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The Emission Spectra of Hexamminechromium(III) Hexacyanocobaltate(III), $[Cr(NH_3)_6][Co(CN)_6]$

Hiroshi KATAOKA

Department of Chemistry, Faculty of Science, Rikkyo University, Nishi-ikebukuro, Toshima-ku, Tokyo 171

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Spin-forbidden absorption bands of $K_3[Co(CN)_6]$ were reexamined employing conventional transmission spectroscopy, diffuse reflectance spectroscopy, and microspectrophotometry. A small but very distinct shoulder ($\varepsilon \approx 0.3$—0.4) obtained at a low temperature at 26000 cm^{-1} was assigned to the $^3T_{1g} \leftarrow {}^1A_{1g}$ transition. Another very small band ($\varepsilon \approx 0.001$) at 16300 cm^{-1} was probably due to an impurity. The emission spectra of $K_3[Co(CN)_6]$ powder in the temperature range from room temperature to that of liquid hydrogen were observed by means of a modified Hitachi 203 fluorescence spectrophotometer. The broad emission band at room temperature showed some vibrational structures at low temperatures. The emission spectra of powders of $[Cr(NH_3)_6](NO_3)_3$ and $[Cr(NH_3)_6][Co(CN)_6]$ were also measured. The following results were obtained: i) Similar emission spectra, which seemed to originate from $[Cr(NH_3)_6]^{3+}$, were observed with both complexes $[Cr(NH_3)_6](NO_3)_3$ and $[Cr(NH_3)_6][Co(CN)_6]$ using mercury lines at 313, 365, and 435 nm for excitation. ii) With 254 nm excitation, such emission spectra as i) were not observed with $[Cr(NH_3)_6](NO_3)_3$, but the same emission spectra as in i) were observed with $[Cr(NH_3)_6][Co(CN)_6]$. iii) The ratio of the emission intensities at 15000 cm^{-1} with 435 and 313 nm excitations was 1 : 0.25—0.30 for $[Cr(NH_3)_6](NO_3)_3$, but it was 1 : 1.5—1.7 for $[Cr(NH_3)_6][Co(CN)_6]$. From these results, it was presumed that, in $[Cr(NH_3)_6][Co(CN)_6]$, there occurred an energy transfer from the complex anion to the complex cation. Furthermore, emission spectra were observed with $[Cr(NH_3)_6](ClO_4)_3$ and the equimolar mixture of complex salts $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ and $[Cr(NH_3)_6](NO_3)_3$–$K_3[Co(CN)_6]$ for the purpose of confirming the energy transfer in $[Cr(NH_3)_6][Co(CN)_6]$. The temperature dependence of the emission intensity was also discussed.

Recently it has been found by many authors that chromium(III) complexes show emission spectra,[1] and several papers have been published presenting evidence for energy transfer in chromium complexes in solutions[2] and in solids.[3,4]

On the other hand, although there have been extensive studies of the absorption spectra of cobalt(III) complexes, there have been few papers on their emission spectra. Those reported up to this time are $Na_5[Co(SO_3)_2(CN)_4]$,[5] $Ag_3[Co(CN)_6]$,[6], and $K_3[Co(CN)_6]$.[7—10] Several papers on energy transfer with cobalt(III) complexes in solutions have also been presented,[11—13] but there have been few papers on that in solids. One of the reasons why the relationship between the absorption and the emission spectrum has not been discussed fully in those reports seem to have been the difficulty of observing the very weak spin-forbidden absorption band. Some authors have observed the spin-forbidden band of $K_3[Co(CN)_6]$,[7,10,14] but differing results have been reported.

In the present work, $K_3[Co(CN)_6]$ was studied in order to establish the relationship between the emission band and the spin-forbidden absorption band. Furthermore, the double complex salt $[Cr(NH_3)_6][Co(CN)_6]$ was studied to get information on the emission spectrum and energy transfer. The reasons why the double complex salt $[Cr(NH_3)_6][Co(CN)_6]$ was selected were as follows: i) The relation between the emission spectrum and the spin-forbidden band of $[Cr(NH_3)_6]^{3+}$ has been elucidated by extensive studies.[15] ii) The absorption spectra of the double complex salt nearly form a superposition of the spectra of the complex cation $[Cr(NH_3)_6]^{3+}$ and the complex anion $[Co(CN)_6]^{3-}$. Therefore, the selective excitation of the complex anion or cation is possible if a suitable wavelength is selected for the excitation. Furtheremore, $[Cr(NH_3)_6](NO_3)_3$, $[Cr(NH_3)_6](ClO_4)_3$, and an equimolar mixture of the complex salts $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ and

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1) For example a) E. Koglin and W. Krasser, *Ber. Bunsenges. Phys. Chem.*, **76**, 401 (1972). b) H. L. Schläfer, M. Martin, H. Gausmann, and H. H. Schmidtke, *Z. Phys. Chem.* (*N.F.*), **76**, 61 (1971). c) S. L. Barker, *Chem. Commun.*, **1971**, 363. d) N.A.P. Kane-Maguire and C. H. Langford, *ibid.*, **1971**, 895. e) G. Gliemann and H. Yersin, *Ber. Bunsenges. Phys. Chem.*, **75**, 1257 (1971). f) F. D. Camassei and L.S. Forster, *J. Chem. Phys.*, **50**, 2603 (1969). g) J. C. Hemple and F. A. Matsen, *ibid.*, **73**, 2502 (1969). h) P. Cancellieri, E, Cervone, C. Furlani, and G. Sartori, *Z. Phys. Chem.* (*N.F.*), **62**, 35 (1968).

2) a) I. Fujita and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, **76**, 115 (1972). b) V. Balzani, R. Ballardini, M. T. Gandolfi and L. Moggi, *J. Amer. Chem. Soc.*, **93**, 339 (1971). c) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970). d) T. Ohno and S. Kato, This Bulletin, **42**, 3385 (1969). e) M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63**, 327 (1959).

3) H. Gausmann and H. L. Schläfer, *J. Chem. Phys.*, **48**, 4056 (1968).

4) H. L. Schläfer, H. Gausmann, and C. H. Möbius, *Inorg. Chem.*, **8**, 1137 (1969).

5) F. Zuloaga and M. Kasha, *Photochem. Photobiol.*, **7**, 549 (1968).

6) A. D. Kirk, H. L. Schläfer, and A. Ludi, *Can. J. Chem.*, **48**, 1065 (1970).

7) G.B. Porter and M. Mingardi, *J. Chem. Phys.*, **44**, 4354 (1966).

8) G. A. Crosby, *J. Chem. Phys.*, **64**, 160 (1967).

9) A. D. Kirk, A. Ludi, and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.*, **73**, 669 (1969).

10) H. Kataoka, Y. Yamamoto, M. Nakahara, and Y. Kondo, *Nippon Kagaku Zasshi*, **92**, 274 (1971).

11) G. B. Porter, *J. Amer. Chem. Soc.*, **91**, 3980 (1969).

12) L. Moggi, F. Bolletta, F. Balzani, and F. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).

13) A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).

14) S. Kida, J. Fujita, K. Nakamoto, and R. Tsuchida, This Bulletin, **31**, 79 (1958).

15) For example a) H. H. Eysel, *Z. Phys. Chem.* (*N.F.*), **72**, 82 (1970). b) A. W. Adamson and T. M. Dunn, *J. Mol. Spectrosc.*, **18**, 83 (1965). c) G. B. Porter and H. L. Schläfer, *Z. Phys. Chem.* (*N.F.*), **40**, 280 (1964). d) H. L. Schläfer, *J. Phys. Chem.*, **69**, 2201 (1965).

$[Cr(NH_3)_6](NO_3)_3$–$K_3[Co(CN)_6]$ were studied for the purpose of confirming the energy transfer.

Recently, energy transfer in the double complex salt composed of $[Ru(bipy)_3]^{2+}$ and $[Cr(ox)_3]^{3-}$ (bipy: bipyridine, ox: oxalate ion) was studied by Fujita and Kobayashi.16) Their observations provided interesting evidence for an electronic excitation energy transfer between complexes with different central metals.

Experimental

Preparation of Materials. $K_3[Co(CN)_6]$, $[Cr(NH_3)_6](ClO_4)_3$, and $[Cr(NH_3)_6](NO_3)_3$ were prepared according to the published methods.17,18) These compounds were recrystallized three times from an aqueous solution.

The double complex salt $[Cr(NH_3)_6][Co(CN)_6]$ was prepared by adding an aqueous solution of $K_3[Co(CN)_6]$ (0.02 mol/l, 500 ml), with rigorous stirring, drop by drop into an aqueous solution of $[Cr(NH_3)_6](NO_3)_3$ (0.02 mol/l, 500 ml).19) The fine precipitate thus obtained was filtered using a 4G-glass filter, washed with a large amount of water, and dried in a vacuum desiccator.

An equimolar mixture of the complexes was obtained by grinding powder of $[Cr(NH_3)_6](NO_3)_3$ and $K_3[Co(CN)_6]$ or $[Cr(NH_3)_6](ClO_4)_3$ and $K_3[Co(CN)_6]$ in an equimolar ratio.

The Growing of a Single Crystal of $K_3[Co(CN)_6]$. Because of the small molar extinction coefficient of the spin-forbidden bands of $K_3[Co(CN)_6]$,7,14) a large single crystal was necessary for measuring its absorption spectrum. This single crystal was grown using equipment similar to that of Galsbøl.20) The solution was prepared by dissolving about 150 g of $K_3[Co(CN)_6]$ in 300 ml of water containing a small amount of KCN at 50—55 °C. The vessel was then covered with a wrap sheet and placed in a thermostated bath at 50 °C. After one day, the solution was decanted into a 300 ml beaker, and then again placed in the thermostated bath as quickly as possible. A small seed21) (*ca.* 1.5 × 1 × 1 mm or larger) was put on the bottom of the beaker, and the surface was covered with a small amount of liquid paraffine in order to avoid evaporation. The solution at 50 °C was slowly cooled to room temperature at a velocity of 2.50±0.01 °C/day. The temperature controller was a Jumo (Western Germany) model MS.D.B.P.8.66. After 10—15 days, a large single crystal weighing 23 g (approximately 25 × 30 × 20 mm) was obtained.22) It was greenish yellow and had some fine cracks, only a small portion being available for measuring the spectra.

Measurements of Absorption and Diffuse Reflectance Spectra. The absorption spectra of aqueous solutions were measured with a Hitachi EPS-3T recording spectrophotometer. The inside of the monochromator was filled with nitrogen gas during the measurement in the 190—220 nm region. The visible and ultraviolet spectra of a single crystal (thickness: 1.5 mm) of $K_3[Co(CN)_6]$ were measured with this spectrophotometer using a microspectrophotometric attachment constructed in this laboratory at room temperature (*ca.* 295 K) and at the temperature of liquid nitrogen (77 K).

The visible and near-infrared spectra of a large single crystal (*ca.* 25 × 30 × 20 mm) were also measured by the conventional method at room temperature using a Cary-14 recording spectrophotometer.

The diffuse reflectance spectra were measured with a Hitachi EPS-3T spectrophotometer, using a reflectance accessory at room temperature.

The infrared spectra in the 700—4000 cm^{-1} region and in the 200—700 cm^{-1} region were obtained with, respectively a JASCO DS-301 infrared spectrophotometer and a JASCO Model IR-F far-infrared spectrophotometer, using the Nujol-mull method.

Measurement of Emission Spectra. For the present purpose, a Hitachi 203 fluorescence spectrophotometer (with two grating monochromators for the excitation and the detection) was modified as follows: i) the sample chamber of the Hitachi 203 spectrophotometer was modified to accommodate a cryostat-type AC-2 apparatus made by Air Products and Chemicals;23,24) ii) the usual Hamamatsu R-212 (maximum sensitive wavelength 340 nm) photomultiplier was replaced with two photomultipliers, a Hamamatsu R-406 (S-1 characteristic, maximum sensitive wavelength 800 nm) and an R-136 (maximum sensitive wavelength 430 nm), for the purpose of detecting weak emission spectra in the near-infrared and red regions; iii) in most cases, the sample was excited with a mercury lamp (120 W, Ushio, UM-102) but in a few cases it was excited with a xenon lamp (150 W, Ushio, UXI-151D), and iv) in order to record the emission spectra automatically a Hitachi wavelength driving apparatus and a Hitachi QPD-53 recorder were used.

The emission spectra were passed through a yellow cut-off filter in order to remove the exciting light, and were detected at the right angle to the exciting light. Furthermore, the correction for the small amount of stray light from the exciting light source was made by means of powdered magnesium oxide, as has been described by Kirk and his co-workers.9) The sample temperature was measured using a calibrated chromel-constantan thermocouple and a reference junction. The entrance and exit slit widths were 0.8 mm in all the measurements. The emission spectra thus obtained were not corrected for the spectrophotometer, incident light intensity, detector, and particle size. The measurement region was 500—780 nm, while the temperatures ranged from room temperature to the temperature of liquid hydrogen (20 K). The measurement error of the temperature was ±0.5% near 250 K, ±1.0% near 150 K, and ±5% near 50 K. The errors of the emission intensity measurement were ±5%.

Wavelength calibrations of the Hitachi EPS-3T spectrophotometer and Hitachi 203 fluorescence spectrophotometer were made by the use of mercury lines.

Results and Discussion

Diffuse Reflectance Spectra. Figure 1 shows the diffuse reflectance spectra of the complex salts $[Cr(NH_3)_6](NO_3)_3$, $[Cr(NH_3)_6](ClO_4)_3$, $K_3[Co(CN)_6]$, and the double complex salt $[Cr(NH_3)_6][Co(CN)_6]$. The diffuse reflectance spectra of an equimolar mixture of complex salts $[Cr(NH_3)_6](NO_3)_3$–$K_3[Co(CN)_6]$ and $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ are shown in Fig. 2.

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16) a) I. Fujita, and H. Kobayashi *J. Chem. Phys,*. **52**, 4904 (1970). b) I. Fujita and H. Kobayashi, private communication.

17) "Inorganic Synthesis," Vol. II, ed. by W. C. Fernelius, (1946), p. 225.

18) M. Mori, *Nippon Kagaku Zasshi*, **74**, 253 (1953).

19) S. M. Jørgensen, *J. Prakt. Chem.*, **30**, 31 (1884).

20) F. Galsbøl, *Rev. Sci. Instrum.*, **36**, 1367 (1965).

21) Small seeds were obtained easily by the evaporation of the concentrated $K_3[Co(CN)_6]$ solution.

22) It was easy to obtain crystals which were thick enough to observe the very weak band, but usually they had many fine cracks and could not be used for the spectral measurement. Thick and transparent crystals could be obtained only very rarely.

23) D. White and K. E. Mann, *Rev. Sci. Instrum.*, **34**, 1370 (1963).

24) T. Ueno and K. Yoshiwara, *Teion Kogaku*, **4**, 106 (1969).

TABLE 1. SPECTRAL DATA OF $K_3[Co(CN)_6]$

	LF-I[d] Band			LF-II[d] Band			CT[e] Band		
	Maxima (cm^{-1})	log ε	$f \times 10^{-3}$	Maxima (cm^{-1})	log ε	$f \times 10^{-3}$	Maxima (cm^{-1})	log ε	$f \times 10^{-1}$
This work	32090	2.28	4.27	38800	2.12	3.30	49800	4.39	6.62
G. B. Porter *et al.*[a]	32100	2.26	—	38600	2.20	—	50000	4.20	—
M. Mingardi *et al.*[b]	32050	—	3.0	38460	—	2.8	48500	—	3.2
S. Kida *et al.*[c]	32500	2.29	—	39000	2.09	—	—	—	—

a) Ref. 7.
b) Ref. 25a).
c) Ref. 14.
d) Spin-allowed ligand field bands.
e) Charge transfer bands.

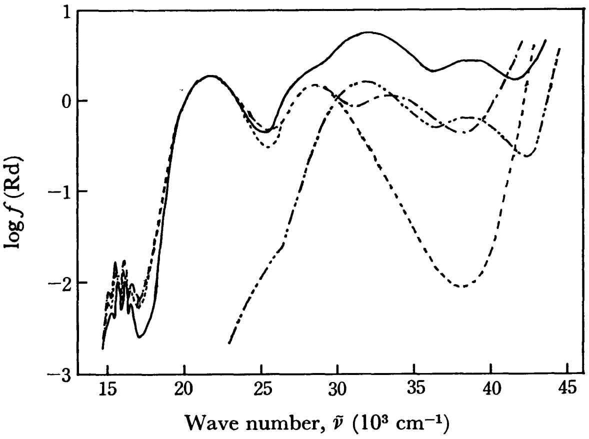

Fig. 1. Diffuse reflectance spectra of $[Cr(NH_3)_6](NO_3)_3$, $[Cr(NH_3)_6](ClO_4)_3$, $K_3[Co(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$.
-·-·-· $[Cr(NH_3)_6](NO_3)_3$ -------- $[Cr(NH_3)_6](ClO_4)_3$
-··-··- $K_3[Co(CN)_6]$ ——— $[Cr(NH_3)_6][Co(CN)_6]$

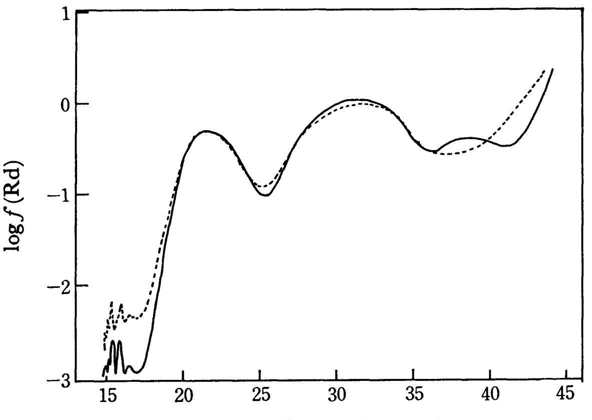

Fig. 2. Diffuse reflectance spectra of equimolar mixture of complex salts.
——— $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$
——— $[Cr(NH_3)_6](NO_3)_3$–$K_3[Co(CN)_6]$

From these figures it is evident that the spectrum of the double complex salt compares well with the spectra of equimolar mixtures, which are considered to be the sum spectra of the individual spectra of the component complexes.

The Absorption Spectrum of $K_3[Co(CN)_6]$. Spin-allowed ligand-field bands and the charge-transfer band of $K_3[Co(CN)_6]$ were measured in an aqueous solution. The position (cm^{-1}) and the logarithms of the molar extinction coefficients of the bands are shown in Table 1, together with other workers' data. The oscillator strength, f, was calculated by the use of:

$$f = 4.32 \times 10^{-9}\int \varepsilon d\tilde{\nu}$$
$$= 5.6 \times 10^{-9}\, \varepsilon_{max} \Delta\tilde{\nu} \quad (1)$$

where ε is the molar extinction coefficient; $\tilde{\nu}$, the wave number, and $\Delta\tilde{\nu}$, the half-band width.[25a)] There is a rather good agreement between the present data and those of others.

Spin-forbidden bands for a number of cobalt(III) complexes have been reported by many workers.[26)] Those of $K_3[Co(CN)_6]$ were also reported by Kida *et al.*[14)] and Porter *et al.*[7)] The former found a shoulder at 24000 cm^{-1} and suggested that it represented a spin-forbidden band. The latter workers obtained a weak band ($\varepsilon \approx 0.01$) at 18500 cm^{-1} and assigned it to the $^3T_{1g} \leftarrow {}^1A_{1g}$ transition. The Tanabe-Sugano diagram[27)] suggests that two spin-forbidden bands ($^3T_{1g}$, $^3T_{2g} \leftarrow {}^1A_{1g}$) exist in the near-ultraviolet and visible regions. It is thus necessary to elucidate whether the weak bands obtained by the above authors originate from similar transitions or from different transitions. In this paper, the spin-forbidden absorption bands of $K_3[Co(CN)_6]$ were reexamined employing conventional transmission spectroscopy, diffuse reflectance spectroscopy, and microspectrophotometry.

With the conventional transmission method, using various concentrations, it was impossible to obtain an absorption spectrum that showed a clear shoulder at 24000 cm^{-1}. Thus, the weak band might have been covered by the tail of the first spin-allowed band. A curve analysis of the first spin-allowed band was made using the equation presented by Shimura and Tsuchida.[28)] Their equation is a modification of Kuhn

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25) a) M. Mingardi and G. B. Porter, *Spectrosc. Lett.*, **1**, 293 (1968). b) M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).

26) a) J. Fujita and Y. Shimura, This Bulletin, **36**, 1281 (1963). b) M. Linhard and M. Weigel, *Z. Phys. Chem.* (*N.F.*), **11**, 308 (1957). c) C. K. Jφrgensen, *Advan. Chem. Phys.*, **5**, 33 (1963). d) D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, *A*, **1966**, 798.

27) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 753, 766 (1954).

28) Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).

and Braun's[29] containing as a correction term δ, the inclination parameter.

On account of the superposition of the first and second spin-allowed ligand field bands of $K_3[Co(CN)_6]$, the true half-width of the first band was expected to be smaller than that obtained from the experimental curve. Thus, curve analyses were done in which the parameters, l (half-width of the band) and δ, were changed in the regions of 3300—5000 cm^{-1} and 0—300 cm^{-1} respectively. The best agreement between the experimental curve and the calculated one in the region 28000—35000 cm^{-1} was found when l and δ were 4900 and 170 cm^{-1} respectively. These two curves are shown in Fig. 3. However, much larger inconsistencies than those found in most cobalt(III) complexes were found in the wave number region below 28000 cm^{-1}. This must have been due to the presence of a small band ($\log \varepsilon \approx 0.4$) at about 27000 cm^{-1}.

An indistinct shoulder appeared at about 25000 cm^{-1} in the diffuse reflectance spectrum of $K_3[Co(CN)_6]$ (Fig. 1). The absorption spectra obtained by microspectrophotometry are shown in Fig. 4. Although no maximum or shoulder in the region in question was found at room temperature, a small but very distinct shoulder was obtained at 26000 cm^{-1} at the temperature of liquid nitrogen. The subtraction of the tail of the first spin-allowed band from this spectrum gave a small band whose maximum was at about 26000 cm^{-1}, its molar extinction coefficient was about 0.3—0.4. This small band may be the spin-forbidden band of $K_3[Co(CN)_6]$.[30]

Furthermore, a very weak band ($\varepsilon \approx 0.001$) was observed at 16300 cm^{-1} using a 10 cm cell and a concentrated solution (1.24 mol/l). This band was also observed at about the same position using a single crystal (thickness, 20 mm). The half-width of this band was about 1000 cm^{-1}.

The single crystal showed two very strong bands, at 4246 and 4279 cm^{-1}, and some other bands at 4155, 4160 , 4290, 6333, and 6341 cm^{-1} in the near-infrared region. The two strong bands at 4246 and 4279 cm^{-1} were assigned by Jones to the combination bands for $(\nu_3+\nu_6)$ and $(\nu_1+\nu_6)$.[34] The two very weak bands in the 6000 cm^{-1} region may be due to the combination band for 2 $(\nu_1, \nu_3, \text{ or } \nu_6)+(\nu_1, \nu_3, \text{ or } \nu_6)$. The next combination band, related to ν_1, ν_3, and ν_6, could be expected to appear in about the 8500 cm^{-1} region; however, no band was observed until the weak and broad band at 16300 cm^{-1} was reached. Therefore, this band might also be due to the spin-forbidden band of K_3-$[Co(CN)_6]$ (Fig. 5).

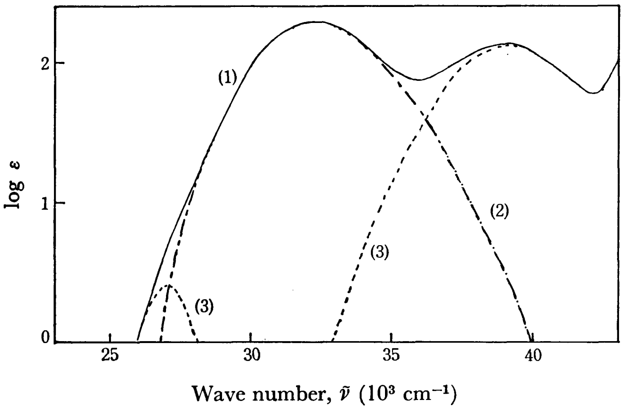

Fig. 3. Curve analysis of $[Co(CN)_6]^{3-}$.
(1): Experimental curve
(2): From Shimura and Tsuchida's equation, where l= 4900 cm^{-1} and δ=170 cm^{-1}
(3): (1)—(2).

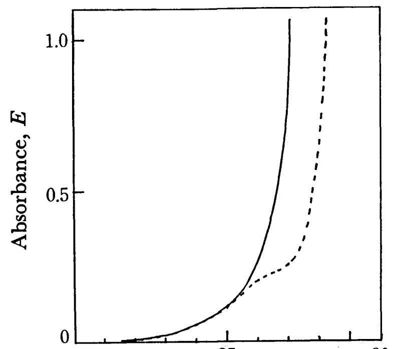

Fig. 4. Absorption spectra of a $K_3[Co(CN)_6]$ crystal by microspectrophotometry.
———: Room temperature
------: Liquid nitrogen temperature

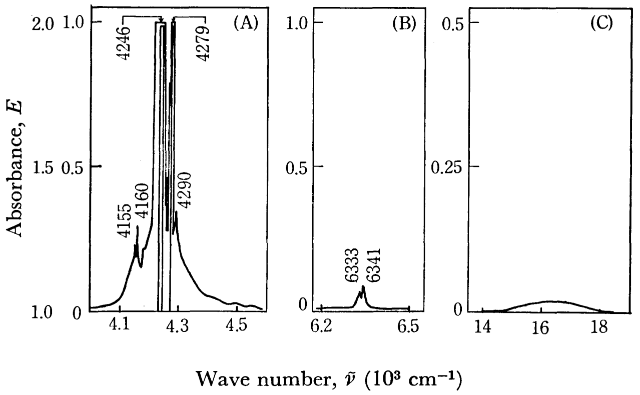

Fig. 5. Absorption spectrum of $K_3[Co(CN)_6]$ in the red and near-infrared regions.
(A), (B) Absorbance scale is left side
(C) Absorbance scale is right side

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[29] W. Kuhn and E. Braun, *Z. Phys. Chem.*, **B8**, 281 (1930).

[30] If a small amount of $K_2[Co(CN)_5H_2O]$ exists in a $K_3[Co(CN)_6]$ crystal, a shoulder might appear at about 26000 cm^{-1}, because $K_2[Co(CN)_5H_2O]$ has the first spin-allowed band at 26300 cm^{-1} ($\varepsilon \approx 260$).[31] It is well-known in the preparation of $K_3[Co(CN)_6]$ that the uptake of the sixth cyanide by $[Co(CN)_5H_2O]^{2-}$ is a slow process at room temperature,[32] but very rapid at 95°C.[33] Thus, the reaction solution was boiled long enough to avoid contamination with $[Co(CN)_5H_2O]^{2-}$. Recrystallization was repeated several times. It is, therefore, more reasonable to attribute the small shoulder at 26000 cm^{-1} to the spin-forbidden band of $K_3[Co(CN)_6]$.

[31] A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

[32] N. K. King and M. E. Winfield, *ibid.*, **83**, 3366 (1961).

[33] L. C. Smith, J. Kleinberg, and E. Griswold, *ibid.*, **75**, 449 (1953).

[34] L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).

However, it is more probable that this band is due to an impurity[35] contained in $K_3[Co(CN)_6]$. This is for the following reasons. i) There is a linear relation, as found by Fujita and Shimura, between the positions of the first spin-forbidden band and the first spin-allowed band of cobalt(III) complexes.[26a] The position of the band in question shifted very much from that expected from this relationship. The band found at 26000 cm^{-1}, however, is in agreement with the relationship, thus, it should be assigned to the $^3T_{1g}\leftarrow{}^1A_{1g}$ transition. The $^3T_{2g}\leftarrow{}^1A_{1g}$ band will exist at higher wave numbers, thus being covered completely by the first spin-allowed band. ii) Based on a theoretical calculation, Alexander and Gray concluded that the spin-forbidden $^3T_{1g}\leftarrow{}^1A_{1g}$ band will appear at about 27000 cm^{-1}.[36] iii) The intensity of this band ($\varepsilon\approx$ 0.001) is abnormally small compared with those of the spin-forbidden bands of other cobalt(III) complexes (ε=0.1—1). iv) The separation between the positions of this band and the phosphorescence band seems to be too small if it is assumed that this band is due to the $^3T_{1g}\leftarrow{}^1A_{1g}$ transition.[37] v) The position (16300 cm^{-1}) and the intensity ($\varepsilon\approx$0.001) of the band found in this work differ very much from the position (18500 cm^{-1}) and the intensity ($\varepsilon\approx$0.01) reported by Porter *et al.*

Energy Level Diagram. The evergy level diagram based on the results of the conventional transmission and diffuse reflectance measurements on $[Cr(NH_3)_6]$-$(ClO_4)_3$, $K_3[Co(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ is shown in Fig. 6. The positions of the maxima of the absorption bands are shown by solid lines and dashed lines, and the half-widths of the bands, by hatched areas. The solid lines and dashed lines represent the electronic states possessing the same multiplicity and different multiplicities with respect to that of each ground state respectively. The electronic configurations of each level are given in parentheses. The wavelengths of the light used for excitation are also shown by the arrows on the left of the diagram.

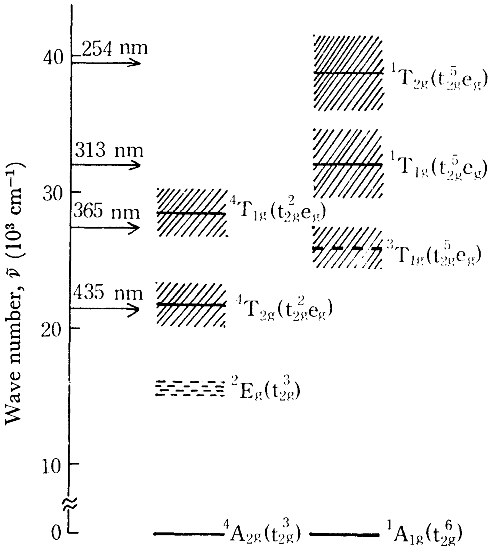

Fig. 6. Energy level diagram of $[Cr(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$

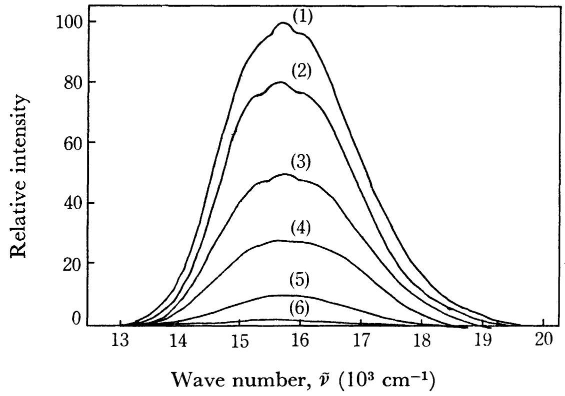

Fig. 7. Emission spectra of $K_3[Co(CN)_6]$ excited with 313 nm light.
Temperature (K): (1): 20, (2) : 100, (3): 151, (4): 190, (5): 235, (6): 295.

Emission Spectrum of $K_3[Co(CN)_6]$. The emission spectra at various temperatures excited with 313 nm light, which has almost the same energy as that of the maximum of the first spin-allowed band, are shown in Fig. 7.[38] It was found that the extremely weak and broad structureless emission band at room temperature gradually increased in intensity with a decrease in the temperature and that it showed some vibrational structures below *ca.* 150 K. Excitations with 365 nm light, and with 254 nm light, which has almost the same energy as that of the maximum of the second spin-allowed band, gave the same spectral pattern as that obtained by excitation with 313 nm light. The temperature dependence of the emission spectra excited with 313 and 254 nm light showed practically the same behavior.

The emission band of $K_3[Co(CN)_6]$ had been observed previously by Porter and Mingardi[7,25a] with a crystal at 4.2 and 77 K at 14000 cm^{-1} and assigned to the $^3T_{1g}\rightarrow{}^1A_{1g}$ phosphorescence of $[Co(CN)_6]^{3-}$, mainly on the basis of the mirror-image relationship between the emission band and the absorption band (18500 cm^{-1}), and on the basis of the lifetime measurement of the emission band (6.8×10^{-4} sec). A broad structureless band with a maximum at 14000 cm^{-1} was also obtained by Kirk *et al.*[9] The discrepancy in the

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[35] One possible impurity may be a binuclear cyanoaquo Co(II)-Co(III) complex with, in the low wave number visible region, a spin-allowed band, a charge transfer band, or an interaction absorption band. According to the conditions of synthesis, the complex with a band at 16300 or 18500 cm^{-1} will be produced.

[36] J. J. Alexander and H. B. Gray, *Coord. Chem. Rev.*, **2**, 29 (1967).

[37] Since the maximum of the absorption band lies at 16300 cm^{-1}, and since the half-width of the band is about 1000 cm^{-1}, the 0–0 position of the band must lie at about 15300 cm^{-1}, which limits the position of the phosphorescence band to wave numbers smaller than this. If a phosphorescence band larger than 15300 cm^{-1} is found, it should be an anti-Stokes band and thus should show a decrease of intensity with a decrease in the temperature. This was not the case in our experiment, as may be seen in Fig. 7.

[38] The maximum of the phosphorescence band of $K_3[Co(CN)_6]$ shifted to a low wave number of about 1000 cm^{-1} when an R–406 tube was used instead of an R–136 tube. However, only the results obtained by the latter tube are shown throughout this work because the sensitivity of the former tube is much lower than that of the latter.

phosphorescence band position between this work ($14700\ cm^{-1}$ using an R–406 tube) and other authors' works may be due to the use of different experimental setups.

As has been stated above, the weak absorption band at $26000\ cm^{-1}$ was assigned to the $^3T_{1g}\leftarrow{}^1A_{1g}$ transition. Thus, the emission band at $14700\ cm^{-1}$ should be assigned to the $^3T_{1g}\rightarrow{}^1A_{1g}$ transition. The position of the emission band might seem to be too far apart from the position of the absorption band, the difference being about $10000\ cm^{-1}$. However, a similar large difference has been observed by Mingardi *et al.*[25a)] in a d^6 cyano-complex, $K_4[Ru(CN)_6]$. They found the corresponding absorption and emission bands at 31000 and $22650\ cm^{-1}$ respectively. The large Stokes shifts 11600 and $17200\ cm^{-1}$ in other d^6 complexes have also been found by DeArmond *et al.* in $[Rh(en)_3]Cl_3$ and $[Ir(en)_3]Cl_3$ (en=ethylenediamine) respectively.[25b)]

Schläfer *et al.* observed the phosphorescence of $K_3[Cr(CN)_6]$ in a glycerol/H_2O (1: 1) rigid solution and in a fine crystal state at −190 °C and assigned the interval (*ca.* $350\ cm^{-1}$) between the vibrational structures of the phosphorescence band to the Cr–C stretching vibration.[39)] The mean interval, $400\ cm^{-1}$, in the phosphorescence spectrum of $K_3[Co(CN)_6]$ in this work may be due to the Co–C stretching or Co–CN bending vibration.

Emission Spectra of $[Cr(NH_3)_6](NO_3)_3$ *and* $[Cr(NH_3)_6](ClO_4)_3$. The emission spectra of $[Cr(NH_3)_6](NO_3)_3$ and $[Cr(NH_3)_6](ClO_4)_3$ are shown in Figs. 8 and 9. The following results were obtained:

i) The emission spectra excited with 313, 365, and 435 nm light showed the same pattern in both complexes.[40,41)] On the other hand, with 254 nm light it was very difficult to distinguish between the emission spectrum and the noise signal at any temperature used in this work.

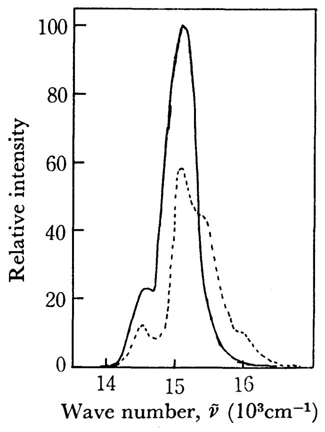

Fig. 8. Emission spectra of $[Cr(NH_3)_6](NO_3)_3$ excited with 313 nm light.
——: 20 K ---------: 295 K

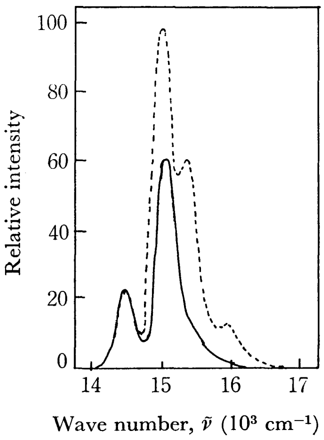

Fig. 9. Emission spectra of $[Cr(NH_3)_6](ClO_4)_3$ excited with 435 nm light.
——: 20 K ------: 295 K

ii) In $[Cr(NH_3)_6](NO_3)_3$, the two emission bands at 15390 and $15970\ cm^{-1}$ decreased in intensity with a decrease in the temperature and almost disappeared at 20 K. However, the other two bands at 14470 and $15040\ cm^{-1}$, increased in intensity with a decrease in the temperature.

iii) In $[Cr(NH_3)_6](ClO_4)_3$, the emission band at $14550\ cm^{-1}$ did not change in intensity with a decrease in the temperature. The other three bands, at 15020, 15390, and $15900\ cm^{-1}$, decreased in intensities with a decrease in the temperature.

As may be seen from the results shown in ii), the two bands at 15390 and $15970\ cm^{-1}$ can be assigned to the transitions from the higher vibrational levels of the ^2E_g state to the ground state. The band at $15390\ cm^{-1}$ may correspond to the $15120\ cm^{-1}$ band reported by Porter *et al.*,[15c)] which was assigned to the 0–0 band. However, it is more reasonable to assign the band at $15040\ cm^{-1}$ to the 0–0 band, judging from the findings on the temperature dependence of the emission spectra (see Fig. 8).

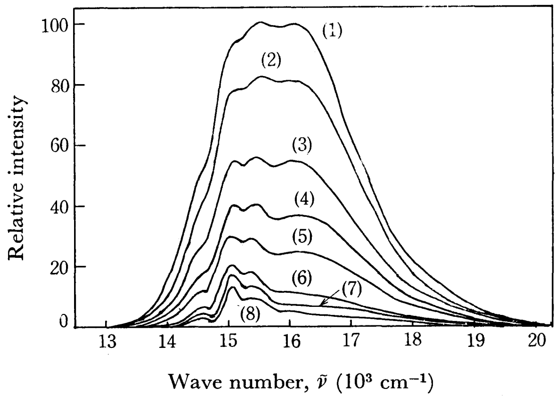

Fig. 10. Emission spectra of equimolar mixture of complex salts $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ excited with 313 nm light.
Temperature (K)
(1): 20, (2): 57, (3): 115, (4): 150, (5): 170, (6): 222,
(7): 235, (8): 295.

[39)] H. L. Schläfer, H. Gausman, H. F. Wasgestian, and H. U. Zander, *Z. Phys. Chem.*, (*N.F.*) **51**, 274 (1966).

[40)] The position of the maxima of the phosphorescence band of $[Cr(NH_3)_6]^{3+}$ shifted to a low wave number of about $200\ cm^{-1}$ when an R-406 tube was used instead of an R-136 tube.

[41)] The emission spectra excited with 435 nm light are shown in $[Cr(NH_3)_6](ClO_4)_3$. This is because the emission intensity was very weak with 313 nm light, which has the same energy as that of the valley between the second spin-allowed band and the charge-transfer band (see Fig. 1).

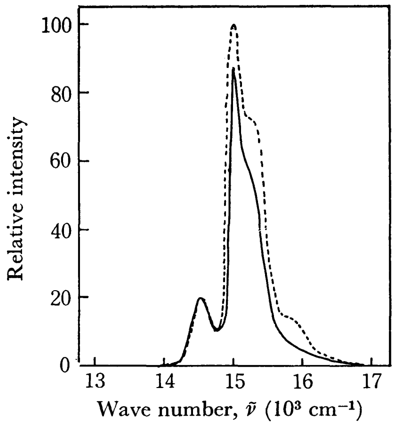

Fig. 11. Emission spectra of equimolar mixture of complex salts $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ excited with 435 nm light. ——: 20K ------: 295 K

Emission Spectra of Equimolar Mixtures of Complex Salts $[Cr(NH_3)_6](NO_3)_3$–$K_3[Co(CN)_6]$ *and* $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$. The emission spectra for these two equimolar mixtures of complex salts were observed. All the results obtained could be explained by considering the superposition of the spectra of the component complexes. Some of the results are shown in Figs. 10 and 11. Figure 10 gives the emission spectra of an equimolar mixture of $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ excited with 313 nm light at various temperatures. It is evident from the figure that the spectra consist of the emission bands of $[Cr(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$. Figure 11 shows the emission spectra of an equimolar mixture of $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ at 20 and 295 K excited with 435 nm light. As may be seen from Fig. 1, $[Co(CN)_6]^{3-}$ absorbs little in this region; thus, only the emission spectrum due to $[Cr(NH_3)_6]^{3+}$ is observed.

Emission Spectra of $[Cr(NH_3)_6][Co(CN)_6]$. The emission spectra of the double complex salt $[Cr(NH_3)_6][Co(CN)_6]$ are shown in Fig. 12.[42] The following results were obtained:

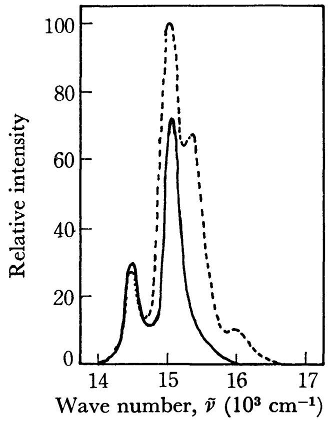

Fig. 12. Emission spectra of $[Cr(NH_3)_6][Co(CN)_6]$ excited with 313 nm light. ——: 20 K ------: 295 K

i) The emission spectra excited with 254, 313, 365, and 435 nm light were different from the emission spectra of the equimolar mixtures of the complex salts excited with 313 nm light, but had nearly the same pattern and position as those of the emission spectra of $[Cr(NH_3)_6](NO_3)_3$ or $[Cr(NH_3)_6](ClO_4)_3$. The only difference was that the two emission bands in the higher wave number region observed as shoulders in $[Cr(NH_3)_6](NO_3)_3$ and $[Cr(NH_3)_6](ClO_4)_3$ showed distinct maxima in this double complex salt. The emission intensity of $[Cr(NH_3)_6]^{3+}$ in the double complex was several times stronger than that of $[Cr(NH_3)_6]^{3+}$ in equimolar mixtures.

ii) The ratio of the emission intensities at 15000 cm^{-1} excited with 435 and 313 nm light was 1: 1.5—1.7 at room temperature, and the ratio hardly changed at 20 K. The ratio was 1: 0.25—0.30 in the case of $[Cr(NH_3)_6](NO_3)_3$.[43]

iii) The two bands at 15400 and 15970 cm^{-1} decreased in their intensities with a decrease in the temperature and almost disappeared at 20 K; the intensity of the emission band at 15000 cm^{-1} also decreased with a decrease in the temperature. However, no temperature dependence of the intensity was observed with the emission band at 14470 cm^{-1}.

Energy Transfer. The fact that the emission spectra of the double complex salt had nearly the same pattern as that of $[Cr(NH_3)_6](NO_3)_3$ or $[Cr(NH_3)_6](ClO_4)_3$ and did not resemble that of $K_3[Co(CN)_6]$, even if 254 nm light, which was mostly absorbed by the complex anion, was used, strongly suggests that some energy transfer occurs from the complex anion to the complex cation in the double complex salt. This becomes clearer when we compare the phosphorescence band of the double complex salt (Fig. 12) with that of the equimolar mixture of the complexes (Figs. 10 and 11) in which the energy transfer cannot be considered and in which the spectrum thus consists of those of the component complexes. Additional evidence is given by the ratio of the intensities of the emission bands at 15000 cm^{-1} excited with 435 and 313 nm light. If the two ratios mentioned above are compared, it is more reasonable to consider that the increase in the ratio from 1: 0.25—0.30 in $[Cr(NH_3)_6](NO_3)_3$ to 1: 1.5—1.7 in $[Cr(NH_3)_6][Co(CN)_6]$ corresponds to the increase in the absorption due to [Co-

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[42] The intensity of the emission band excited with 254 nm light was weak because of the low intensity of the light source in this region. However, it was confirmed that the pattern and position of this band were similar to those of the emission band excited with 313 nm light. Thus, the emission spectrum excited with 254 nm light was not shown; that excited with 313 nm light was shown instead.

[43] The intensities of the 313 and 435 nm emission lines of the Ushio UM-102 mercury lamp were almost the same (private communication from Ushio, Incorporated). The sensitivities of the photomultiplier R-136 at 313 and 435 nm were 1: 2 (Hamamatsu Corporation Information Bulletin, **1972**, 8). When powdered magnesium oxide was irradiated with these mercury light, the Hitachi 203 fluorescence spectrophotometer out-put indicated the 1: 2 ratio at these wavelengths. Therefore, the transmittance of the fluorescence spectrophotometer was considered to be nearly the same at these wavelengths. From these results, it was concluded that the ratios of the emission band at 15000 cm^{-1} excited with 313 and 435 nm were not much different from the true value if we neglect the problems concerning the samples, that is, the inner-filter effect, the particle size effect, etc. A more detailed experiment concerning the quantitative aspects of this work using ferrioxalate solutions in a chemical actinometer is now under way in this laboratory.

$(CN)_6]^{3-}$.44)

As possible energy transfer paths, the following two are suggested. They satisfy the spin conservation rule in consideration of the energy level diagram shown in Fig. 6:

$$\begin{tikzcd}
 & & {}^4T_{1g} \arrow[r, dashed] & {}^4T_{2g} \arrow[r, squiggly] & {}^2E_g \\
{}^1T_{2g} \arrow[r, dashed] & {}^1T_{1g} \arrow[ur] \arrow[dr] & & & \\
 & & {}^4T_{2g} \arrow[r, squiggly] & {}^2E_g &
\end{tikzcd}$$

where→means energy transfer; ---→, internal conversion, and ⇝, intersystem crossing. However, if the formation of the molecular orbitals between the complex cation and the complex anion are considered, the following two paths are also possible, as in the case of $[Ru(bipy)_3]_3[Cr(ox)_3]_2$ (bipy: 2,2′-bipyridyl, ox: oxalate ion) studied by Fujita and Kobayashi:16)

$$\begin{tikzcd}
 & & & {}^4T_{2g} \arrow[r, squiggly] & {}^2E_g \\
{}^1T_{2g} \arrow[r, dashed] & {}^1T_{1g} \arrow[r, squiggly] & {}^3T_{1g} \arrow[ur] \arrow[dr] & & \\
 & & & {}^2E_g &
\end{tikzcd}$$

It is interesting to note that the latter paths are prohibited if importance is attached to the simple consideration of the spin conservation rule, although they are usually considered to be more favorable from the point of view of the longer lifetime of ${}^3T_{1g}$.

Temperature Dependence of the Emission Intensity. The temperature dependence of the emission intensity of $K_3[Co(CN)_6]$, $[Cr(NH_3)_6](NO_3)_3$, $[Cr(NH_3)_6](ClO_4)_3$, and $[Cr(NH_3)_6][Co(CN)_6]$ is shown in Figs. 13—16.

These data may be classified into two groups according to whether the emission intensity increases or decrease with a decrease in the temperature. The emission intensity in $K_3[Co(CN)_6]$ and $[Cr(NH_3)_6](NO_3)_3$ increases with a decrease in the temperature. These phenomena can be explained in terms of the usual emission process competing with the nonradiative relaxation process.

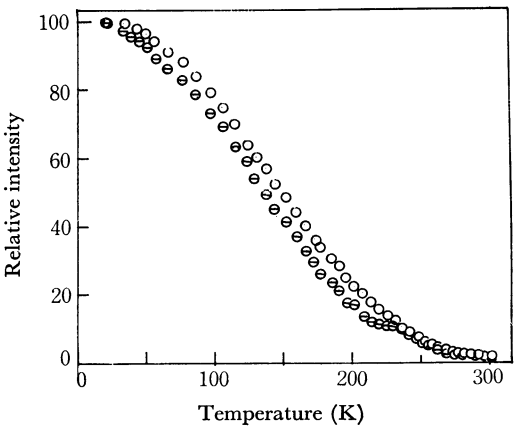

Fig. 13. Temperature dependence of the emission intensity of $K_3[Co(CN)_6]$ at 15700 cm^{-1}.
○: excited with 313 nm light
⊖: excited with 254 nm light
Relative intensity of the emission spectra was obtained by normalizing its value at 20 K to 100.

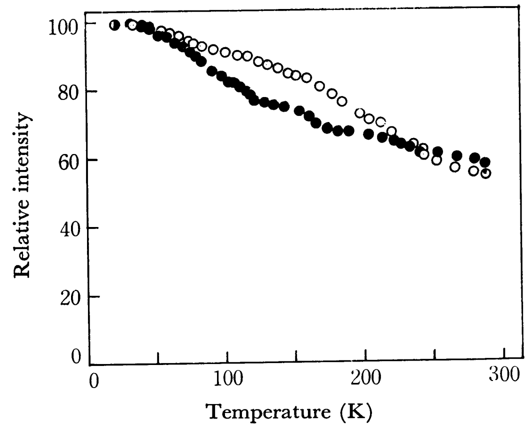

Fig. 14. Temperature dependence of the emission intensity of $[Cr(NH_3)_6](NO_3)_3$ at 15040 cm^{-1}.
●: excited with 435 nm light
○: excited with 313 nm light
Relative intensity of the emission spectra was obtained by normalizing its value at 20 K to 100.

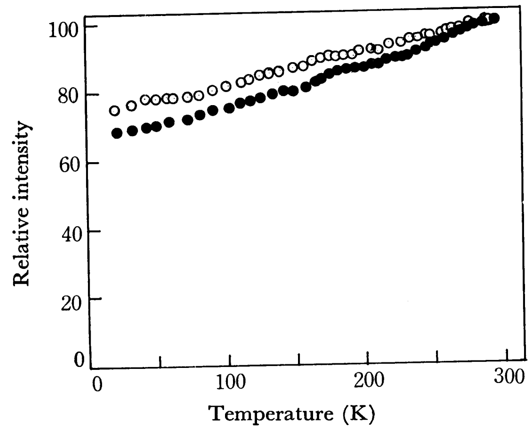

Fig. 15. Temperature dependence of the emission intensity of $[Cr(NH_3)_6](ClO_4)_3$ at 15000 cm^{-1}.
●: excited with 435 nm light
○: excited with 313 nm light
Relative intensity of the emission spectra was obtained by normalizing its value at room temperature to 100.

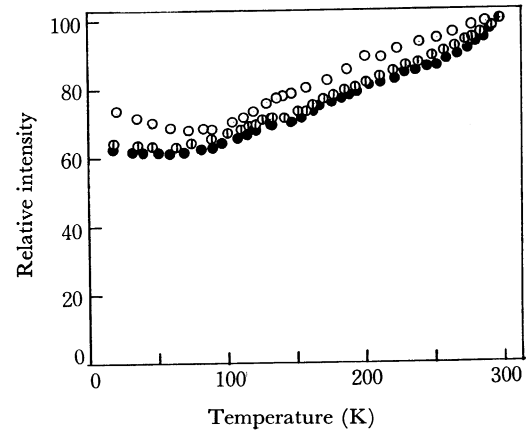

Fig. 16. Temperature dependence of the emission intensity of $[Cr(NH_3)_6][Co(CN)_6]$ at 15000 cm^{-1}
●: excited with 435 nm light
⦶: excited with 365 nm light
○: excited with 313 nm light
Relative intensity of the emission spectra was obtained by normalizing its value at room temperature to 100.

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44) Kirk and Schläfer proposed a crystal perturbation theory against an energy transfer in order to explain an abnormal emission spectrum of $[Cr(atp)_6][Cr(CN)_6]$ (atp: antipyrin). Their case must be the result of a special ligand which prohibits the energy transfer, as they pointed out.45)

45) A.D. Kirk and H.L. Schläfer, *Z. Phys. Chem.*, **52**, 2411 (1970).

However, the temperature dependence of the emission intensity of $[Cr(NH_3)_6](ClO_4)_3$ and $[Cr(NH_3)_6][Co(CN)_6]$ is anomalous; that is, the intensity decreases with a decrease in the temperature except in the cases of the bands at 14550 and 14470 cm^{-1} respectively. The explanation of this anomalous temperature effect is very difficult. Flint studied the emission spectra of crystalline $2[Cr(en)_3]Cl_3 \cdot KCl \cdot 6H_2O$ and $[Cr(en)_3]Cl_3 \cdot 3H_2O$ (en=ethylenediamine) at temperatures down to 5 K.[46] He found that the emission band at 14880 cm^{-1} (N–band) having vibronic structure to lower energy due to $^2E \rightarrow ^4A_2$ was quenched at temperatures below 200 K, and that a new broader emission band appeared at *ca.* 14500 cm^{-1} (B–band) and increased in intensity with a decrease in the temperature. He explained this new emission band as being due to a transition within a new Cr(III) center associated with lattice defects. Probably a similar explanation would hold for $[Cr(NH_3)_6](ClO_4)_3$ and $[Cr(NH_3)_6][Co(CN)_6]$. That is, if we assume that, in our case, the bands 15020 and 15000 cm^{-1} correspond to the N–bands, the anomalous decrease in the intensity with the decrease in the temperature can be explained. Therefore, the bands at 14550 and 14470 cm^{-1} should be assigned to the B–bands. The fact that the B–bands in our case do not show any increase in intensity with a decrease in the temperature may be explained by the overlap of the decreasing lower-energy part of the N–band.

The temperature dependence of the emission intensity of equimolar mixtures of complex salts, $K_3[Co(CN)_6]$–$[Cr(NH_3)_6](ClO_4)_3$, are shown in Fig. 17. In these cases, the temperature dependence can be explained by a superposition of those of the component complexes.

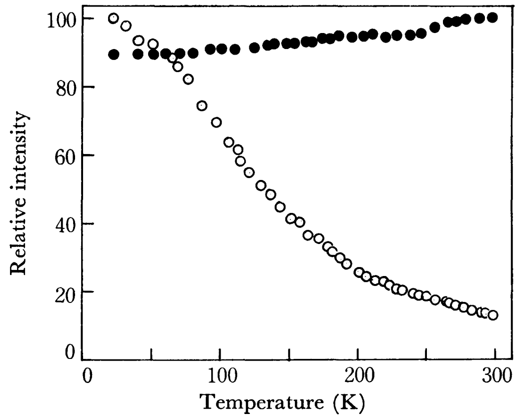

Fig. 17. Temperature dependence of the emission intensity of equimolar mixture of complex salts $[Cr(NH_3)_6](ClO_4)_3$–$K_3[Co(CN)_6]$ at 15040 cm^{-1}

●: excited with 435 nm light

○: excited with 313 nm light

Relative intensity of the emission spectra excited with 435 nm light was obtained by mornalizing its value at room temperature to 100, and relative intensity of the emission spectra excited with 313 nm light was obtained by normalizing its value at 20 K to 100.

The author wishes to express his gratitude to Professor Y. Kondo and Professor M. Nakahara for their stimulating suggestions and discussion during this work. He is also indebted to Dr. A. Kuboyama (The Government Chemical Industrial Research Institute) for the use of a Cary-14 spectrophotometer, and to Mr. A. Urushiyama for his help with the microscopic measurements. Special thanks are also due to Professor H. Kobayashi and Dr. I. Fujita (Tokyo Institute of Technology) for pre-prints of their reports. He also wishes to thank Professor Gene S. Lehman for his kindness in reading the original manuscript.

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[46] C. D. Flint, *J. Chem. Phys.*, **52**, 168 (1970).