# Luminescence Spectra of Cobalt(III) Cyano Complexes

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Luminescence spectra of $M_3[Co(CN)_6]$ (M=K, Rb, Cs), *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$, and *trans*-$Na_5[Co(CN)_4(SO_3)_2]$ were measured at 20 K. Single crystal luminescence spectra of the hexacyanocobaltates(III), centered at 14100—14200 $cm^{-1}$, exhibited vibrational structure associated with three components, and the separation between the members of the progression was about 400 $cm^{-1}$. Luminescence spectra of powdered *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$ and *trans*-$Na_5[Co(CN)_4(SO_3)_2]$ were structureless and broad centered at 13200 and 14400 $cm^{-1}$, respectively. Comparison of these luminescence spectra with the corresponding spin-forbidden bands indicated that the 0-0 transition lies at 18300—18600 $cm^{-1}$ for hexacyanocobaltates(III), at 16500—17000 $cm^{-1}$ for *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$, and at 17700—18200 $cm^{-1}$ for *trans*-$Na_5[Co(CN)_4(SO_3)_2]$. The vibrational structure in luminescence spectra of hexacyanocobaltates(III) can be interpreted in terms of the $\nu_8$, $\nu_9$, $\nu_{12}$, and $\nu_{13}$ ungerade skeletal modes, a lattice mode, and the totally symmetric $\nu_2$ vibrational mode. Analysis of the relative intensity of the vibrational structure in the luminescence spectra gave information about the change in the Co–C internuclear equilibrium distance from the ground state to the excited luminescent state. The relationship between luminescence and photochemical behavior of cobalt(III) complexes was also considered.

In recent years, there has been a rapidly expanding interest in the luminescence of transition-metal coordination compounds.1) A luminescence spectrum provides a great deal of useful information not only about an excited state but also about a ground state. There have been many studies on luminescence spectra of chromium(III) complexes from the viewpoints of both their spectroscopic and photochemical aspects.1,2) On the other hand, although there have also been extensive spectroscopic and photochemical studies of cobalt(III) complexes, there has been few papers on their luminescence.

Luminescence of cobalt(III) complex was first reported on $K_3[Co(CN)_6]$ by Porter and Mingardi3) in 1966. They observed a broad and structureless band centered at 14400 $cm^{-1}$, and assigned it as ${}^3T_{1g}\rightarrow{}^1A_{1g}$ phosphorescence on the basis of the band position and the lifetime. Later, the luminescence spectrum of $[Co(CN)_6]^{3-}$ was studied by some workers,4–9) but most of them have also only reported it to be structureless and broad. The author has reported vibrational structure of the luminescence spectrum of powdered $K_3[Co(CN)_6]$ at 20 K, which exhibited a progression with about 400 $cm^{-1}$ spacing interpreted in terms of the Co–C stretching frequency for the first time.7) Recently, Hipps and Crosby9) have also reported vibrational structure whose spacing between the members of the progression was 420 $cm^{-1}$ in the luminescence spectrum of $K_3[Co(CN)_6]$ at 4.2 K.

Another example of luminescence of cobalt(III) complex was *trans*-$Na_5[Co(CN)_4(SO_3)_2]$ reported by Zuloaga and Kasha.10) They reported a broad and structureless spectrum centered at 14300 $cm^{-1}$ at 77 K and assigned it as the ${}^3T_{1g}\rightarrow{}^1A_{1g}(O_h)$ phosphorescence. As mentioned above, investigations of luminescence of cobalt(III) complexes have been very limited.

This paper deals with the luminescence of cobalt(III) complexes, the luminescence of one among them, *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$, having been observed for the first time. For single crystals of $K_3[Co(CN)_6]$, $Rb_3[Co(CN)_6]$, and $Cs_3[Co(CN)_6]$, the luminescence spectra were measured with particular care for the fine structure to make clear what kind of vibration was responsible for the intensity. Also, the position of the 0-0 transition of the ${}^3T_{1g}\leftrightarrow{}^1A_{1g}(O_h)$ of hexacyanocobaltates(III) and of *cis*- and *trans*-tetracyanodisulfitocobaltates(III) are presented.

Finally, the possible relationship between photochemical behavior and luminescence is discussed.

## Experimental

*Preparation of Materials.* $K_3[Co(CN)_6]$,11) $Rb_3[Co(CN)_6]$,12) $Cs_3[Co(CN)_6]$,12) *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$,13) *trans*-$Na_5[Co(CN)_4(SO_3)_2]$,14) *fac*-$[Co(CN)_3(NH_3)_3]$,15) *cis*-$[Co(CN)_2(en)_2]ClO_4$,16) $[Co(CN)(NH_3)_5]Cl_2$,17) and $[Co(NH_3)_6]Cl_3$18) were prepared according to the published methods. These compounds, except for *fac*-$[Co(CN)_3(NH_3)_3]$, were recrystallized several times. Single crystals of $K_3[Co(CN)_6]$, $Rb_3[Co(CN)_6]$, and $Cs_3[Co(CN)_6]$ were obtained by slow evaporation of aqueous solutions.

*Measurement of Luminescence Spectra.* Excitation light from a Ushio UM-102 mercury lamp (120 W) was isolated by a Spex Micromate grating monochromator (10 cm, f 2.5, blazed at 300 nm, 1200 l/mm), then passed through a Toshiba UV-D25 filter, and projected on the sample at an incident angle of 45°. Luminescent light at right angles to the excitation light was passed through a yellow cut-off filter to reduce scattered excitation light, and was dispersed by a JASCO CT-100 grating monochromator (100 cm, f 8.6, blazed at 750 nm, 1200 l/mm). The light from the monochromator was detected by a cooled Hamamatsu R-649S (S-20) photomultiplier, a Hamamatsu C-716 preamplifier, and a Hamamatsu C-767 photon counter, and recorded by a Yokogawa 3051 recorder equipped with a Yokogawa 3053-12 DC unit. Sometimes a set of a Hamamatsu R-666 photomultiplier, with GaAs photocathode, and a JASCO L-125 lock-in amplifier was used for the detection system. The sample was cooled with an Air Products and Chemicals Cryo-Tip AC-2 for measurements at liquid hydrogen temperature and with the optical cryostat designed in our laboratory for those at liquid nitrogen temperature. The sample temperature was measured using a chromel/constantan and a chromel/Au-0.07%Fe thermocouple.

Spectral slit width was about 8 cm$^{-1}$ for hexacyanocobaltates(III) and *trans*-$Na_5[Co(CN)_4(SO_3)_2]$, and about 16 cm$^{-1}$ for other compounds.

The luminescence spectra thus obtained were corrected by the standard lamp method.

*Measurements of Visible and Ultraviolet Absorption, Diffuse Reflectance, Infrared, and Raman Spectra.* The absorption spectra of aqueous solutions were measured with a Hitachi EPS-3T spectrophotometer. The spin-forbidden band of a single crystal of $K_3[Co(CN)_6]$ was measured with a JASCO CT-50 grating monochromator (50 cm, f 5.6, blazed at 300 nm, 1200 l/mm) equipped with a Hamamatsu R-649S photomultiplier connected with the photon counting system at liquid helium temperature. The sample was cooled with the optical cryostat.

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

The infrared spectra in the 200—700 cm$^{-1}$ region were obtained with a JASCO IR-F far-infrared spectrophotometer using the Nujol mull method.

Raman spectra were measured on powdered samples with a He-Ne laser Raman spectrophotometer.[19]

## Results and Discussion

*Luminescence Spectra of $K_3[Co(CN)_6]$.* The 20 and 77 K, 313 nm excited luminescence spectra measured on a single crystal are shown in Fig. 1. The peak position of 14200 cm$^{-1}$ was almost the same as that of other authors,[4—9] and the half band width of the total band was about 2600 cm$^{-1}$. The luminescence band increased gradually in intensity with a lowering in the temperature from room temperature to about 30 K, and decreased slightly with lowering in the temperature from about 30 to 20 K. This can be explained as having been caused by the competition between non-radiative relaxation and sharpening of the each component bands; that is, from room temperature to about 30 K, the dominant effect is depression of the non-radiative process, which increases luminescence intensity, and from about 30 to 20 K, sharpening of each component band is dominant, which decreases luminescence intensity. Even at room temperature, a structureless and very weak spectrum was observed. At 77 K, the spectrum exhibited vibrational structure with about 400 cm$^{-1}$ spacing between the members of the progression. When the temperature was lowered from 77 to 20 K, the $A_n$ progression at 77 K was resolved into two components, $a_n$ and $b_n$ progressions; moreover, a weak $c_n$ progression appeared between the $A_n$ progression. The average spacing of 394 cm$^{-1}$ between the members of each progression was slightly decreased with increase in $n$, and the fundamental vibrational frequency was extrapolated to about 405 cm$^{-1}$ as shown in Fig. 2.

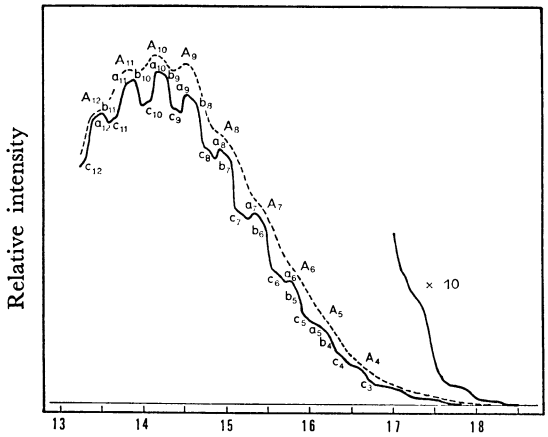

Fig. 1. Luminescence spectra of $K_3[Co(CN)_6]$.
——, 20 K; ----, 77 K.

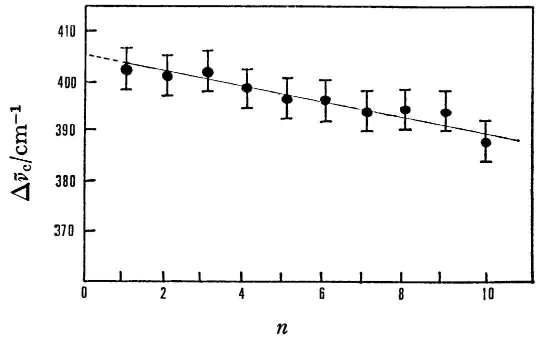

Fig. 2. Energy differences between $c_n$ peaks, $\Delta\tilde{\nu}_c = \tilde{\nu}_{c_{n+1}} - \tilde{\nu}_{c_n}$, in $K_3[Co(CN)_6]$ at 20 K.

*Luminescence Spectra of $Rb_3[Co(CN)_6]$ and $Cs_3[Co(CN)_6]$.* The 313 nm excited luminescence spectra of the rubidium and caesium salts were measured on single crystals at 20, 77 K, and room temperature. The spectral pattern was practically the same as that of the potassium salt. At 20 K, the maximum positions of the total bands were at 14100 and 14200 cm$^{-1}$ for the rubidium and caesium salts, respectively. The vibrational structure, consisting of three components, was observed, but it was not so clear as in the potassium salt. The energy separation between the members of the progression was about 400 cm$^{-1}$ as in the potassium salt. Even at 77 K, the spectra showed vibrational structure.

*Position of the 0-0 Transition.* Since the three salts of hexacyanocobaltates(III) showed the same vibrational pattern, the potassium salt, whose spectrum was the best resolved of the three, will be discussed.

The ${}^3T_{1g} \leftarrow {}^1A_{1g}$ spin-forbidden band of $K_3[Co(CN)_6]$ has been reported at different peak energy by some authors. Kida *et al.*[20] found a shoulder at 24000 cm$^{-1}$, while Porter and Mingardi,[3] and Jain *et al.*[21] observed weak bands at 18500 and 20833 cm$^{-1}$, respectively; and these three bands have been assigned as the ${}^3T_{1g} \rightarrow {}^1A_{1g}$ spin-forbidden transition. Recently, this spin-forbidden band was carefully reexamined by Kataoka[8] by microspectrophotometry at 77 K. A small shoulder, which was not observed at room temperature, appeared clearly at 26000 cm$^{-1}$ when the temperature lowered to 77 K, and was assigned as the ${}^3T_{1g} \leftarrow {}^1A_{1g}$ spin-forbidden band.

The first component of the luminescence band, which lies at highest energy, was observed at *ca.* 18200 cm$^{-1}$ in the 20 K sepctrum obtained. This indicates that the 0-0 transition lies at some 100 cm$^{-1}$ higher than 18200 cm$^{-1}$. Comparison of the absorption peak values with a position of the 0-0 transition obtained from the luminescence spectrum clearly shows that the positions of 18500 and 20833 cm$^{-1}$ in absorption are too low in energy; while the peak positions observed at 24000 and 26000 cm$^{-1}$ are consistent with the 0-0 transition obtained from this luminescence measurement. On the other hand, the calculated value for $^3T_{1g} \leftarrow {}^1A_{1g}$ spin-forbidden band is *ca.* 27000 cm$^{-1}$.[22)] Consequently, it is more probable to assign the 26000 and/or 24000 cm$^{-1}$ band than the 18500 and 20833 cm$^{-1}$ bands as the $^3T_{1g} \leftarrow {}^1A_{1g}$ spin-forbidden band.

It is expected that the 0-0 transition would not obtain any appreciable intensity either in luminescence or in absorption. Thus, in order to obtain a more exact position of the 0-0 transition, vibrational structure measurement in the spin-forbidden absorption band is required. That is, comparison of the vibrational structures in both the luminescence and absorption spectra can be expected to give the 0-0 band position between their first components.

To determine the position of the 0-0 transition, the 4.2 K single crystal absorption was measured, but no vibrational structure was observed in the 17000—23000 cm$^{-1}$ region. Consequently, the position of the 0-0 transition was not exactly determined, but would lie between 18300 and 18600 cm$^{-1}$.

*Assignment of Vibrational Structure.* To assign the vibrational structure associated with the luminescence spectrum, the normal modes of vibration of $[Co(CN)_6]^{3-}$ must be considered. Raman and infrared spectra of this complex have been studied by many workers,[23—29)] but there has been some uncertainty in position and assignment, especially for low energy region skeletal vibration. The assignments of some workers are listed in Table 1.

There are five vibronic active skeletal modes, $\nu_7(t_{1u})$, $\nu_8(t_{1u})$, $\nu_9(t_{1u})$, $\nu_{12}(t_{2u})$, and $\nu_{13}(t_{2u})$; thus the fine structure of the spectrum would consist of $(\nu_7, \nu_8, \nu_9, \nu_{12}, \nu_{13}) + n\nu_2(a_{1g})$ $(n=0, 1, 2, \ldots)$ peaks.[30)] In these vibrational modes, it can be considered that the contribution of the deformation modes, $\nu_8$, $\nu_9$, $\nu_{12}$, and $\nu_{13}$, to the intensity would be large.[31—33)] It is possible that the lattice motion would couple with the electronic level; but its contribution to the intensity, which is proportional to the degree of destruction of the center of symmetry, would be much weaker than that of the ungerade skeletal vibration.

The luminescence spectra seem to consist of three kinds of progressions, and members of each progression have about 400 cm$^{-1}$ spacing. These progressions may be vibronic bands originated from one or more electronic levels. The ground state, $^1A_{1g}$, is not split by any perturbation, but the excited luminescent state, $^3T_{1g}$, splits into E, $T_2$, $T_1$, and $A_1$ by spin-orbit interaction. For $K_3[Co(CN)_6]$, the separation between the E and other upper levels, $T_2$, $T_1$, and $A_1$, have been reported as 30, 318, and about 500 cm$^{-1}$, and the lifetimes of the E, $T_2$, and $T_1$ as 463, 2615, and 28.3 μs, respectively, determined from the temperature dependence analysis of the lifetime.[9)] On the basis of these separations and lifetimes, the contribution to the luminescence intensity of each level, $I_i$, is given by[34)]

$$I_i \propto k_i \cdot g_i \cdot \exp(-\Delta E/kT) = 1/\tau_i \cdot g_i \cdot \exp(-\Delta E/kT), \qquad (1)$$

where $k_i$ is the rate constant of the luminescence process, $\tau_i$ is the lifetime, and $g_i$ is the multiplicity. Thus the calculated intensity ratios of $I_{T_2}/I_E$ and $I_{T_1}/I_E$ are $2.1 \times 10^{-2}$ and $2.9 \times 10^{-9}$ at 20 K and $1.5 \times 10^{-1}$ and $6.6 \times 10^{-2}$ at 77 K. This indicates that, at 20 K, the luminescence from the $T_2$ and other upper levels would contribute less to the spectrum. Thus it is possible to neglect the $T_2$, $T_1$, and $A_1$ levels as luminescent ones.

Comparison of the energy separations betweeen adjacent components of the luminescence spectrum with those of the ungerade skeletal vibrations indicates that the most reasonable assignments are as follows. The most intense component, $a_n$ progression, can be assigned as the transition to $(\nu_9 + n\nu_2)$ or $(\nu_{13} + n\nu_2)$ level, or it may consist of two peaks corresponding to those, since the $\nu_9$ and $\nu_{13}$ modes have nearly the same energy. Similarly, $b_n$ progression is assigned as the transition to $(\nu_8 + n\nu_2)$ or $(\nu_{12} + n\nu_2)$ level, or again it may consist of two peaks corresponding to those; while the weak component, $c_n$ progression, cannot be assigned as any of the skeletal vibrational modes. The energy difference between the $a_n$ and $c_n$ progression is about 175 cm$^{-1}$; and the lattice modes appeared strongly at 172 and 189 cm$^{-1}$,[26)] hence the $c_n$ progression can be assigned as the transition to the ($a_n$+lattice mode) level.

*Calculation of the Relative Intensity of the Luminescence Band.* The intensity ratio of the individual component bands from the 0-th vibrational state in the electronic state A to the *n*-th vibrational state in the electronic state B is given by[35)]

TABLE 1. RAMAN AND INFRARED SPECTRA OF $[Co(CN)_6]^{3-}$ ($\tilde{\nu}$/cm$^{-1}$)

| | $\nu_2(a_{1g})$ $\nu$Co-C | $\nu_3(e_g)$ $\nu$Co-C | $\nu_7(t_{1u})$ $\nu$Co-C | $\nu_8(t_{1u})$ $\delta$Co-C-N | $\nu_9(t_{1u})$ $\delta$C-Co-C | $\nu_{12}(t_{2u})$ $\delta$Co-C-N | $\nu_{13}(t_{2u})$ $\delta$C-Co-C | Ref. |
|---|---|---|---|---|---|---|---|---|
| $K_3[Co(CN)_6]$ | 404 | 394[a)] | 565 | 414 | 129 | 380 | 104 | 26) |
| | 408 | 330<br>(358) | 564 | 416 | 90[a)] | 440 | 69[a)] | 23) |
| | | | 562 | 414 | 128 | | 108 | 27) |
| | | | | | 92 | | 72 | 28) |
| | 408 | | 562 | 415 | | | | This work |
| $Rb_3[Co(CN)_6]$ | 406 | | 561 | 414 | | 443 | | This work |
| $Cs_3[Co(CN)_6]$ | 413 | | 560 | 415 | | 437 | | This work |

a) Calculated value.

$$\frac{I(\mathrm{B}_n\leftarrow\mathrm{A}_0)}{I(\mathrm{B}_0\leftarrow\mathrm{A}_0)} = \frac{I_n}{I_0} = \left[\frac{1}{2}\alpha(\Delta r)^2\right]^n \frac{1}{n!}, \tag{2}$$

where $\alpha=4\pi^2 m\bar{\nu}c/h$ and $\Delta r$ is the difference in the equilibrium nuclear distance between the A and B states.

$$\text{Setting } \frac{1}{2}\alpha(\Delta r)^2 = K,$$

$$\frac{I_n}{I_0} = K^n\frac{1}{n!}. \tag{3}$$

The relative intensity of individual members of the $a_n$ progression in the luminescence band, calculated from Eq. 3, is shown in Fig. 3 together with the observed spectrum of $K_3[Co(CN)_6]$ at 20 K. The calculated relative intensities shown by the heights of vertical lines in Fig. 3 are the one when $K=10.7$, and those of the other marks are the ones when $K=11.7$ and 12.7. When the maximum of the band occures at the $n$-th component, it can be seen that $n=K$ in Eq. 3, so that $K=10.7$ means that the first component of 18200 cm$^{-1}$ in the luminescence spectrum should involve no $\nu_2$ vibration. It is clear from Fig. 3 that the intensity ratio when $K=10.7$ is the best fit; thus it is highly probable that the 0-0 transition lies at 18300—18600 cm$^{-1}$.

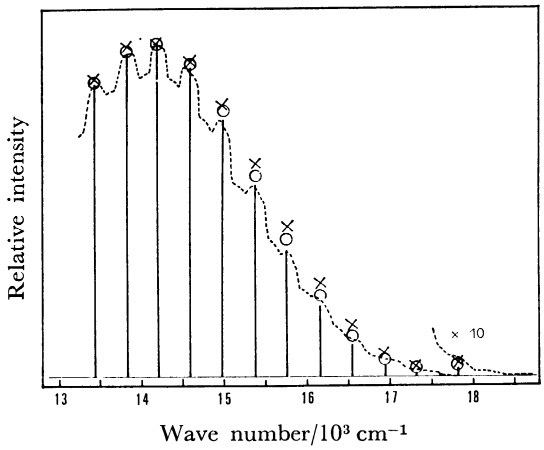

Fig. 3. Calculated relative intensity of $K_3[Co(CN)_6]$. Broken line indicates the observed spectrum. Vertical line, $K=10.7$; ○, $K=11.7$; ×, $K=12.7$.

By fitting the relative intensities of the individual components in the observed luminescence band to the calculated ones, the change in the Co–C equilibrium nuclear distance, $\Delta r$, between the luminescent excited state and the ground state can be computed. The calculated change in the distance is 0.3 Å, when $K=10.7$. This value can be compared to 0.20—0.23 Å in Pt-F distance in $[PtF_6]^{2-}$.[36)]

*Luminescence Spectrum of* cis-*$K_3Na_2[Co(CN)_4(SO_3)_2]$*. The 20 K, 365 nm excited luminescence spectrum is shown in Fig. 4. A broad and structureless band was observed at 13200 cm$^{-1}$, and its half band width was about 2000 cm$^{-1}$. The higher energy threshold value of the luminescence band was observed at 16500 cm$^{-1}$. The intensity of the luminescence was somewhat weaker than that of the hexacyanocobaltates(III).

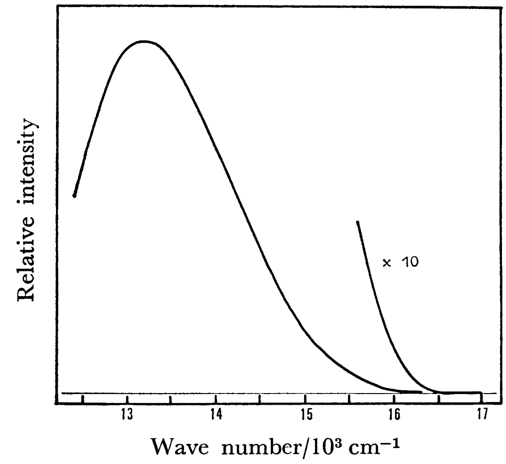

Fig. 4. Luminescence spectrum of *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$ at 20 K.

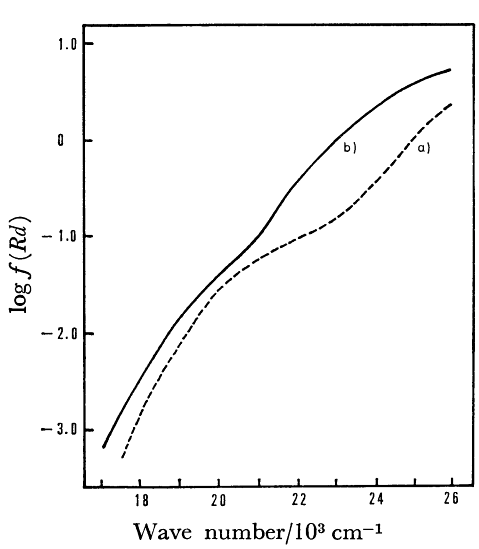

Fig. 5. Spin-forbidden bands of a) *cis*-$K_3Na_2[Co(CN)_4(SO_3)_2]$ and b) *trans*-$Na_5[Co(CN)_4(SO_3)_2]$ measured by diffuse reflectance method.

On the other hand, in the absorption spectrum obtained by the diffuse reflectance method, a weak shoulder was observed at *ca.* 20000 cm$^{-1}$, as shown in Fig. 5. In the figure the reflectance spectrum of *trans*-$Na_5[Co(CN)_4(SO_3)_2]$ is also shown.

The luminescence can be assigned as the transition from the lowest triplet state, $^3T_{1g}(O_h)$, to the $^1A_{1g}(O_h)$ ground state, on the basis of its position and intensity. It is consistent with the position of the luminescence band that the weak shoulder at *ca.* 20000 cm$^{-1}$ in absorption was regarded to be the spin-forbidden band, hence it can be assigned as the $^3T_{1g}\leftarrow{}^1A_{1g}(O_h)$ spin-forbidden transition, which is the reverse process of luminescence. The 0-0 transition would lie at 16500—17000 cm$^{-1}$ on the basis of the threshold value of the luminescence band and the maximum position of both luminescence and absorption.

*Luminescence Spectrum of* trans-*$Na_5[Co(CN)_4(SO_3)_2]$*. The 20 K, 365 nm excited luminescence spectrum is shown in Fig. 6. A broad and structureless band as in the cis salt was observed at 14400 cm$^{-1}$, and its

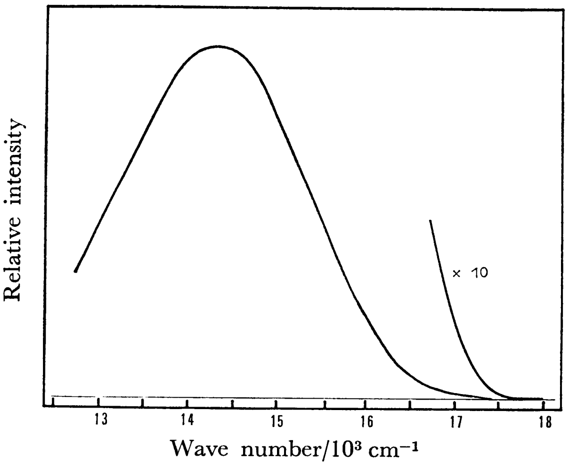

Fig. 6. Luminescence spectrum of *trans*-$Na_5[Co(CN)_4(SO_3)_2]$ at 20 K.

half band width was about 2300 cm$^{-1}$. The threshold value was observed at *ca.* 17700 cm$^{-1}$. Intensity of the luminescence was comparable to that of the hexacyanocobaltates(III). The diffuse reflectance spectrum showed a weak shoulder at *ca.* 20000 cm$^{-1}$, as shown in Fig. 5.

The luminescence spectrum of this complex salt has already been measured at 77 K by Zuloaga and Kasha,[10] and the spectrum obtained in the present work was essentially the same as that in this previous investigation. The luminescence can be assigned as $^3T_{1g}\rightarrow{}^1A_{1g}(O_h)$ phosphorescence and the weak shoulder observed in the absortpion spectrum can be assigned as the reverse process of the luminescence, that is the $^3T_{1g}\leftarrow{}^1A_{1g}(O_h)$ transition. The 0-0 transition would lie at 17700–18200 cm$^{-1}$ on the basis of the threshold value of the luminescence band and the maximum position of both luminescence and absorption bands. Finally, it is interesting to note that there is some difference in ligand field strength between this complex and hexacyanocobaltates(III), but the luminescence of both appeared at almost the same position in spite of their defference in energy of the $^3T_{1g}\leftarrow{}^1A_{1g}(O_h)$ spin-forbidden band.

*Luminescence of Other Cobalt(III) Complexes.* Luminescence spectra of *fac*-$[Co(CN)_3(NH_3)_3]$, *cis*-$[Co(CN)_2(en)_2]\,ClO_4$, $[Co(CN)(NH_3)_5]\,Cl_2$, and $[Co(NH_3)_6]Cl_3$, excited by 365 and 313 nm light were measured in the 12000—20000 cm$^{-1}$ region, but no luminescence was observed even at 20 K. Thus the luminescent complexes are probably restricted to those having four or more cyano ligands.

*Relationship between Luminescence and Photochemical Behavior.* Photochemical reaction of cobalt(III) complexes in aqueous solution have been extensively studied by many authors.[1b,1c,37] Generally, they can be classified into the following two types:

(A) Redox reaction from Co(III) to Co(II) with release of ligands,

(B) Ligand substitution reaction without reduction of central cobalt atom.

Cobalt(III) complexes almost all belong to type (A), for example, $[Co(NH_3)_6]^{3+}$,[38] $[Co(en)_3]^{3+}$,[38] $[CoCl(NH_3)_5]^{2+}$,[39,40] $[CoBr(NH_3)_5]^{2+}$,[40,41] $[CoI(NH_3)_5]^{2+}$,[42,43] $[Co(ox)_3]^{3-}$,[44] *etc.* But to date there have been reported a few that belong to type (B), for example, $[Co(CN)_6]^{3-}$,[45] $[CoCl(CN)_5]^{3-}$,[40,46] $[CoBr(CN)_5]^{3-}$,[40,46] and $[Co(CN)_5I]^{3-}$,[46] as listed in Table 2. It is interesting to note that all of them that belong to type (B) contain five or more cyano ligands.

In the photochemical reaction of type (A), the oxidation state of the cobalt atom changes from +3 to +2, hence it is considered that the reaction occurs from a ligand-to-metal charge transfer(LMCT) state. This means that the LMCT level mainly is the most populated state after irradiation of ultraviolet light and that the potential minimum of the LMCT level is lower than that of the ligand field leves, as shown in Fig. 7a). In the complexes of type (A), ligand

Table 2. Relationship between photochemical behavior and luminescence of cobalt(III) complexes

| Complex | Type of photochemical reaction[a] | Phosphorescence[b] |
|---|---|---|
| $[Co(NH_3)_6]^{3+}$ | A | – |
| $[Co(en)_3]^{3+}$ | A | – |
| $[CoCl(NH_3)_5]^{2+}$ | A | – |
| $[CoBr(NH_3)_5]^{2+}$ | A | – |
| $[CoI(NH_3)_5]^{2+}$ | A | – |
| $[Co(CN)(NH_3)_5]^{2+}$ | × | – |
| *cis*-$[Co(CN)_2(en)_2]^+$ | × | – |
| *fac*-$[Co(CN)_3(NH_3)_3]$ | × | – |
| *cis*-$[Co(CN)_4(SO_3)_2]^{5-}$ | × | + |
| *trans*-$[Co(CN)_4(SO_3)_2]^{5-}$ | × | + |
| $[CoCl(CN)_5]^{3-}$ | B | +[c] |
| $[CoBr(CN)_5]^{3-}$ | B | +[c] |
| $[Co(CN)_5I]^{3-}$ | B | +[c] |
| $[Co(CN)_6]^{3-}$ | B | + |
| $[Co(ox)_3]^{3-}$ | A | – |

a) A, Type (A); B, Type (B); ×, Not investigated.
b) +, Phosphorescent; –, non-phosphorescent.
c) Unpublished data.

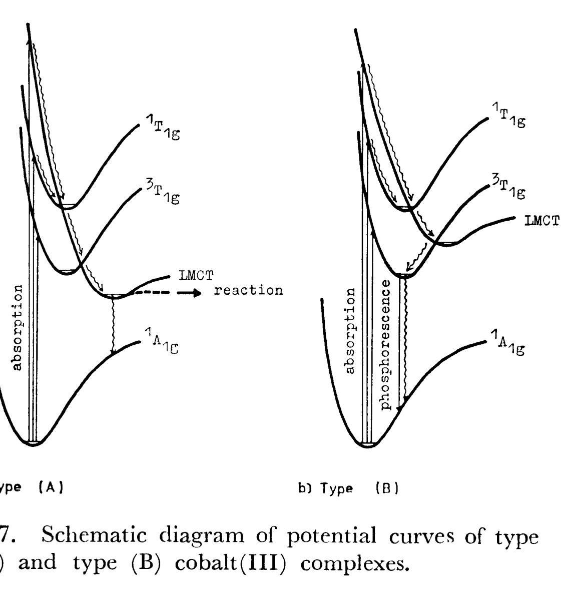

Fig. 7. Schematic diagram of potential curves of type (A) and type (B) cobalt(III) complexes.

substitution reaction also may occur, the cobalt atom maintaining its oxidation state of $+3$ when the complex is irradiated with a ligand field absorption band; but even in those cases when this reaction has occured, the quantum yield is lower than in the redox reaction by from 10 to 100 times. In the solid state, although there are only a few cobalt(III) complexes that undergo photochemical reaction,[47,48] the situation of electronic level of these complexes does not differ as much as in an aqueous solution. Thus in the solid state, the irradiated energy may be finally populated also to the LMCT level and would deactivate non-radiatively. Therefore, it may be concluded that the complexes of type (A) do not luminesce the $^3T_{1g} \rightarrow {}^1A_{1g}$ phosphorescence.

On the other hand, in complexes that belong to type (B), the cobalt(III) atom is not reduced, but the ligand substitution reaction does occur; hence it is considered that the energy irradiated is not populated to the LMCT level, but to the ligand field level, and a photochemical reaction occurs from this level in aqueous solution. This indicates that the lowest ligand field triplet level, $^3T_{1g}(O_h)$, would be the main populated state and lower than the LMCT level, as shown in Fig. 7b). Hence, in the solid state, the $^3T_{1g} \rightarrow {}^1A_{1g}(O_h)$ luminescence would be observed. Actually, the luminescent complexes belong to type (B), as shown in Table 2.

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