

## Construction of a Temperature-Variable Microspectrophotometer and Its Application to *trans*-[Co(N)<sub>2</sub>(O)<sub>4</sub>]<sup>-</sup>-Type Complexes

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**Abstract.** A temperature-variable microspectrophotometer has been newly constructed. The measurable range of the instrument is from 440 to 700 nm, and the temperature can be varied from room temperature to 92K. Absorption spectra of *trans*-K[Co(mal)<sub>2</sub>(py)<sub>2</sub>] · 2H<sub>2</sub>O, *trans*-K[Co(ox)<sub>2</sub>(py)<sub>2</sub>] · 3H<sub>2</sub>O, and *trans*-K[Co(ida)<sub>2</sub>] · 2H<sub>2</sub>O have been measured. The oscillator strength of <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>E<sub>g</sub> transition band steeply decreases with a decreasing temperature, while that of the <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>A<sub>2g</sub> transition band slightly decreases. The oscillator strength of <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>E<sub>g</sub> in the bis (malonato) complex decreases more steeply than the corresponding one in the bis (oxalato) complex. From the temperature dependence of the oscillator strengths, a perturbing mode of each transition band has been evaluated.

### Introduction

Transition metal complexes exhibit weak absorption bands due to a ligand field transition in a visible region. The ligand field transition is inherently forbidden, since the initial and final states have the same parity (*i.e.* even). The appearance of the weak absorption bands is explained in terms of a vibronic mechanism in which the even-parity states mix with an odd-parity state through an odd-parity molecular vibration (*i.e.* a perturbing mode).<sup>1)</sup> A direct method to investigate the vibronic mechanism in mixed-ligand complexes is to measure the vibrational fine structure of a ligand field transition band at helium temperature. Urushiyama *et al.*<sup>2,3)</sup> have observed the vibrational fine structures of <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>A<sub>2g</sub> (D<sub>4h</sub>) transition band in *trans*-[Co(CN)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> and *trans*-[Co(CN)<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> complexes at 4.2K. However, there are few mixed-ligand complexes which exhibit fine structures of transition bands.

An alternative method is to measure a temperature dependence of band intensities.

The intensity of a transition band is usually characterized by an oscillator strength,  $f$ , which is calculated by an integral of the band area ;<sup>1)</sup>

$$f = 4.322 \times 10^{-9} \int \epsilon(\tilde{\nu}) d\tilde{\nu}, \quad 1)$$

where  $\epsilon(\tilde{\nu})$  is a molar extinction coefficient at wavenumber  $\tilde{\nu}$ . If a ground state is in thermal equilibrium, the oscillator strength of a vibronically allowed transition band at a given temperature,  $T$  K, is written as follows,<sup>1)</sup>

$$f(T) = f(0) \coth(h\nu/2kT), \quad 2)$$

where  $f(0)$  is the oscillator strength at 0 K, and  $\nu$  is a frequency of a perturbing mode in a vibronic mechanism. The symbols  $h$  and  $k$  are Plank and Boltzman constants, respectively. The function  $\coth$  is called hyperbolic cotangent ; the  $f(T)$  value decreases with an increasing  $\nu$  value and a decreasing temperature. Dubicki and Day<sup>4)</sup> have reported electronic spectra of tetragonal Cr(III) complexes at various temperatures. They have found that the intensity of a  ${}^4B_{1g} \rightarrow {}^4E_g$  transition band follows the  $\coth$  law and discussed the relation of odd-parity vibrations to odd-parity states which lend intensity to the ligand field transition bands.

In this paper, a construction of a temperature-variable microspectrophotometer and absorption spectra of *trans*-[Co(OO)<sub>2</sub>(py)<sub>2</sub>]<sup>-</sup> complexes (OO = mal<sup>2-</sup>, ox<sup>2-</sup>) at various temperature will be reported. These bis (pyridine) complexes are interesting, because they show no splitting of  ${}^1A_{1g} \rightarrow {}^1T_{1g}(Oh)$  transition band, although typical *trans*-[Co(N)<sub>2</sub>(O)<sub>4</sub>]-type complexes such as *trans*-[Co(*ida*)<sub>2</sub>]<sup>-</sup> exhibit marked splitting in the corresponding band.

## Experimental

*Instrument.* The temperature-variable microspectrophotometer consists of a Hitachi 323 Recording Spectrophotometer and a specially designated sample compartment containing a microscope. Schematic diagram is shown in Fig. 1. The spectrophotometer is used as a monochromator and a recorder. Monochromatic light beam is divided into two by a sector mirror (8), after passing a slit (7) inserted newly in the spectrophotometer. The divided beams are reflected by quartz total reflection prisms (9) and introduced into the sample compartment through quartz windows (13). One beam is converged on a sample crystal by a condenser (14) and then led to a photomultiplier (19) (Hamamatsu TV. Co., headon type R376) by a objective (16) (the lenses used for the condenser and objective are Olympus LWDC plan 40x with 2mm work distance). On the other hand, the reference light beam is attenuated through a glid filter (11) and an iris diaphragm (12), and led to the photomultiplier by two quartz total reflection prisms (17).

The photomultiplier is stored in a metal tube and settled upper the sample compartment. High voltage is supplied to the photomultiplier by a power unit of the spectro-

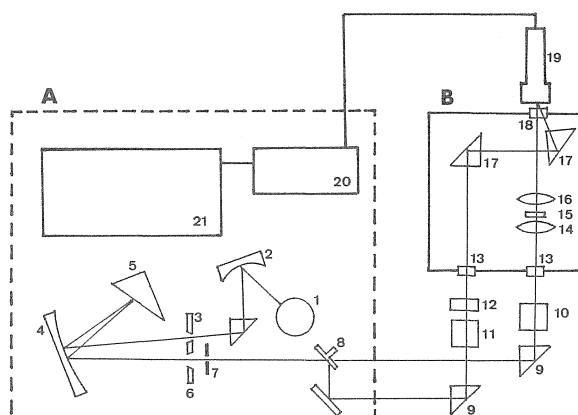


Fig. 1 Schematic diagram of a microspectrophotometer

A: Hitachi 323 Recording Spectrophotometer,

B: Sample Compartment.

- |                                    |                                     |
|------------------------------------|-------------------------------------|
| 1. light source                    | 12. iris diaphragm                  |
| 2. mirror                          | 13. quartz window                   |
| 3. entrance slit                   | 14. condenser                       |
| 4. collimator                      | 15. sample stage (copper)           |
| 5. prism                           | 16. objective                       |
| 6. exit slit                       | 17. total reflection prism (quartz) |
| 7. slit                            | 18. quartz window                   |
| 8. sector mirror                   | 19. photomultiplier                 |
| 9. total reflection prism (quartz) | 20. main amplifier                  |
| 10. Rochon prism                   | 21. recorder                        |
| 11. glid filter                    |                                     |

photometer. Signals is fed from the photomultiplier to a main amplifier (20) and a recorder (21) of the spectrophotometer.

A sample is put on a quartz plate ( $\phi 26$ mm, thickness 0.5mm), and the plate is covered with a copper holder, which is settled on a copper stage. A copper pipe ( $\phi 8$ mm) in which liquid nitrogen flows is attached under the copper stage. Silicone grease (Toray, HVG) is filled in any openings to raise heat conductivity. One side of a sample crystal is joined to the copper holder by a bridge of silicone grease.

Liquid nitrogen is supplied to the copper pipe by evaporating liquid nitrogen in a dewar bottle by a heater (300W). The sample compartment is evacuated with an oil diffusion pump (ULVAC, VPC-250) below  $10^{-2}$  Pa to prevent the objective from freezing. A bellows tube has been inserted into an exhaust pipe to absorb vibrations of the vacuum pump. An outer wall of the sample compartment has been made of a stainless-steel pipe (thickness 10mm) to protect an optical system from distortion, and all apparatuses in the compartment have been constructed on a stainless-steel plate (thickness 30mm). A thermocouple (CRC) is attached with Apiezon grease N (James G, Biddle Co.) near a sample crystal on a quartz plate, and temperature is measured by using a digital thermometer (Yokokawa, E. W., YEW TYPE 2572).

*Measurement.* The complexes were prepared according to the literatures; *trans-K* [*Co(ox)*<sub>2</sub>(*py*)<sub>2</sub>] · 3*H*<sub>2</sub>*O*,<sup>5)</sup> *trans-K* [*Co(mal)*<sub>2</sub>(*py*)<sub>2</sub>] · 2*H*<sub>2</sub>*O*,<sup>5)</sup> *trans-K* [*Co(ida)*<sub>2</sub>] · 2*H*<sub>2</sub>*O*,<sup>6)</sup> *trans-[Co(Cl)*<sub>2</sub>(*en*)<sub>2</sub>] *Cl* · 2*H*<sub>2</sub>*O* · *HCl*.<sup>7)</sup> Sample crystals were grown from saturated aqueous solutions. The size of a crystal was longer than 0.3mm. The sample crystals were checked with a polarization microscope prior to the measurement of spectra. By inserting a Rochon prism into an optical path, polarized absorption spectra of *trans-[Co(Cl)*<sub>2</sub>(*en*)<sub>2</sub>] *Cl* · *H*<sub>2</sub>*O* · 2*HCl* were measured at a room temperature, to examine the function of the instrument.

*Curve analysis.* Spectral curves were analyzed into symmetrical Gaussian functions by an iterative procedure,<sup>8)</sup> and spectral areas were calculated by integrating the Gaussian functions. Wavenumbers of perturbing modes were evaluated from the temperature dependence of transition band areas by a least-squares method. Calculations were carried out at Data Processing Center, Kanazawa University.

## Results and Discussion

*Construction of Instrument.* A base line measured at transmittance is almost flat in the region of 700 to 440 nm. The transmitted light decreases at a wavelength shorter than 440nm. The decrease seems to be responsible to the used glass objectives. The base line varied about 1.5% at transmittance by cooling.

Temperature was regulated within 1.5 degree by changing the flow rate of liquid nitrogen (in the range of *ca.* 190 to 160K, temperature often varied within 3.0 degree). The lowest temperature attained on a quartz plate was 92K. Polarized absorption spectra of *trans-[Co(Cl)*<sub>2</sub>(*en*)<sub>2</sub>] *Cl* · *H*<sub>2</sub>*O* · 2*HCl* well agreed with those of the literature.<sup>9)</sup>

*Absorption Spectra of trans-[Co(N)*<sub>2</sub>(*O*)<sub>4</sub>] -*type Complexes.* Since the complexes have approximately *D*<sub>4h</sub> symmetry, an octahedral *T*<sub>1g</sub> state splits into *E*<sub>g</sub> and *A*<sub>2g</sub>. According to an angular overlap model,<sup>(10)</sup> a <sup>1</sup>*A*<sub>1g</sub> → <sup>1</sup>*A*<sub>2g</sub> transition band is predicted to appear at a lower energy than a <sup>1</sup>*A*<sub>1g</sub> → <sup>1</sup>*E*<sub>g</sub> transition band in complexes with a *trans-[Co(N)*<sub>2</sub>(*O*)<sub>4</sub>] chromophore.

The observed spectra of *trans-K* [*Co(mal)*<sub>2</sub>(*py*)<sub>2</sub>] · 2*H*<sub>2</sub>*O* are shown in Fig. 2. The temperature was decreased to 118.6K. The spectrum at 288.5K exhibits a broad absorption band, and resembles a solution spectrum of the complex at a room temperature. However, the spectrum at 118.6K exhibits an obvious shoulder, which is assignable to <sup>1</sup>*A*<sub>1g</sub> → <sup>1</sup>*A*<sub>2g</sub>, at a lower frequency side of the absorption band. Therefore, the intensity of the transition band observed in the spectrum at a room temperature is mainly originated to <sup>1</sup>*A*<sub>1g</sub> → *E*<sub>g</sub>. As the temperature decreases, the maximum position shifts to a lower frequency and the intensity of the transition band decreases.

The spectra of *trans-K* [*Co(ox)*<sub>2</sub>(*py*)<sub>2</sub>] · 3*H*<sub>2</sub>*O* are illustrated in Fig. 3. Since the complex has the same chromophore as the bis (malonato) complex, a similar splitting of the <sup>1</sup>*A*<sub>1g</sub> → <sup>1</sup>*T*<sub>1g</sub> (*Oh*) band is anticipated. However, an apparent shoulder was not discern-

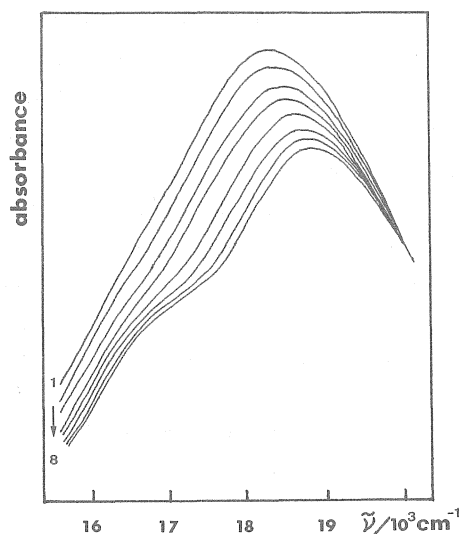


Fig. 2. Absorption spectra of  $\text{trans-}K[\text{Co}(\text{mal})_2(\text{py})_2] \cdot 2\text{H}_2\text{O}$  at 1) 266.4K, 2) 247.6K, 3) 224.4K, 4) 207.9K, 5) 177.8K, 6) 153.6K, 7) 132.0K, 8) 118.6K.

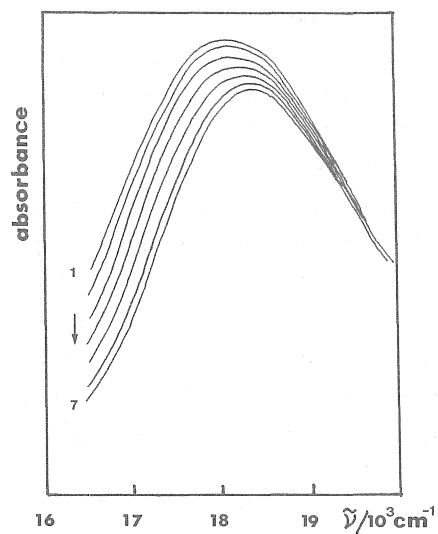


Fig. 3. Absorption spectra of  $\text{trans-}K[\text{Co}(\text{ox})_2(\text{py})_2] \cdot 3\text{H}_2\text{O}$  at 1) 268.1K, 2) 247.9K, 3) 220.4K, 4) 197.7K, 5) 167.3K, 6) 126.9K, 7) 111.1K.

ible even at 111.1K. This fact indicates that the intensity of the  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  transition component is much weaker than that of the  ${}^1A_{1g} \rightarrow {}^1E_g$  transition component.

The absorption spectra of  $\text{trans-}K[\text{Co}(\text{ida})_2] \cdot 2\text{H}_2\text{O}$  are shown in Fig. 4. A well-resolved splitting of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}(\text{Oh})$  band was observed even at a room temperature. The temperature was decreased to 130.2K.

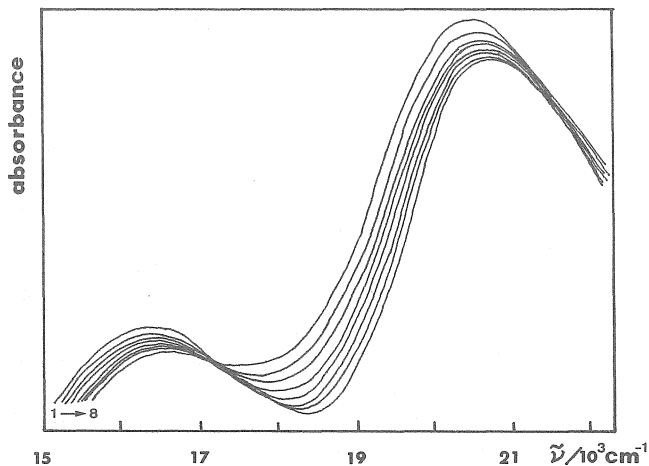


Fig. 4. Absorption spectra of  $\text{trans-}K[\text{Co}(\text{ida})_2] \cdot 2\text{H}_2\text{O}$  at 1) 266.1K, 2) 247.6K, 3) 226.9K, 4) 204.5K, 5) 186.7K, 6) 168.3K, 7) 149.0K, 8) 130.2K.

As to the  $trans-[Co(ida)_2]^-$  and  $trans-[Co(mal)_2(py)_2]^-$  complexes, the absorption curves were analyzed into symmetrical Gaussian curves by an iterative procedure.<sup>8)</sup> Absorption spectra are usually plotted against either wavelength or wavenumber. When the spectra plotted against wavenumber were analyzed, calculated curves disagreed with the observed ones at the feet of the Gaussian curves. Therefore, a weak band which appears near an intense band can not be reliably separated in this manner. On the other hand, an analysis employed wavelength resulted in a good agreement even at the feet of the Gaussian curves. Consequently, the curve analysis was carried out by using absorption spectra plotted against wavelength in this study. As to  $trans-K[Co(ox)_2(py)_2]$ , an analysis into two Gaussian curves was unsuccessful, since the splitting of the absorption band was unclear even at 111.1K. The absorption spectra of this complex in the  ${}^1A_{1g} \rightarrow {}^1T_{1g}(Oh)$  region were analyzed as a single Gaussian function which corresponded to  ${}^1A_{1g} \rightarrow {}^1E_g$  transition band. It is notably to point out that the fitness between the observed and calculated curves became poor with decreasing temperature.

The spectral areas which are integrals of Gaussian curves decrease with decreasing temperature. If it is assumed that a single perturbing mode is specially effective in an intensity-borrowing mechanism, the frequency of the mode is evaluated according to the coth law of Eq. 2. The coth curves obtained by a least-squares method are illustrated in Fig. 5. The oscillator strength of  ${}^1A_{1g} \rightarrow {}^1E_g$  in the bis (malonato) complex decreases most steeply with a perturbing mode of  $275\text{cm}^{-1}$ , as the temperature decreases. The perturbing

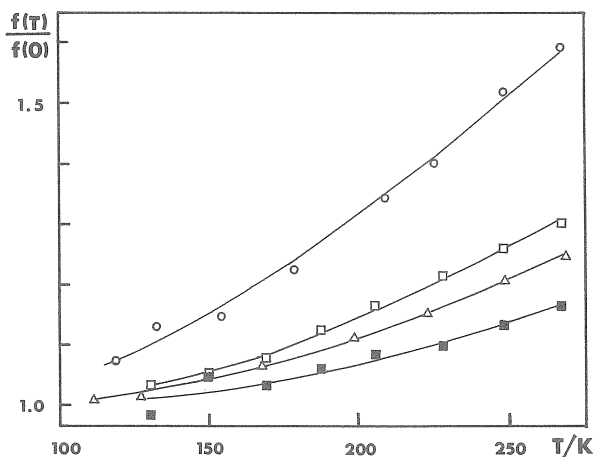


Fig. 5. Temperature dependence of oscillator strengths ;  
 ○ :  ${}^1A_{1g} \rightarrow {}^1E_g$  transition band of  $trans-K[Co(mal)_2(py)_2] \cdot 2H_2O$ ,  
 △ :  ${}^1A_{1g} \rightarrow {}^1E_g$  transition band of  $trans-K[Co(ox)_2(py)_2] \cdot 3H_2O$ ,  
 □ :  ${}^1A_{1g} \rightarrow {}^1E_g$  transition band of  $trans-K[Co(ida)_2] \cdot 2H_2O$ ,  
 ■ :  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  transition band of  $trans-K[Co(ida)_2] \cdot 2H_2O$ .

mode responsible to  ${}^1A_{1g} \rightarrow {}^1E_g$  in the bis (oxalato) complex is estimated as  $407\text{cm}^{-1}$ . This value is much larger than the value obtained in the bis (malonato) complex. Since the two bis (pyridine) complexes have a similar skeletal structure, the difference may be due to the rigidity of the chelate rings. The oxalato ligand forms a tight five-membered chelate ring, while the malonato ligand forms a flexible six-membered chelate ring. As to the bis(ida) complex which contains four five-membered chelate rings, the perturbing mode for the  ${}^1A_{1g} \rightarrow {}^1E_g$  transition is evaluated as  $372\text{cm}^{-1}$ .

The oscillator strength of  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  in the bis (ida) complex changes with a perturbing mode of  $475\text{cm}^{-1}$ . The value is larger than the values found in  ${}^1A_{1g} \rightarrow {}^1E_g$ . Though the  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  transition band in the bis (malonato) complex was not analyzed on account of large errors, a perturbing mode of this transition band is estimated to *ca.*  $500\text{cm}^{-1}$  from the temperature dependence similar to that of the corresponding band in the bis(ida) complex. Therefore, it is concluded that the perturbing modes of  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  have higher frequency than those of  ${}^1A_{1g} \rightarrow {}^1E_g$  in the *trans*-[Co(N)<sub>2</sub>(O)<sub>4</sub>]<sup>-</sup>-type complexes.

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