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Phosphorescence Spectra of $[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(NH_3)_6][CdCl_5]$. Splitting of Their 0–0 Bands

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Synopsis. High resolution $^2E \rightarrow {}^4A_2$ phosphorescence spectra of $[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(NH_3)_6][CdCl_5]$ were measured. The 0–0 bands split into two components separated by 3.7 and 3.4 cm^{-1} for $[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(NH_3)_6][CdCl_5]$, respectively. The same spacings were also resolved in the ν_8 bands. The splitting in both cases is assigned as that of the ^2E phosphorescent electronic level.

There have been many studies of $^2E \rightarrow {}^4A_2$ phosphorescence spectra of hexaamminechromium(III) salts.[1–5] The phosphorescence spectrum of $[Cr(NH_3)_6][Co(CN)_6]$ was studied by Kataoka[1] in our laboratory, and by Cervone *et al.*[2] from the viewpoint of energy transfer from $[Co(CN)_6]^{3-}$ to $[Cr(NH_3)_6]^{3+}$, but no assignment of the vibronic bands was made. Flint *et al.*[3] investigated the phosphorescence spectra of $[Cr(NH_3)_6][CdCl_5]$, $[Cr(NH_3)_6][Co(CN)_6]$, and $[Cr(NH_3)_6](N_3)_3$, where the complex cation is in non-cubic environment, and they have given an assignment of vibronically active fundamentals. On the other hand, X-ray studies of $[Cr(NH_3)_6][Co(CN)_6]$[6] and $[Cr(NH_3)_6][CdCl_5]$[7] showed that the $[Cr(NH_3)_6]^{3+}$ ion occupies $\bar{3}$ site symmetry in the lattice. A ^2E level does not split by the sole action of the trigonal field or the spin orbit interaction, but splits into two Kramers doublets through the interplay of the two. Hence a splitting of the 0–0 band would be expected, but to date no splitting has been observed in $[Cr(NH_3)_6][Co(CN)_6]$ and $[Cr(NH_3)_6][CdCl_5]$.

Experimental

The materials were prepared according to the published methods[1,7] from carefully recrystallized $[Cr(NH_3)_6](NO_3)_3$, $K_3[Co(CN)_6]$, and $CdCl_2 \cdot 2.5H_2O$.

Phosphorescence spectra were recorded using excitation from a mercury lamp, the line being isolated by a Spex Michromate (f 2.5, 10 cm). The detection monochromator was a Jasco CT-100 (f 8.5, 100 cm) equipped with a cooled Hamamatsu R-649S (S-20) photomultiplier connected with Hamamatsu C-767 photon counter. Spectral slit width was 0.8 cm^{-1} for this measurement.

Results and Discussion

$[Cr(NH_3)_6][Co(CN)_6]$. The 20 K, 365 nm excited phosphorescence spectrum measured on a powdered sample ranging from the 0–0 to ν_7 band is shown in Fig. 1 together with the assignment of the vibronic bands observed. Down to 77 K, the 0–0 band clearly split into two components separated by 3.7 cm^{-1}, and the same spacing was also observed in the $\nu_8(e_u)$ band. The two components of each of these bands at 77 and 20 K are shown in Fig. 2. In the 0–0 band, these components, completely separated, had comparable intensities and their intensity ratios at 77 and 20 K are given by $\exp(-\Delta E/kT)$. Hence, the splitting of both the 0–0 band and the $\nu_8(e_u)$ band can be assigned as that of the ^2E phosphorescent electronic level, and can be interpreted as being due to the combined effect of the trigonal distortion of the $[Cr(NH_3)_6]^{3+}$ ion in the lattice and the spin orbit interaction. Splitting of the $^4A_2$ ground state is expected to be much smaller than that of the ^2E state.[8] In other vibronic bands, the splitting of the ^2E level could not be resolved because of their broadness.

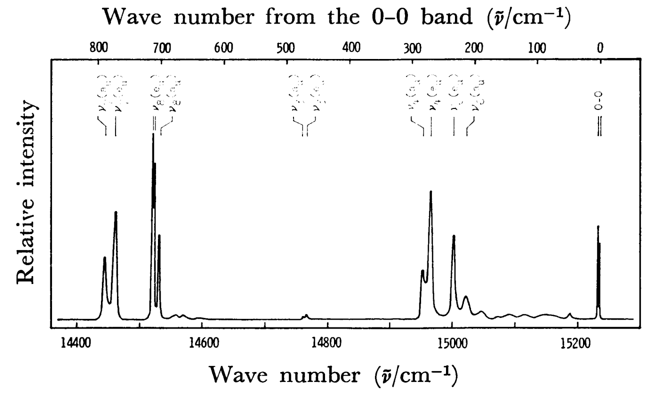

Fig. 1. Phosphorescence spectrum of $[Cr(NH_3)_6][Co(CN)_6]$ at 20 K.

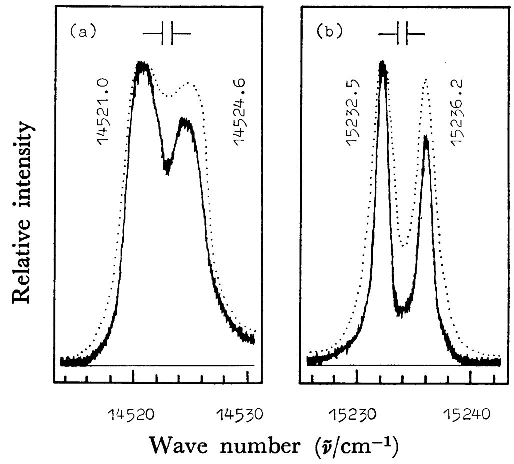

Fig. 2. Phosphorescence spectra of $[Cr(NH_3)_6][Co(CN)_6]$ at 20 K. (a) $\nu_8(e_u)$ band, (b) 0–0 band. Dotted line indicates outline of the spectra at 77 K. Lower energy component of each band is normalized.

$[Cr(NH_3)_6][CdCl_5]$. This complex salt is photosensitive even in a solid state. During a few minutes exposure to the excitation source, the original bands decreased in intensity and new bands appeared. For

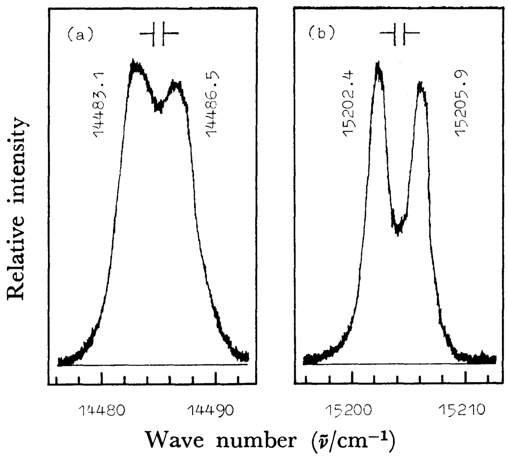

Fig. 3. Phosphorescence spectra of $[Cr(NH_3)_6][CdCl_5]$ at 77 K. (a) ν_8 band, (b) 0–0 band.

this reason, an excitation wavelength less susceptible to decomposing was selected, and measurement was done as quickly as possible, changing the sample for measuring each band. The 77 K, 313 nm excited phosphorescence spectra of a powdered sample of the 0–0 and ν_8 bands are shown in Fig. 3. Splitting of the 0–0 and ν_8 bands with a spacing of 3.4 cm^{-1} was also observed as in $[Cr(NH_3)_6][Co(CN)_6]$. The two components of these bands can be reasonably assigned as the transition from two levels, originated from the ^2E state, to the $^4A_2$ ground state, but neither of them can be a constituent band of a photodecomposition product, because long exposure gave no shift of the 0–0 and ν_8 bands, and intensity ratios of the two were constant.

The 0–0 band splitting observed is very small compared with 27 cm^{-1} for $[Cr(NH_3)_6](N_3)_3$,[3] 48 cm^{-1} for $[Cr(en)_3](ClO_4)_3$,[9] and 18 cm^{-1} for $2[Cr(en)_3]Cl_3 \cdot KCl \cdot 6H_2O$.[8,9] This indicates that the deviation from cubic symmetry is very small as expected from the X-ray studies. Since the structural studies were done at room temperature, it can be considered that phase transition might occur at low temperature, although observation of the bands while the sample was being cooled indicated no change in the spectral pattern in detail other than sharpening of the bands. This suggests that no phase transition occurred, or if it did occur, the structural difference should be little.

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