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VIBRATIONAL STRUCTURE OF THE LIGAND FIELD ABSORPTION BAND OF SOME Co(III) COMPLEXES

Kunimasa FUKUDA and Akio URUSHIYAMA

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

The vibrational structures of the ligand field absorption bands of the Co(III) complexes, $[Co(NH_3)_6]^{3+}$, $[CoF(NH_3)_5]^{2+}$, $[CoCl(NH_3)_5]^{2+}$, trans-$[CoCl_2(NH_3)_4]^+$, and trans-$[CoBr_2(NH_3)_4]^+$ were studied at 4.2 K. It was found that the vibrational structures observed in the present studies consist of the uniquantal progressions of the totally symmetric CoN stretching vibrations of the complexes.

The vibrational fine structures of the ligand field absorption bands of the Co(III) complexes in O_h site symmetry have been observed by several workers.1) However, no study has been reported for the mixed ligand complexes. This communication presents the vibrational structures of the ligand field absorption bands of the Co(III) ammine complexes in various symmetries.

Low temperature absorption spectra were measured using a grating monochromater (Model CT-50: Japan Spectroscopic Co.) and a photon counting system (Model HTV-C767: Hamamatsu TV. Co.) and a liquid helium optical cryostat. The samples were mounted over a pinhole (ϕ 0.3 mm for single crystal, ϕ 2.0 mm for silicone grease mull) of the cooling stage of the cryostat, and the transmission spectra were recorded. The vibrational fine structures of the components of the $^1T_{1g}$ band of $[Co(NH_3)_6]^{3+}$, $[CoF(NH_3)_5]^{2+}$, $[CoCl(NH_3)_5]^{2+}$, trans-$[CoCl_2(NH_3)_4]^+$ and trans-$[CoBr_2(NH_3)_4]^+$ could be observed clearly at low temperatures. However, no structure could be detected on the components of the $^1T_{2g} \leftarrow {}^1A_{1g}$ band in the present studies.

The crystal absorption spectrum of $[Co(NH_3)_6][Co(CN)_6]$ is shown in Fig. 1. Clear vibrational structure is superimposed on the $^1T_{1g} \leftarrow {}^1A_{1g}$ band as already reported by Wentworth.1b) Most of the lines can be explained in terms of the

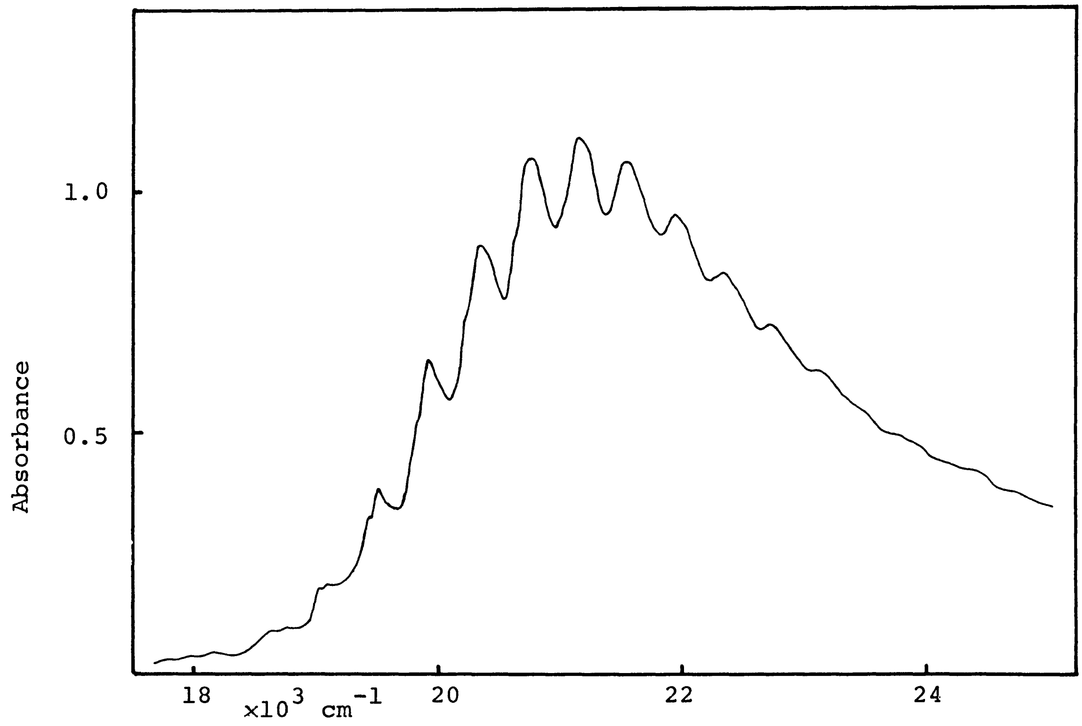

Fig. 1. Crystal absorption spectrum of $[Co(NH_3)_6][Co(CN)_6]$ at 4.2 K, with polarized light parallel to the c axis.

uniquantal progression of $\nu_1(a_{1g})$ of the combination, $\nu_i+(N+n)\nu_1(a_{1g})$ where ν_i denotes the non totally symmetric vibrations, N=integer and n=0,1,2,$\cdots$, assuming a vibronic coupling scheme. The average spacing of 402 cm^{-1} is thought to be a reasonable value for the $\nu_1(a_{1g})$ vibration$^{3)}$ in the $^1T_{1g}$ excited state. Each line could be resolved into two or more components, which may be correlated with the different nontotally symmetric vibrations (ν_i) effective in vibronic intensity. The crystal is hexagonal with space group $R\bar{3}$ and the precise symmetry of $[Co(NH_3)_6]^{3+}$ is S_6.$^{2)}$ However, the polarized absorption spectra with light polarized parallel and perpendicular to the crystal c axis appeared to be almost identical, indicating a very small distortion from O_h symmetry.

The crystal absorption spectra of $[CoF(NH_3)_5]Cl\cdot 2H_2O$ in the 16000-25000 cm^{-1} region are shown in Fig. 2. No X-ray crystallographic work has been reported for this crystal. However, the polarized absorption spectra were measured on its extinction directions as shown in the figure. A distinct splitting of the first spin-allowed band was observed. The band at lower energy is assigned to the $^1E[^1T_{1g}] \leftarrow {}^1A_1$ transition and the higher energy one to the $^1A_2[^1T_{1g}] \leftarrow {}^1A_1$ transition in C_{4v} symmetry. A good deal of vibrational structure was observed for each of the bands. The vibrational structure appeared to be rather complicated.

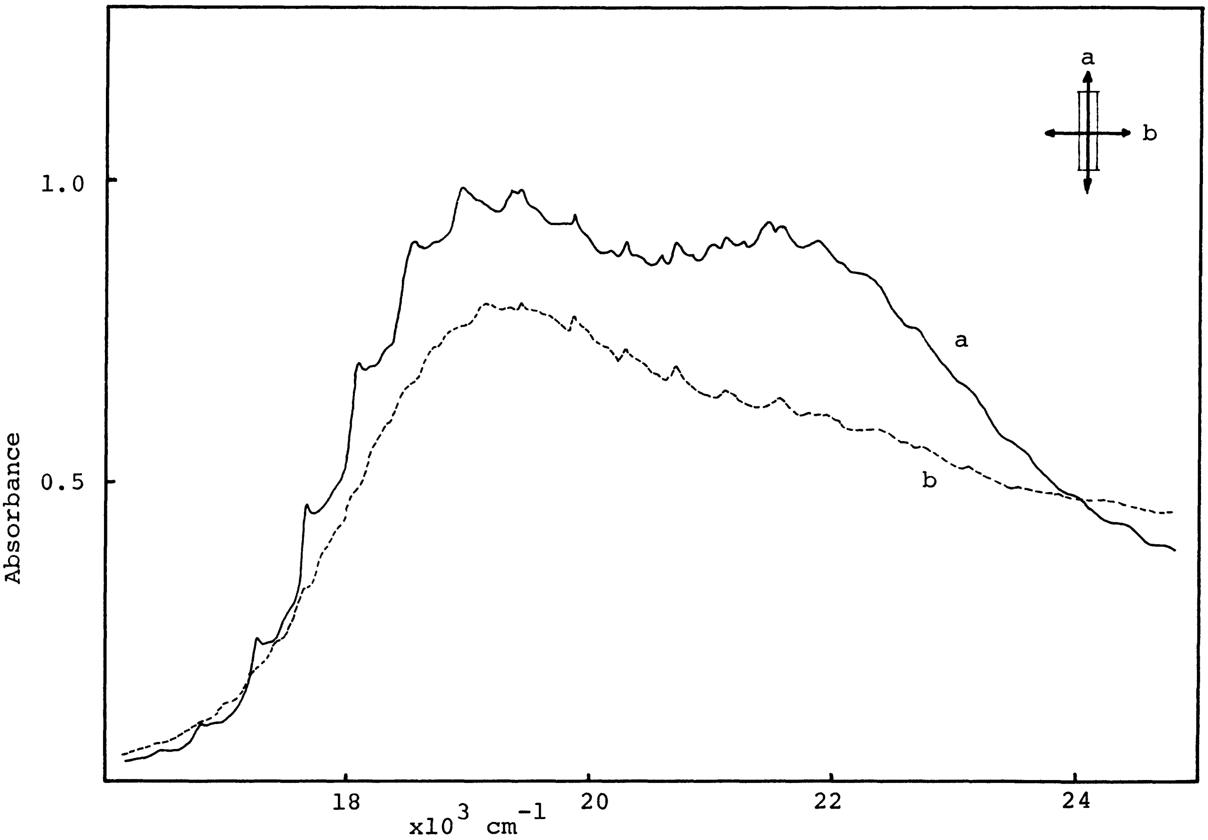

Fig. 2. Polarized absorption spectra of $[CoF(NH_3)_5]Cl_2\cdot 2H_2O$ at 4.2 K.

However, most of the lines are thought to consist of the uniquantal progressions of the $\nu_3(a_1)$[3a)] vibration for each band. That is, the spacings on the ^1E and $^1A_2$ bands were both found to be ~420 cm^{-1}. In the case of $[CoCl(NH_3)_5]Cl_2$, the average spacing was estimated to be 405 cm^{-1} for each band, although the spectra are not shown in the figure. These frequencies can be assigned to the $\nu_3(a_1)$ vibration of the skeletons. It was found that two or more components consist of the $\nu_3(a_1)$ progression on each of the bands. The predominant sharp lines on the ^1E_g band appeared to be clearly polarized. Each of the components may be correlated with the nontotally symmetric vibrations effective in vibronic intensities of the bands.

The crystal absorption spectra of trans-$[CoBr_2(NH_3)_4]_3[Co(CN)_6]$ and trans-$[CoCl_2(NH_3)_4]_3[Co(CN)_6]$ are illustrated in Figs. 3 and 4, respectively. These dihalogenocomplexes in D_{4h} symmetry showed two components which are assigned as $^1E_g[^1T_{1g}] \leftarrow {}^1A_{1g}$ in the 14000-18500 cm^{-1} region and $^1A_{2g}[^1T_{1g}] \leftarrow {}^1A_{1g}$ in the 18500-22000 cm^{-1} region. Vibrational structure was observed exclusively on the $^1A_{2g}$ bands. In the case of trans-$[CoBr_2(NH_3)_4]^+$, a predominant progression with spacings of ~400 cm^{-1} was found on the lower energy slope of the $^1A_{2g}$ band.

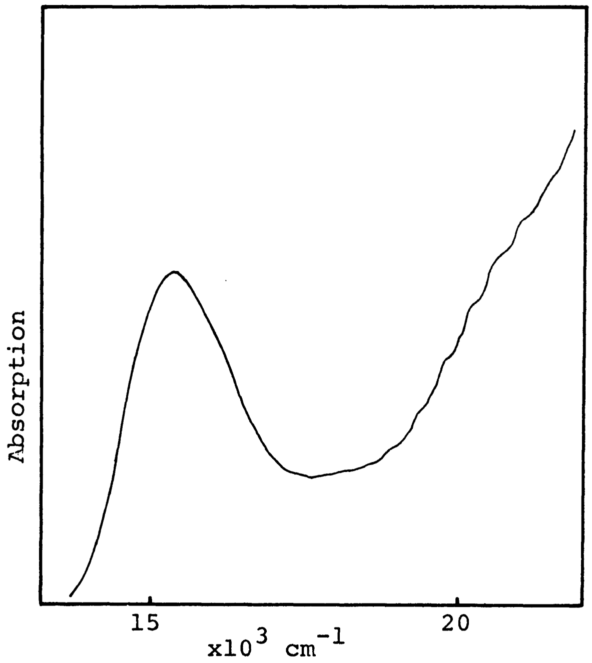

Fig. 3. Crystal absorption spectrum of trans-[$CoBr_2(NH_3)_4$]$_3$[$Co(CN)_6$] at 4.2 K (mull method).

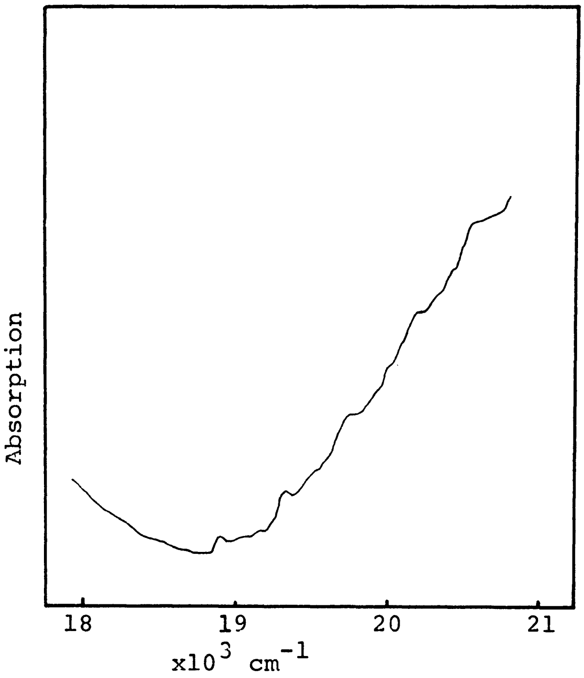

Fig. 4. Crystal absorption spectrum of trans-[$CoCl_2(NH_3)_4$]$_3$[$Co(CN)_6$] at 4.2 K (mull method).

For trans-[$CoCl_2(NH_3)_4$]$^+$, the interval was estimated to be ~425 cm^{-1}. These vibrational frequencies can naturally be correlated with the $\nu_2(a_{1g})$[3a] vibrations of the trans-CoX_2N_4 groups. At least three components were found to consist of the $\nu_2(a_{1g})$ progression. The observed lines may be assignable on the basis of the infrared absorption data.

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