it is considered that in a dichro salt, the band which could not been found overlaps with the component (2) in the band at $15.75\times10^3\,cm^{-1}$.

It has been shown for a series of aqua and chloro amminecobalt(III) complexes that the positions of components of the first absorption band qualitatively follow Yamatera's rule and also that an excellent quantitative agreement between the rule and experiments can be obtained by using parameter values which are derived by taking into account the effect of coexisting ligands.

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