The Vibrational Fine Structure of the $^1T_{1g}\leftarrow{}^1A_{1g}$ Absorption Band of [Co(NH$_3^*$)$_6$]$^{3+}$

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The crystal absorption spectra of [Co(NH$_3$)$_6$][Ir(CN)$_6$] and [Co(ND$_3$)$_6$][Ir(CN)$_6$] were studied at 4.2 K. The vibrational fine structure observed on the $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption band of the hexaamminecobalt(III) complexes was interpreted in terms of a vibronic intensity scheme in comparison with the vibrational frequencies of the complexes. The deuteration shifts helped to confirm the assignments of the structure. It was found that, as well as the skeletal vibrations of the CoN$_6$ group, the NH$_3$ (and ND$_3$) rocking and the H–N–H symmetric deformation modes are effective in the vibronic intensity mechanism of the bands.

The vibrational fine structure of the $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption band of [Co(NH$_3$)$_6$]$^{3+}$ was first studied by Wentworth.[1] He observed, in his low-temperature spectroscopic work, that at least twelve members of a progression with a spacing of about 420 cm^{-1} were superimposed on the band. Since then, several reports[2] have appeared concerning the temperature dependence of the band intensity and the vibronic interaction with the odd skeletal modes of the CoN$_6$ group. Recently, we examined the transmission spectra of [Co(NH$_3$)$_6$]-[Co(CN)$_6$] at 4.2 K and resolved each progressional line into several components.[3] As a result of these transmission studies, it is thought that measurements with a higher resolution may give definite information as to the structure of the band.

It is our experience that the clarity of the fine structure observed on the $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption band of the hexaamminecobalt(III) complexes is very dependent on particular crystal lattices. In the present paper, the low-temperature crystal-absorption spectra of [Co-(NH$_3$)$_6$][Ir(CN)$_6$] and [Co(ND$_3$)$_6$][Ir(CN)$_6$] will be reported. These crystals showed the most extensive structure in our studies. The observed fine structure was interpreted on the basis of the infrared and Raman data of the complexes.

Experimental

Single-crystals of [Co(NH$_3$)$_6$][Ir(CN)$_6$] were obtained when aqueous solutions of [Co(NH$_3$)$_6$]Cl$_3$ and K$_3$[Ir(CN)$_6$] were mixed extremely slowly in a glass tube. The infrared and Raman spectra suggested that the skeletons of the complexes are retained through the procedure. Found: Co, 11.7%. Calcd for [Co(NH$_3$)$_6$][Ir(CN)$_6$]: Co, 11.6%. The deuterium-substituted compound was similarly obtained from D$_2$O solutions. The infrared and Raman bands of the hexa-amminecobalt(III) complex shifted toward the low-wave-number side (Table 1). Weissenberg photographs showed that the crystal of [Co(NH$_3$)$_6$][Ir(CN)$_6$] belongs to the trigonal crystal system, $a=7.35(2)$ Å, $\alpha=97.9(1)°$, with the space group of R3 or R$\bar{3}$. The crystals of [Co(ND$_3$)$_6$][Ir(CN)$_6$] are found to be very similar in appearance to those of [Co-(NH$_3$)$_6$][Ir(CN)$_6$] under a microscope. The low-temperature polarized absorption spectra of appropriate crystal samples were measured by the method previously reported.[3] All the spectra were taken with a spectral slit width of less than 160 μm, which corresponds to a resolution of 10 cm^{-1}. The fine structure observed on the band of [Co(ND$_3$)$_6$]$^{3+}$ was obscured after several days' exposure of the sample crystal in room air. The temperatures of an indium plate in which the samples were set with Apiezon N grease on a pinhole ($\phi=0.1$ mm) were monitored by means of a thermocouple (Au: Fe chromel). The sample dimensions were estimated by the use of a micrometer ocular. The infrared and Raman spectra were taken with a JASCO IR-F spectrometer and Narumi 750Z-1200 Raman spectrometer respectively.

Results and Discussion

Figures 1 and 2 show the crystal absorption spectra of [Co(NH$_3$)$_6$][Ir(CN)$_6$] and [Co(ND$_3$)$_6$][Ir(CN)$_6$] respectively in the $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption region of the hexaamminecobalt(III) complexes. The counter complex anion, [Ir(CN)$_6$]$^{3-}$, can be expected to show no absorption in the visible region.[4] Some structure was detected also on the $^1T_{2g}\leftarrow{}^1A_{1g}$ absorption bands in the near-ultraviolet region. However, no detailed analysis was possible because of the low resolution. The absorption spectra taken with the polarized lights whose electric vectors are parallel and perpendicular to the crystal [111] axis were observed to be almost identical in the two samples.

It was found that the $^1T_{1g}\leftarrow{}^1A_{1g}$ band of [Co(NH$_3$)$_6$]$^{3+}$ consists of the progressional members of,

TABLE 1. VIBRATIONAL FREQUENCIES OF HEXAAMMINECOBALT(III) COMPLEXES[a]

	δ_s(NH$_3$), (ND$_3$) cm^{-1}	ρ_r(HNH), (DND) cm^{-1}	ν_1(a$_{1g}$) cm^{-1}	ν_2(e$_g$) cm^{-1}	ν_3(t$_{1u}$) cm^{-1}	ν_4(t$_{1u}$) cm^{-1}	ν_6(t$_{2u}$) cm^{-1}
[Co(NH$_3$)$_6$]$^{3+}$	1329[b], 1324[b]	851[b]	480[b]	441[b]	480[b]	331[b]	252[e]
[Co(ND$_3$)$_6$]$^{3+}$	1020[c]	667[c]	452[d]		446[d]	294[c]	232[e]

a) Vibrations are denoted according to K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, John Wiley and Sons, New York (1978). b) T. V. Long, II, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, **9**, 459 (1970). c) K. H. Schmidt and A. Muller, *J. Mol. Struct.*, **22**, 343 (1974). d) Present work on [Co(ND$_3$)$_6$][Ir(CN)$_6$]. e) W.A. Yeranos, *Inorg. Chem.*, **7**, 1259 (1968).

apparently, five structure components, (na), (nb), (nc), (nd), and (nf). The average spacing of the progression was estimated to be 401 cm^{-1}. In the case of $[Co(ND_3)_6]^{3+}$, the spacing of the progression was reduced to 370 cm^{-1}, and a new component, (ne), appeared distinctly in the lower-wavenumber vicinity of the $(n+1\ d)$ components. However, the energy differences between the components of (na), (nb), (nc), and (nd) exerted no significant change on the deuteration of the ligands.

Assuming a vibronic intensity scheme, the positions of the structure components can be expressed as $^1A_{1g}(O)\rightarrow$ $^1T_{1g}(O')+\nu_i+n\nu_j$, where $\nu_i=$the frequency of the odd vibration, $\nu_j=$the frequency of the even vibration, and $n=$the integer. A large displacement of the potential surface of the electronic excited state from that of the ground state along the Q_j internal coordinate gives a long Frank-Condon progression with a spacing corresponding to that of ν_j on the band. An electronic excitation to the anti-bonding e_g orbital may relax the Co–N bonds and result in some frequency reductions in the electronic excited state.

The vibrational frequencies of the complexes studied are summarized in Table 1. The observed average spacings of 401 and 370 cm^{-1} may be correlated to the $\nu_1(a_{1g})$ vibrations of the CoN$_6$ skeletons of $[Co(NH_3)_6]^{3+}$ and $[Co(ND_3)_6]^{3+}$ respectively. However, as in the case of the $^4T_{2g}\leftarrow^4A_{2g}$ absorption band of $[Cr(NH_3)_6]^{3+}$ discussed by Wilson et al.,[5] there is,

indeed, a possibility that the $\nu_2(e_g)$ mode is involved in the progression of the bands. In general, the $\nu_1(a_{1g})$ and the $\nu_2(e_g)$ M–N stretching modes of the hexacoordinated transition metal complexes are observed to have almost the same frequencies.[6] Therefore, further spectroscopic studies are necessary for more reliable assignments of the progression observed on the bands associated with the $t_{2g}\rightarrow e_g$ electronic transition of the complexes.

It is known[6] that the frequencies of the CoN$_6$ skeletal vibrations of the hexaamminecobalt(III) complex are lowered by about 10% on the deuteration of the ligands, whereas the NH$_3$ rocking, the H–N–H deformation, and the N–H stretching frequencies are reduced by as much as 20—28% on the deuteration. If the observed intervals between the components are compared with those of the infrared frequencies shown in the table, the following assignments seem reasonable:

$(na)\ \cdots\ ^1A_{1g}(O)\ \longrightarrow\ ^1T_{1g}(O')\ +\ \nu_{lattice}\ +\ n\nu_1(\nu_2)$

$(nb)\ \cdots\ \qquad\qquad\qquad\qquad +\ \nu_6\ +\ n\nu_1(\nu_2)$

$(nc)\ \cdots\ \qquad\qquad\qquad\qquad +\ \nu_4\ +\ n\nu_1(\nu_2)$

$(nd)\ \cdots\ \qquad\qquad\qquad\qquad +\ \nu_3\ +\ n\nu_1(\nu_2)$

$(ne)\ \cdots\ \qquad\qquad\qquad\qquad +\ \nu(NH_3,\ ND_3\ rocking)$

$\qquad\qquad\qquad\qquad\qquad\qquad +\ n\nu_1(\nu_2)$

$(nf)\ \cdots\ \qquad\qquad\qquad\qquad +\ \nu(H\text{–}N\text{–}H\ sym.\ def.)$
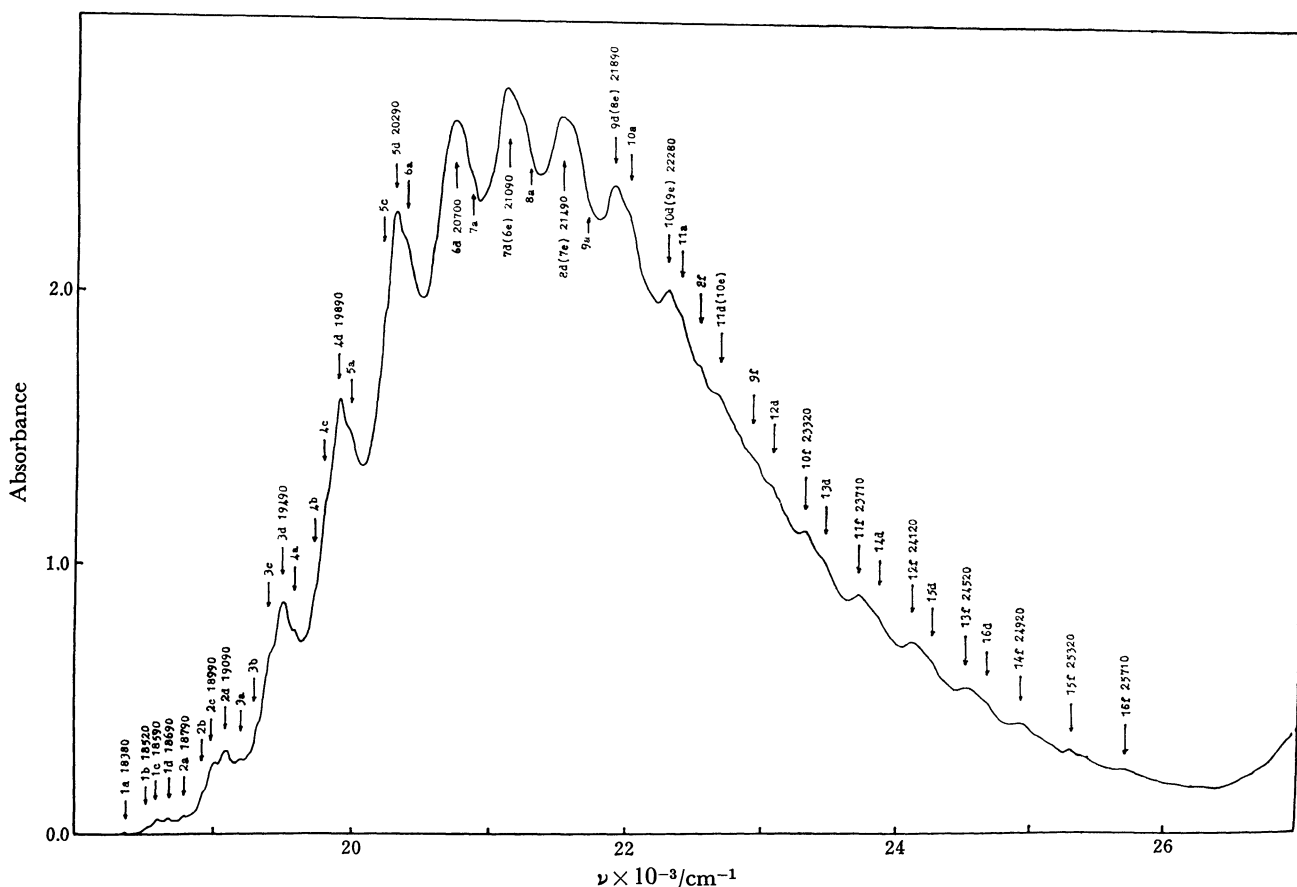
$\qquad\qquad\qquad\qquad\qquad\qquad +\ n\nu_1(\nu_2)$.

Fig. 1. Crystal absorption spectrum of $[Co(NH_3)_6][Ir(CN)_6]$ at 4.2 K with the polarized light whose electric vector parallel to the crystal [111] axis (crystal thickness is 0.14 mm).
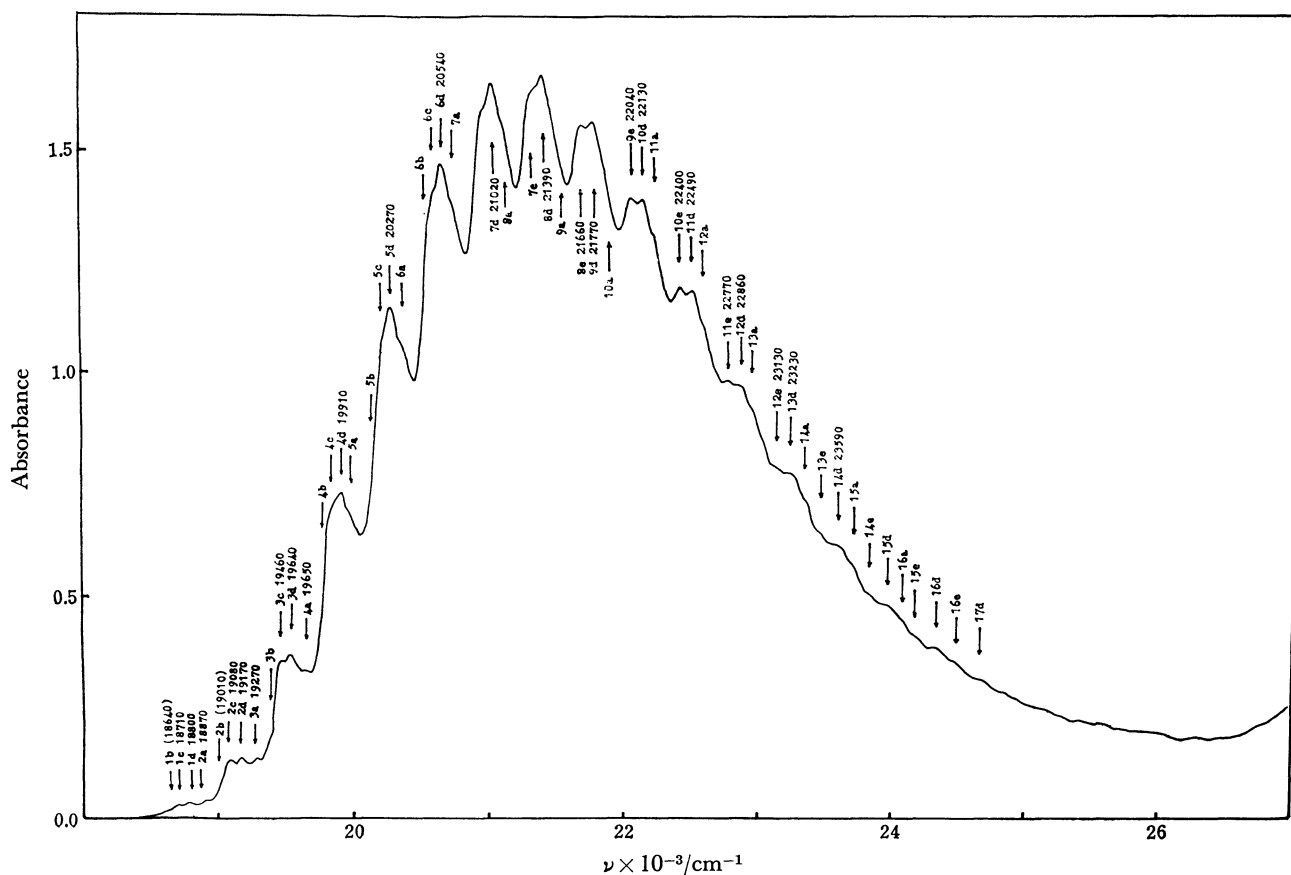
Fig. 2.   Crystal absorption spectrum of $[Co(ND_3)_6][Ir(CN)_6]$ at 4.2 K with the polarized light whose electric
vector parallel to the crystal [111] axis (crystal thickness is 0.08 mm).

The weak components, (na), were assigned to lattice vibrations of the crystals. In the case of $[Co(NH_3)_6]^{3+}$, the (ne) components are thought to be obscured due to their locations close to $(n+1\ d)$. The components of (nf) were also obscured on the band of $[Co(ND_3)_6]^{3+}$. A preliminary measurement of the $^4T_{2g}\leftarrow{}^4A_{2g}$ absorption band of $[Cr(NH_3)_6]^{3+}$ showed distinct structure components on the higher-wavenumber side of the band very similar to the (ne) and (nf) components in the present cases. As a matter of course, no structure components corresponding to (ne) and (nf) were reported in the fine structure of the $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption band of $[PtF_6]^{2-}$ studied by Patterson et al.[7] In the present measurements, the O–O' lines could not be detected even if the thickness of the samples was increased to 0.8 mm.

Flint et al.[8] have studied the structure of the $^4A_{2g}\leftarrow{}^2E_g$ emission of $[Cr(NH_3)_6]^{3+}$ and have detected the dominant vibronic components of the NH_3 rocking and the H–N–H sym. def. modes, as well as the skeletal modes of the CrN_6 group. They proposed that the spin-allowed absorption band of $^4T_{2g}\leftarrow{}^4A_{2g}$ should also involve the vibronic components attributable to the NH_3 rocking and the H–N–H sym. def. vibrations, since the mixing of the $^4T_{2g}$ state into the ^2E_g state is responsible for the intensity of the $^4A_{2g}\leftarrow{}^2E_g$ transition. The present experimental results are in line with their

suggestion also in the case of the $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption band of $[Co(NH_3)_6]^{3+}$ and $[Co(ND_3)_6]^{3+}$.

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