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Optical and ESR Spectra for High-Spin Tetrahedral Complexes of Co(III) and Co(II) in Keggin-Structure Heteropolytungstate

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The ligand-field spectra for the cobalt complexes in the single crystals of $K_3H_2[Co^{III}W_{12}O_{40}]\cdot 16H_2O$ and $K_4H_2[(Co^{II}, Zn^{II})W_{12}O_{40}]\cdot nH_2O$ have been observed at several temperatures above 1.4 K and assigned under D_2 site symmetry. In the spectrum of the elongated $Co^{III}O_4$ complex, two absorption bands of 8250 and 8953 cm^{-1} strengthen with increasing temperature by vibronic mechanism. The X-band ESR spectra of both complexes have also been measured at 77 K. The signal from the Co(III) complex is not observed. The signal of the high-spin Co(II) complex of tetrahedral symmetry is unequivocally observed even at relatively high temperature of 77 K. From the analysis of the ESR spectrum, it is concluded that the $Co^{II}O_4$ tetrahedron of D_2 symmetry is flattened and deviated slightly from axial symmetry.

The tetrahedral high-spin complexes of both Co(III) and Co(II) are known to exist in the heteropolyanions of Keggin type as $[Co^{III}W_{12}O_{40}]^{5-}$ and $[Co^{II}W_{12}O_{40}]^{6-}$, respectively. The high-spin complex of Co(III) ($3d^6$, $S=2$) is very few. Another example is found only in Co(III)-doped garnets.[1,2] The high-spin Co(II) complex ($3d^7$, $S=3/2$) is also interesting especially from the viewpoint of ESR study because ESR data of high-spin complexes are relatively few compared with those of low-spin complexes.[3–6] It would be of great interest, therefore, to study these Co(III) and Co(II) complexes by means of the optical and ESR spectra.

Concerning the low-temperature properties of these complexes, there have been some reports on the magnetic susceptibility of powder samples[7,8] and the brief report on the ESR frozen spectrum of the Co(II) complex.[9] In the previous paper,[10] we have first reported the single-crystal absorption spectra of the pure Co(III) and Co(II) complexes at 77 K.

Yanonni[11] has reported that the crystal of Co(III) complex belongs to hexagonal system ($P6_222$, $Z=3$) at room temperature and the tetrahedron of $Co^{III}O_4$ is elongated, having three pairs of oxygen–oxygen distance of 2.69, 3.20, and 3.31 Å. From these data, Simmons[7] has concluded that the symmetry of this tetrahedron is D_2 which is nearly S_4. Unfortunately, the exact orientation of the tetrahedron with respect to the crystal axes has not been shown in the reports.[11,12] The crystals of both complexes of Co(III) and Co(II) are known to be isomorphous, but the exact symmetry of the $Co^{II}O_4$ tetrahedron is unknown.

In this report, we will discuss the single-crystal optical spectra at various temperatures above 1.4 K and the ESR spectra at 77 K both of the pure Co(III) complex and of the pure and diluted Co(II) complexes in the potassium salts of the Keggin-structure heteropolyanions.

Experimental

The potassium salts were prepared and crystallized by the method in the literature.[10,13] For comparison, $(K,H)_5[Ga^{III}W_{12}O_{40}]\cdot mH_2O$[14] and $K_2\{(C_4H_9)_4N\}_4[Co^{II}W_{12}O_{40}]\cdot lCH_3CN$[15] were also crystallized from aqueous and CH_3CN solutions, respectively. Mixed crystal of Co(III) with Ga(III) could not be obtained.

For the spectroscopic measurements, a JASCO CT-100 grating spectrometer was used with a HTV-R376 photomultiplier for the visible range or with a HTV-P819 PbS detector in the near-infrared range. Photoelectric signals were amplified and converted into logarithmic scale. A Glan–Taylor prism served as a polarizer. The samples were immersed in liquid helium for measurements at 1.4 and 4.2 K. For measurements at higher temperatures, the method in the literature[16] was used. That is, the samples were placed in a glass vessel immersed in liquid helium, and cooled by exchange helium gas inserted into the vessel or heated with an electric heater on the copper sample holder. The temperatures were measured with a Ge resistor and a thermocouple of Chromel vs. Au–Fe.

X-Band ESR spectra were recorded on a JEOL-FE2XG spectrometer equipped with a liquid-nitrogen-insertion Dewar. DPPH served as a magnetic field calibrant.

Results and Discussion

Co(III) Complex. The spectra of the Co(III) complex are shown in Figs. 1—3 and listed in Table 1. The relative intensities among the Figures are not shown, but the spectra in Fig. 3 are very weak compared with those in Figs. 1 and 2, as reported in the previous paper.[10] In Fig. 1, the D-band is assigned, as described previously,[10] to the spin-forbidden transition of $^5A\rightarrow{}^3T_1$. This transition may gain intensity by mixing of the $^3T_1$ state with the nearby $^5T_2$ state. The actual intensity of the A-band is larger for $E/\!/c$ than for $E\perp c$, but the reverse of that is found for the B- and C-bands. The B- and C-bands

Table 1. Observed Energies for $K_3H_2[Co^{III}W_{12}O_{40}]\cdot 16H_2O$ (in cm^{-1})

$E\perp c$	$E//c$
Visible (1.4 K)	
17753[a] 17191	≈17600
15586	
	≈15300
14635	
	≈14200
14085	
Near-infrared (4.2 K)	
≈10000[a]	≈10000
≈9000[a]	
≈8250	8249.9
6579	6587.0
6371.0[a]	
	6361.9
(200 K)	
8953[b]	
6959[b]	

a) Shoulder. b) Unpolarized.

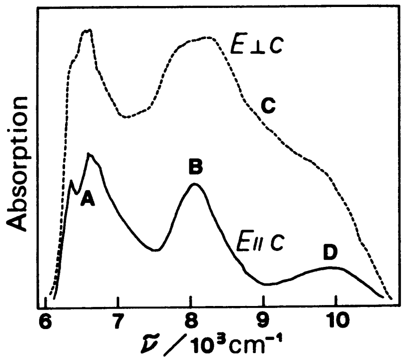

Fig. 1. Absorption spectra of the $^5E\rightarrow{}^5T_2$ transition of $K_3H_2[Co^{III}W_{12}O_{40}]\cdot 16H_2O$ at 4.2 K. E denotes the electric vector of the incident light. c denotes the crystal c-axis.

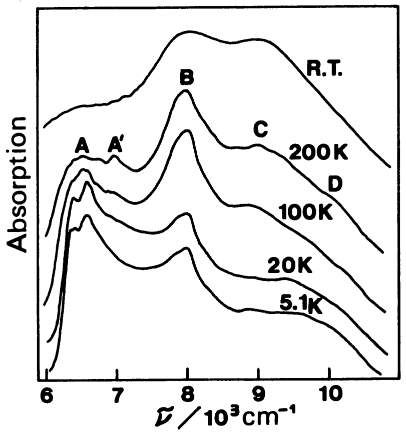

Fig. 2. Temperature dependence of the $^5E\rightarrow{}^5T_2$ transition of $K_3H_2[Co^{III}W_{12}O_{40}]\cdot 16H_2O$ (unpolarized). For comparison, the spectrum of $[Co^{III}W_{12}O_{40}]^{5-}$ in CH_3CN solution at room temperature is also shown uppermost. In aqueous solution, the spectrum is almost unchanged.

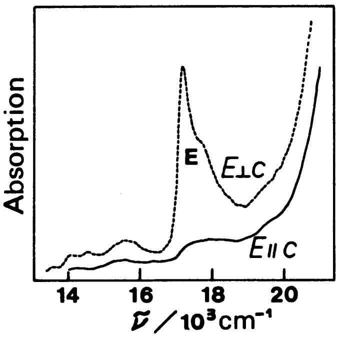

Fig. 3. Absorption spectra of the spin-forbidden transitions of $K_3H_2[Co^{III}W_{12}O_{40}]\cdot 16H_2O$ at 1.4 K. Note that the ordinate is enlarged compared with that in Fig. 1.

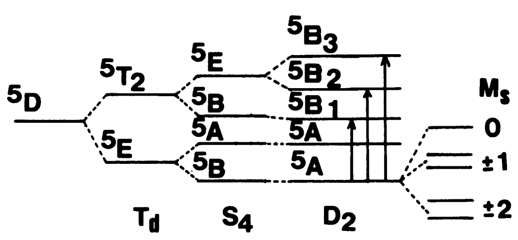

Fig. 4. Schematic energy levels of the ^5D state.

extremely strengthen with increasing temperature; the spectrum at 200 K becomes comparable to that of the complex soluted in CH_3CN (Fig. 2).

To interpret these spectra, the energy levels for Co(III) in the complex of D_2 site symmetry are considered (Fig. 4). The energy-level order in the ligand field of an elongated tetrahedron of S_4 symmetry ($^5E>{}^5B>{}^5A>{}^5B$) has been determined for yttrium iron garnet[17] and adopted for the interpretation of the spectrum of Co(III) in yttrium gallium garnet.[2] Simmons[7] has discussed the order of the magnitude for these energy levels in the ligand field of S_4 or D_2 symmetry. Defining the elongated axis of the $Co^{III}O_4$ tetrahedron as the z-axis and taking the z-axis parallel to the c-axis of the crystal, then, for electric dipole radiation, the $^5A\rightarrow{}^5B_1$ transition is expected to be allowed in z-polarization ($E//c$) and the transitions of $^5A\rightarrow{}^5B_2$ and $^5A\rightarrow{}^5B_3$ allowed in y- and in x-polarization ($E\perp c$), respectively. Moreover, considering the contribution of a internal vibration of B_1-type either to the ground state or to each excited state, then the $^5A\rightarrow{}^5B_2$ and $^5A\rightarrow{}^5B_3$ transitions are allowed vibronically also in x- and in y-polarization, respectively. Some vibrations of the $Co^{III}O_4$ tetrahedron have been reported.[18]

From these results, it seems most reasonable that the A-, B-, and C-bands are assigned as the $^5A \rightarrow {}^5B_1$, $^5A \rightarrow {}^5B_2$, and $^5A \rightarrow {}^5B_3$ transitions, respectively. The B-and C-bands may strengthen by the vibronic mechanism at higher temperatures. Note that the alternate interpretation of the $^5B_2$ and $^5B_3$ levels is possible in the present study.

The A-band is composed of the two peaks (6361.9, 6587.0 cm^{-1}) in the $E/\!/c$ spectrum. There are two possibilities of the assignment of these peaks. One is that the lower-energy peak is the zero-phonon line of the $^5A \rightarrow {}^5B_1$ transition and the higher-energy peak is the one-phonon line, and the other is that the peaks are derived from the splitting of the $^5B_1$ state by the spin-orbit interaction

The A′-band which strengthens with increasing temperature may be a phonon band associated with the A-band.

The E-band in Fig. 3 which is very weak compared with the A- and B-bands as described in the previous paper[10] is allowed in the $E \perp c$ spectrum. The spectra at 4.2 K are almost the same as those at 1.4 K (not shown). This band has been assigned to the transitions to the $^3A_2$, $^3A_1$, and ^1E states only on the basis of the energy-level fitting in T_d symmetry.[10] However, the intensities of the spin-forbidden transitions to the $^3T_1$ and $^3T_2$ states will be larger than those to the $^3A_2$, $^3A_1$, and ^1E states because of the strong spin-orbit interaction between the $^5T_2$ state and the $^3T_1$ and $^3T_2$ states. Moreover, the positions of the $^3T_1$ and $^3T_2$ states can not be determined only from the energy-level fitting in T_d symmetry because of the splitting of these states in D_2 symmetry as observed in the $^5T_2$ state. Therefore, the E-band seems to be ascribed to the splitting components of the higher excited levels of $^3T_1$ and $^3T_2$ in T_d symmetry.

From the results described above, it is concluded that the spectra of the Co(III) complex are explained in the ligand field of the elongated tetrahedron of D_2 symmetry.

ESR signal from Co(III) is not observed at 77 K. The preliminary measurement at 5.5 K shows also no signal. Sturge et al.[2] have suggested that the ^5B ground state in S_4 symmetry would have the $M_s = \pm 2$ states the lowest. This holds also in D_2 symmetry (Fig. 4). In the Co(III)-doped garnets, Sturge et al.[2] have observed the forbidden transition of $\Delta M_s = 4$ between the two states of $M_s = \pm 2$ using 24 GHz (K-band) and 56 GHz frequencies, but Chiba et al.[4] have not observed using ≈9.5 GHz (X-band). Therefore, the possible explanation for no signal observed from Co(III) in the present study is that the energy separation between the two states of $M_s = \pm 2$ is too large for X-band frequencies.

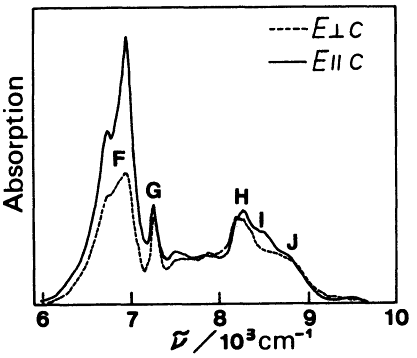

Fig. 5. Absorption spectra of the $^4A_2 \rightarrow {}^4T_1(F)$ transition of $K_4H_2[(Co^{II}, Zn^{II})W_{12}O_{40}] \cdot nH_2O$ at 4.2 K.

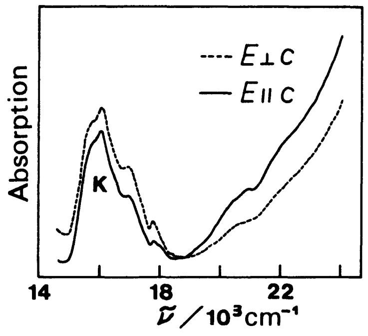

Fig. 6. Absorption spectra of the $^4A_2 \rightarrow {}^4T_1(P)$ transition of $K_4H_2[(Co^{II}, Zn^{II})W_{12}O_{40}] \cdot nH_2O$ at 1.4 K. Note that the ordinate is shortened compared with that in Fig. 5.

Co(II) Complex. The spectra are shown in Figs. 5 and 6 and listed in Table 2. The ESR spectra are shown in Fig. 7. The F-band in Fig. 5 is attributed to the vibrational band of the water of crystallization, because the corresponding band is also observed for $(K,H)_5[Ga^{III}W_{12}O_{40}] \cdot mH_2O$ but not observed for $K_2\{(C_4H_9)_4N\}_4[Co^{II}W_{12}O_{40}] \cdot lCH_3CN$.

As is found in Figs. 5 and 6, the crystal of Co(II) diluted with Zn(II) shows hardly any poralization anisotropy. Its ESR spectrum shows nonaxial symmetry with three effective g-values (**a** in Fig 7). The angular dependence is hardly found for $H/\!/c$ or for $H \perp c$ (not shown). That is, ESR spectrum similar to **a** in Fig. 7 is always observed independent of the direction of magnetic field. Contrary to the mixed crystal, the significant angular dependence is observed in the preliminary ESR measurement for the single crystal of pure Co(II) complex. From these observations, the $Co^{II}O_4$ tetrahedron may have nonaxial symmetry and oriented fairly irregurally in the crystals doped with Zn(II).

By assuming D_2 symmetry as nonaxial symmetry of the $Co^{II}O_4$ tetrahedron, the splitting of energy levels could be shown in Fig. 8. On the basis of these energy

Table 2. Observed Energies for $K_4H_2[(Co^{II}, Zn^{II})W_{12}O_{40}]\cdot nH_2O$ (in cm^{-1})

	$E\perp c$	$E/\!/c$
Visible (1.4 K)		
	22276	22222
		21692
	21645	
		20846
	20530	
		20358
	19720	
	19209[a]	
	18447	
	18278[a]	
		18041[a]
	17771	17784
	17473[a]	
	17229[a]	
	16938	16900
	16041	16021
	15788	15765[a]
	15596[a]	15535[a]
	15373[a]	15363[a]
	15216[a]	15207[a]
Near-infrared (4.2 K)		
	8809.8	8802.8
	8597.7	
		8503.4
	8280.9	8280.2
	8165.9	8165.3[a]
	7258.5	7250.6

a) Shoulder.

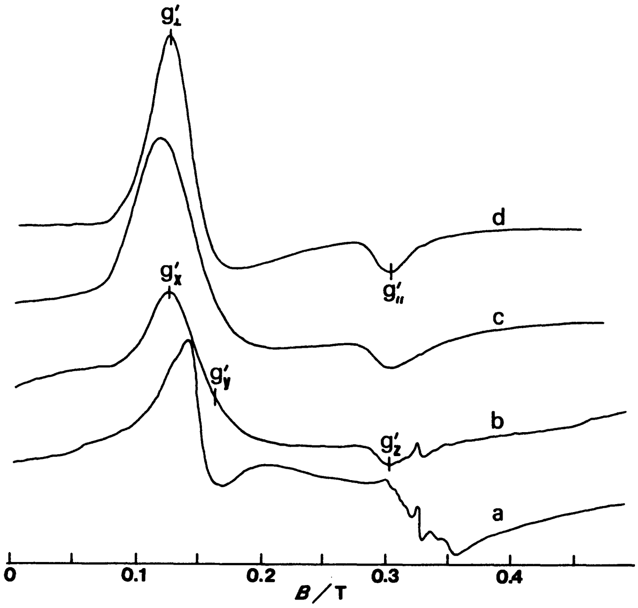

Fig. 7. ESR spectra of Co(II) complexes at 77 K. a: $K_4H_2[(Co^{II},Zn^{II})W_{12}O_{40}]\cdot nH_2O$ (single crystal), b: powder pattern of a, c: $K_4H_2[Co^{II}W_{12}O_{40}]\cdot 17H_2O$ (powder), d: $K_2\{(C_4H_9)_4N\}_4[Co^{II}W_{12}O_{40}]\cdot lCH_3CN$ (powder).

levels, the absorption bands in the $^4A_2\rightarrow{}^4T_1(F)$ region shown in Fig. 5 may be assigned to the transitions all of which are allowed for electric dipole radiation as follows: The G-band is due to the $^4B_1\rightarrow{}^4A$ transition, and the H-band is assigned to the lower branch splitted from the ^4E state in S_4 symmetry ($^4B_2$ or $^4B_3$) and the I- or J-shoulder to the upper branch ($^4B_2$ or $^4B_3$).

In Fig. 6, the spectral shape of the K-band which is mainly due to the $^4A_2\rightarrow{}^4T_1(P)$ transition is very similar to that of the solution spectrum.[10] In this visible region there may be many spin-forbidden transitions which gain intensity by interaction with spin-allowed bands, therefore, it is not possible to discuss the details of the K-band in the present study.

The ESR spectrum of the Zn-doped complex, $K_4H_2[(Co^{II},Zn^{II})W_{12}O_{40}]\cdot nH_2O$, shows a nonaxial pattern with $g'_x=5.20$, $g'_y=4.02$, and $g'_z=2.15$ (**b** in Fig. 7). On the other hand, the tetrabutylammonium salt of the pure Co(II) complex, $K_2\{(C_4H_9)_4N\}_4[Co^{II}W_{12}O_{40}]\cdot lCH_3CN$, shows an axial pattern with $g'_\perp=5.09$ and $g'_{/\!/}=2.17$ (**d** in Fig 7). Similar spectrum with $g'_\perp=5.02$ and $g'_{/\!/}=2.14$ is observed in the preliminary experiment at 5.5 K (not shown). It is interesting that the ESR spectrum of the high-spin Co(II) complex is unequivocally observed even at relatively high temperature of 77 K. It seems that the spin-lattice relaxation time of Co(II) in this complex is rather long. The powder pattern of the pure Co(II) complex in $K_4H_2[Co^{II}W_{12}O_{40}]\cdot 17H_2O$ crystallized from aqueous solution is intermediate between **b** and **d** (**c** in Fig. 7).

In the same manner as the halo complexes,[3,5] the resonances in Fig. 7 can be assigned as the transition between the lowest $M_s=\pm 1/2$ states (Fig. 8). By the method of Drulis et al.[5] using the g'_x, g'_y, and g'_z values observed, the parameters can be calculated in the spin Hamiltonian, $H=D\{S_z^2-1/3S(S+1)\}+E(S_x^2-S_y^2)+\beta(g_xS_xH_x+g_yS_yH_y+g_zS_zH_z)$, for the Zn-doped Co(II) complex (**b** in Fig. 7). On the assumption of $g_x=g_y=g_\perp$ and $g_z=g_{/\!/}$, the parameters can be estimatd as follows: $g_\perp=2.32$, $g_{/\!/}=2.20$, and $E/D=0.0858$. Similar result is obtained from the equations of Fukui et al.[6]

From the facts that $g_\perp$ is larger than $g_{/\!/}$ and that the $M_s=\pm 1/2$ states may be the lowest, the $Co^{II}O_4$

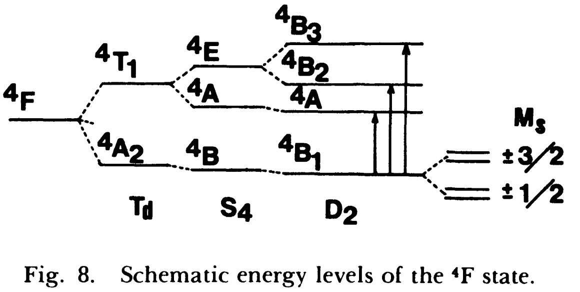

Fig. 8. Schematic energy levels of the ^4F state.

tetrahedron may be flattened.[5,19] This is in contrast with the $Co^{III}O_4$ tetrahedron described above. The nonaxiality parameter (E/D) of 0.0858 is one of the smallest among the reported values.[5,6] Therefore, the $Co^{II}O_4$ tetrahedron in the Zn-doped complex may be only slightly deviated from axial symmetry.

The $g_\perp$ and $g_{/\!/}$ values give g_{eff}=2.28 and μ_{eff}=4.41. Simmons[7] has obtained the values of g_{eff}=2.20 and μ_{eff}=4.27—4.28 from the magnetic susceptibility.

From the equation of $g_{eff}=2.001-(8\lambda)/10D_q$, where D_q=460 cm^{-1},[10] the spin-orbit coupling constant λ is estimated to be −160 cm^{-1}. The fact that the $|\lambda|$ value is smaller than the free-ion value of 178cm^{-1} is consistent with the result that the Racah parameter B of 650cm^{-1} for the Co(II) complex[10] is smaller than the free-ion value B_0 of 971cm^{-1}. Considering the magnitude of $|\lambda|$, there is also possibility that the absorption bands ranging from the H-band to the J-shouder in Fig. 5 are accounted for the spin-orbit splitting of the ^4E state in nearly S_4 symmetry.

For comparison, the values of $g_\perp$=2.55, $g_{/\!/}$=2.17, g_{eff}=2.43, and μ_{eff}=4.71 are obtained for $K_2\{(C_4H_9)_4N\}_4[Co^{II}W_{12}O_{40}]\cdot lCH_3CN$ (**d** in Fig. 7).

Comparison between Co(III) and Co(II) Complexes. By lowering of symmetry from T_d to S_4, the $^5T_2$ state for Co(III) complex and the $^4T_1(F)$ state for Co(II) complex are estimated to split by ≈2100 and ≈1300cm^{-1}, respectively.[20] This larger splitting for Co(III) complex may be due to the Jahn-Teller effect in the ^5E ground state or in the $^5T_2$ excited state. As described above, the $Co^{III}O_4$ tetrahedron is elongated and shows D_2 symmetry, but the $Co^{II}O_4$ tetrahedron is probably flattened and shows D_2 symmetry which is nearly S_4.

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References

1) D. L. Wood and J. P. Remeika, *J. Chem. Phys.*, **46**, 3595 (1967).

2) M. D. Sturge, F. R. Merritt, J. C. Hensel, and J. P. Remeika, *Phys. Rev.*, **180**, 402 (1969).

3) A. Bencini, C. Benelli, D. Gatteschi, and C. Zanchini, *Inorg. Chem.*, **18**, 2137 (1979).

4) Y. Chiba, T. Yoshida, and M. Date, *J. Phys. Soc. Jpn.*, **50**, 3925 (1981).

5) H. Drulis, K. Dyrek, K. P. Hoffmann, S. K. Hoffmann, and A. Weselucha-Birczyńska, *Inorg. Chem.*, **24**, 4009 (1985).

6) K. Fukui, H. Ohya, N. Hirota, H. Ogoshi, and K. Aoyagi, 25th ESR Conference of Japan, Sapporo, December 1986, Abstr. No. 15A04.

7) V. E. Simmons, Ph. D. Thesis, Boston University, 1963.

8) L. C. W. Baker, V. E. S. Baker, S. H. Wasfi, G. A. Candela, and S. H. Kahn, *J. Chem. Phys.*, **56**, 4917 (1972).

9) G. M Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970).

10) K. Kojima and J. Matsuda, *Bull. Chem. Soc. Jpn.*, **58**, 821 (1985).

11) N. F. Yanonni, Ph. D. Thesis, Boston University, 1961.

12) H. So and M. T. Pope, *J. Chem. Phys.*, **55**, 2786 (1971).

13) L. C. W. Baker and T. P McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956).

14) O. W. Rollins, *Inorg. Chem.*, **11**, 3114 (1972).

15) K. Nomiya, M. Miwa, R Kobayashi, and M. Aiso, *Bull. Chem. Soc. Jpn.*, **54**, 2983 (1981).

16) N. Kojima, T. Ban, and I. Tsujikawa, *J. Phys. Soc. Jpn.*, **44**, 919 (1978); N. Kojima, Doctor Thesis, Kyoto University, 1978.

17) R. Pappalardo, *Nuovo Cimento*, **26**, 748 (1962).

18) K. Nomiya, R. Kobayashi, and M. Miwa, *Bull. Chem Soc. Jpn.*, **56**, 2272 (1983).

19) W. D. Horrocks, Jr. and D. A. Burlone, *J. Am. Chem. Soc.*, **98**, 6512 (1976).

20) The value of ≈2100 cm^{-1} is the energy separation between the A-band and the center of the B- and C-bands (Fig. 1), and the value of ≈1300 cm^{-1} is that between the G-band and the center of the H-, I-, and J-bands (Fig. 5).