Absorption Spectra of Tetrahedral Co(III) and Co(II) Complexes in Heteropolytungstates

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The absorption spectra of Co(III) and Co(II) in the single crystals of the Keggin-structure compounds, $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ and $K_6[Co^{II}W_{12}O_{40}]\cdot mH_2O$, have been measured at 77 K. The spectra of these complexes in aqueous solutions have also been observed. All the spectra have been interpreted using crystal-field theory by assuming that a Co(III) or Co(II) ion is in T_d symmetry. The parameters, D_q, B, and C/B can be evaluated as 780 cm^{-1}, 630 cm^{-1}, and 4.7 respectively for the Co(III) complex, and 460 cm^{-1}, 650 cm^{-1}, and 4.5 respectively for the Co(II) complex.

A few reports have been published on the absorption spectra of high-spin Co(III) complexes in the tetrahedral ligand fields; Co(III) both in garnets[1] and in xNa_2O–SiO_2 glasses ($x \geq 1.5$),[2] and 12-tungstocobaltate(III) $[Co^{III}W_{12}O_{40}]^{5-}$.[3-5] Only the solution spectra have been measured for the last complex.

We report the absorption spectra of $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ in single crystals at 77 K as well as in aqueous solution at room temperature. These spectra are interpreted on the basis of the crystal-field theory.

On the other hand, 12-tungstocobaltate(II) $[Co^{II}W_{12}O_{40}]^{6-}$ contains Co(II) complex with tetrahedral arrangement of oxygen atoms and the spectra of this anion have been reported only in solutions.[3,4,6,7]

The absorption spectra of $K_6[Co^{II}W_{12}O_{40}]\cdot mH_2O$ in single crystals as well as in aqueous solution are also discussed.

Experimental

$K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ and $K_6[Co^{II}W_{12}O_{40}]\cdot mH_2O$ were prepared by the method in the literature.[8] Single crystals of both compounds were grown by slow evaporation of each aqueous solution. The shapes of crystals are hexagonal prisms. Co(III) complex prisms (light yellow) tend to grow more elongate along the hexagonal principal axis than Co(II) complex prisms (emerald green). Co(III) complex prisms are easy to break by polishing. X-Ray powder diffraction data for Co(III) compounds agree with Yanonni's data.[9]

Single-crystal spectra were measured at 77 K using a Shimadzu model MPS-50L spectrophotometer equipped with simple glass Dewars. A Nalumi RM-21 type grating monochromater with a Hamamatsu R-376 photomultiplier was also used to measure the strong band for the Co(II) complex in the visible region. Polished specimens of 0.30—0.70 mm thickness were immersed in liquid nitrogen. Filters of POLAROID HN-42T (visible region) and HR-INFRARED (near-infrared region) were used to measure preliminary polarized spectra. Spectra of aqueous solutions of 3.50×10^{-5} mol dm^{-3} were recorded both on a Hitachi 340 spectrophotometer (ultraviolet to near-infrared region) and on a Shimadzu UV-260 spectrophotometer (ultraviolet region) using 1-cm optical length quartz cells.

Energy matrices including the electrostatic[10] and crystal-field contributions were diagonalized using a HITAC M-160H computer.

Results and Discussion

Spectra of Co(III) and Co(II) Complexes in Aqueous Solutions. The absorption spectra of $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ and $K_6[Co^{II}W_{12}O_{40}]\cdot mH_2O$ in aqueous solutions agree well with the previous data,[3-7] except that very strong bands around 50000 cm^{-1} and shoulders around 45450 cm^{-1} are observed (Fig. 1 and Tables 1 and 2). These bands and shoulders are probably attributed to the transitions within $W_{12}O_{40}$ skeletons, because a similar band and shoulder are observed in the spectrum of aqueous solution of sodium metatungstate $Na_6[H_2W_{12}O_{40}]\cdot 29H_2O$ prepared by the method of Ref. 11 which has the Keggin-structure isopolyanion $[H_2W_{12}O_{40}]^{6-}$. The band for the Co(III) complex is shifted to lower wavenumbers than that of the Co(II) complex, likewise a 38000-cm^{-1} band in Fig. 1 due to the transition within the same skeleton.[3-5,7] It is interesting that these transition energies are

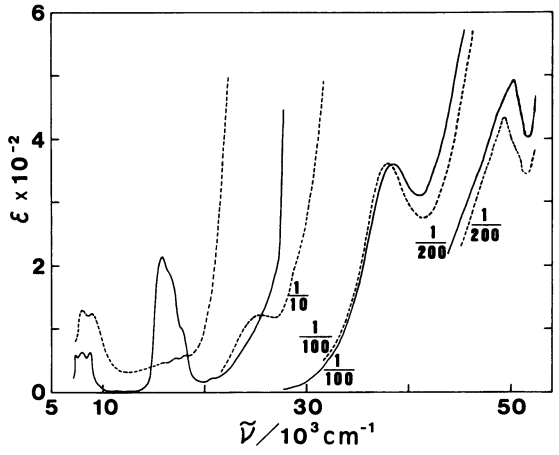

Fig. 1. Aqueous solution spectra of $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ (----) and $K_6[Co^{II}W_{12}O_{40}]\cdot mH_2O$ (——). Fractional numbers show reduced scale for ε.

Table 1. Observed and calculated[a] transition energies for $[Co^{III}W_{12}O_{40}]^{5-}$ (in 10^{-3} cm^{-1})

Observed		Calculated[b]
Solution	Single crystal[c]	
49.50		CT[e]
45.45[d]		CT[e]
38.03		CT[e]
	27.28	CT[f] [27.18[h] 26.90[i] 26.76[h] 26.34[j] 24.11[k] 23.53[l] 23.07[h] 22.74[m] 22.45[n] 22.01[l] 21.54[o] 19.79[l]][g]
25.15		
	24.10	
	22.41	
	19.50	
	17.86[d]	17.54[p] 17.51[q]
17.12	17.21	17.38[j]
15.38		16.80[m] 16.29[h]
	15.27	15.79[l]
	14.18	14.91[i]
	10.80[d]	
9.15		9.07[l]
8.11		7.80[r]
	7.76	
	6.51	
	5.48	
	5.08	Vib[s]
	4.40	

a) Calculated higher energy levels are omitted. b) Calculation has been carried out with the parameters $D_q=780$ cm^{-1}, $B=630$ cm^{-1}, and $C/B=4.7$. c) Unpolarized spectrum. d) Shoulder. e) Charge-transfer transition within $W_{12}O_{40}$ skeleton. f) Charge-transfer transition between a ligand oxygen atom and a central Co(III) ion. g) These transitions are probably masked. h) $^5E\rightarrow{}^3T_2$. i) $\rightarrow{}^3E$. j) $\rightarrow{}^1E$. k) $\rightarrow{}^1T_1$. l) $\rightarrow{}^3T_1$. m) $\rightarrow{}^1T_2$ n) $\rightarrow{}^1A_2$. o) $\rightarrow{}^1A_1$. p) $\rightarrow{}^3A_2$. q) $\rightarrow{}^3A_1$. r) $\rightarrow{}^5T_2$. s) Vibrational peaks due to water.

Table 2. Observed and calculated[a] transition energies for $[Co^{II}W_{12}O_{40}]^{6-}$ (in 10^{-3} cm^{-1})

Observed		Calculated[b]
Solution	Single crystal[c]	
50.40		CT[e]
45.45[d]		CT[e]
38.31		CT[e]
25.91[d]	26.46	CT[f] [26.52[l] 28.98[h] 23.57[j] 21.22[k] 22.89[k]][g]
	25.84	
20.33	20.41	19.99[j]
	19.46	18.48[k]
17.79		18.07[j]
	17.39	
16.84[d]	16.81	16.51[j]
16.05	16.18	15.98[l]
15.34[d]	15.70	15.73[m]
	15.22	
		13.49[k]
	12.71	12.96[l]
8.76	8.58[d]	
8.10	7.97	7.83[n]
7.25	7.24	
	5.56	
	5.16	Vib[p] 4.60[g,o]
	4.27	

a) Calculated higher energy levels are omitted. b) Calculation has been carried out with the parameters $D_q=460$ cm^{-1}, $B=650$ cm^{-1}, and $C/B=4.5$. c) Unpolarized spectrum. d) Shoulder. e) Charge-transfer transition within $W_{12}O_{40}$ skeleton. f) Charge-transfer transition between a ligand oxygen atom and a central Co(II) ion. g) These transitions are probably masked. h) $^4A_2\rightarrow{}^2A_2$. i) $\rightarrow{}^2E$. j) $\rightarrow{}^2T_2$. k) $\rightarrow{}^2T_1$. l) $\rightarrow{}^2A_1$. m) $\rightarrow{}^4T_1(^4P)$. n) $\rightarrow{}^4T_1(^4F)$. o) $\rightarrow{}^4T_2(^4F)$. p) Vibrational peaks due to water.

affected by the oxidation state of cobalt ion in spite of the transitions within $W_{12}O_{40}$ skeletons.[5] Weak absorptions at 17120 cm^{-1} and 15380 cm^{-1} for the Co(III) complex are due to spin-forbidden d-d transitions and become well resolved in the single-crystal spectra described below.

Spectra of $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ in Single Crystals.[12] On the assumption that CoO_4 has T_d symmetry (it is known to be distorted[9]), the calculation of transition energies shown in Fig. 2 and Table 1 has been carried out in terms of the following estimations: (1) A band in the near-infrared region is assigned to the $^5E\rightarrow{}^5T_2$ transition, which determines the D_q value directly. (2) C/B is fitted in the vicinity of the value of 4.8.[10,15,16] (3) B is fitted in order to explain the spectra in the 13000—20000 cm^{-1} region(Figs. 2 and 3). From (1), (2), and (3), we evaluate the parameters D_q, B, and C/B as 780 cm^{-1}, 630 cm^{-1}, and 4.7 respectively. Simmons[4] has estimated the values of D_q and B as about 800 cm^{-1} and about 600 cm^{-1} respectively. Wood and Remeika[1] have reported the D_q values of 710 cm^{-1} (calculated) and 830 cm^{-1} (observed). The B value of 630 cm^{-1} is rather small compared with the value of

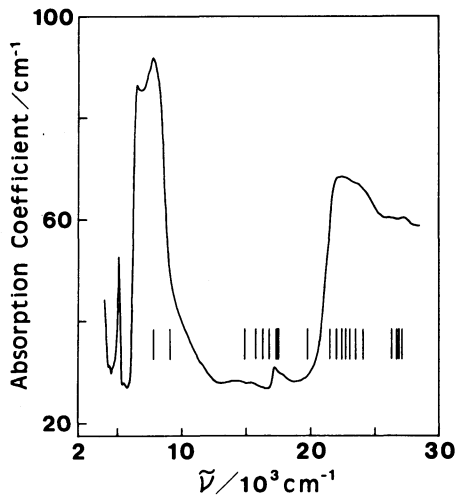

Fig. 2. Single-crystal spectrum of $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ at 77 K together with the calculated energy level positions (vertical lines). Details are shown in Table 1.

1053 cm^{-1} for the free Co(III) ion, which indicates the presence of a strong nephelauxetic effect. With this B

value, the bands in the visible region seem to be assigned fairly well (Fig. 2). A relatively intense band near 17500 cm^{-1} may be due to the $^5E \rightarrow {}^3A_2, \rightarrow {}^3A_1$, and $\rightarrow {}^1E$ transitions. In Fig. 3, anisotropy is observed in the 17500-, 15270-, and 14180-cm^{-1} band.

The $^5E \rightarrow {}^5T_2$ band in the solution spectrum apparently shifts to blue by about 1500 cm^{-1} compared with that of the single-crystal spectrum. It is not clear whether two peaks of this band in the former correspond directly to two peaks of the similar band in the latter, unless the single-crystal spectra are measured at higher temperatures.

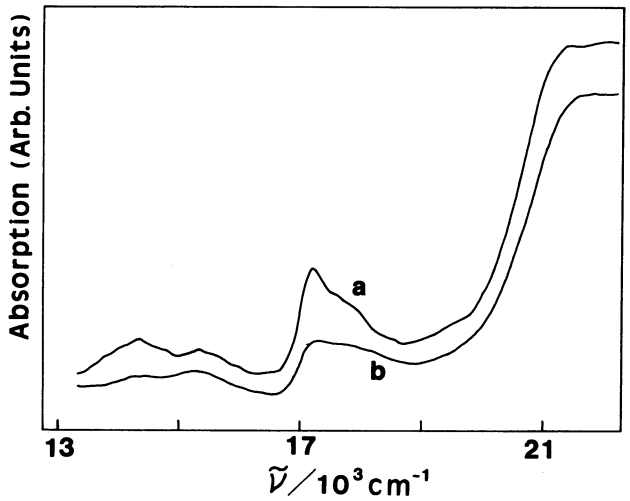

Fig. 3. Polarized single-crystal spectra of $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ in the visible region at 77 K. Electric vector $\boldsymbol{E}$ is perpendicular (a) and parallel (b) to the hexagonal principal axis.

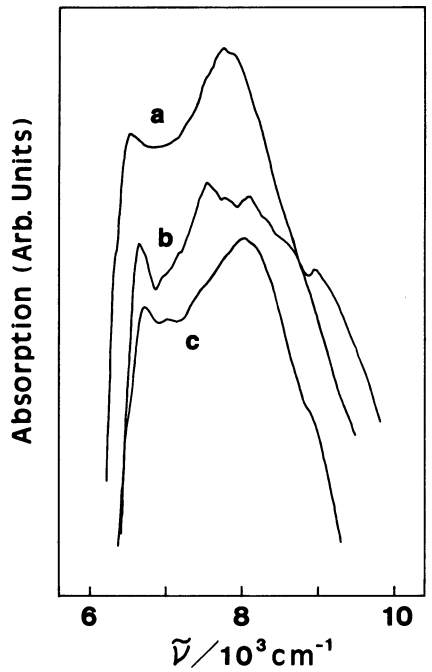

Fig. 4. Polarized single-crystal spectra of $K_5[Co^{III}W_{12}O_{40}]\cdot nH_2O$ in the $^5E \rightarrow {}^5T_2$ transition region at 77 K. The curve a is unpolarized and $\boldsymbol{E}$ is perpendicular (b) and parallel (c) to the hexagonal principal axis. The curves b and c have been shifted expediently upwards along the ordinate.

In the polarized spectra of Fig. 4, four to five peaks are observed and show anisotropy. It is of interest that the spectrum with $\boldsymbol{E}$ parallel to the hexagonal principal axis is similar to the unpolarized spectrum, unlike the $^4A_2 \rightarrow {}^4T_1$ (^4F) band for the Co(II) complex described below. Unfortunately, it is not possible to discuss the details of the reason for the splitting of this band, though the contribution of the distortion probably due to the Jahn-Teller effect[4] may be greater than that of the spin-orbit coupling. If it is possible to find out the reason for this splitting, both the D_q value and the energy of the $^5E \rightarrow {}^3T_1$ spin-forbidden transition expected to be at 9070 cm^{-1} will be confirmed.

A band around 23000 cm^{-1} in Fig. 2 is rather resolved and considerably lower both in intensity and in energy than a corresponding 25510-cm^{-1} band in the solution spectrum. These findings are of interest, though as to the intensity of the 23000-cm^{-1} band there remains some uncertainty arising from the fact that the samples are too fragile to be polished down thin specimens enough for optical measurement. Simmons[4] has proposed that this band may be due to a charge-transfer transition from a ligand oxygen atom to a central Co(III) ion, together with possibilities of other interpretations. On the other hand, the band has been assigned to a reciprocal charge-transfer transition by Dietzel and Coenen.[2] Although a number of spin-forbidden transitions are expected near this band, a charge-transfer transition between a ligand oxygen atom and a central Co(III) ion perhaps contributes mainly to this band.

Three bands at 5480 cm^{-1}, 5080 cm^{-1}, and 4400 cm^{-1} are attributed to the vibrational bands of water by referring to the previous data.[17-20]

Spectra of $K_6[Co^{II}W_{12}O_{40}]\cdot mH_2O$ in Single Crystals.[12] The transition energies calculated with the parameters D_q, B, and C/B of which values are 460 cm^{-1}, 650 cm^{-1}, and 4.5 respectively, explain the observed spectra fairly well (Fig. 5 and Table 2). The D_q value of 460 cm^{-1} is relatively large in comparison with other Co(II) tetrahedral complexes, but it agrees with that of Co(II) in yttrium gallium garnet[1] and is comparable with that of $Co(NCS)_4^{2-}$.[3,21] or $Co(NO_3)_4^{2-}$.[22] Simmons[4] has estimated the D_q and B values as 484 cm^{-1} and 672 cm^{-1} respectively. Nomiya *et al.*[7] has determined it to be 410 cm^{-1}. Likewise for the Co(III) complex, the B value of 650 cm^{-1} is rather small compared with the value of 971 cm^{-1} for the free Co(II) ion. The C/B value of 4.5 is typical for Co(II) tetrahedral complexes.

The $^4A_2 \rightarrow {}^4T_2$ transition is expected to be at 4600 cm^{-1}, but is not observed because of its low intensity[23] and of masking effect by the vibrational bands

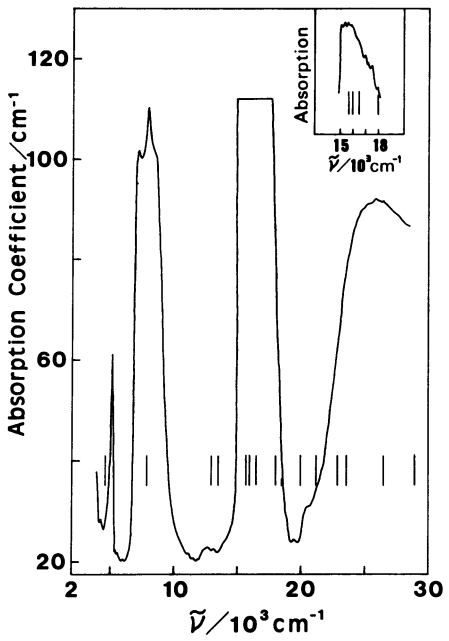

Fig. 5. Single-crystal spectrum of $K_6[Co^{III}W_{12}O_{40}]\cdot mH_2O$ at 77 K together with the calculated energy level positions (vertical lines). Details are shown in Table 2. The inset is the spectrum measured using the grating monochromater.

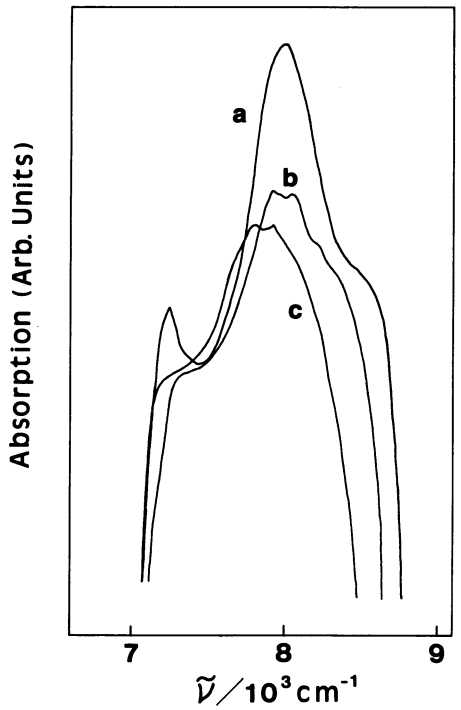

Fig. 6. Polarized single-crystal spectra of $K_6[Co^{II}W_{12}O_{40}]\cdot mH_2O$ in the $^4A_2\rightarrow{}^4T_1(^4F)$ transition region at 77 K. The curve a is unpolarized and $\boldsymbol{E}$ is perpendicular (b) and parallel (c) to the hexagonal principal axis. The curves b and c have been shifted expediently upwards along the ordinate.

due to water at 5560 cm^{-1}, 5160 cm^{-1}, and 4270 cm^{-1}.

The $^4A_2\rightarrow{}^4T_1(^4F)$ band splits into three to four peaks which show slight anisotropy (Figs. 5 and 6 and Table 2). The magnitude of the splitting by about 1340 cm^{-1} is predominantly due to the spin-orbit coupling in the excited state. The first-order value for this splitting is given by 6λ. Therefore, $|\lambda|$ is 223 cm^{-1} for this complex, the value of which is even larger than the free ion value of 178 cm^{-1}.[4,23] When the B value is decreased from the free ion value, $|\lambda|$ is also expected to be decreased. The reason for the above contradiction is probably that $|\lambda|$ is overestimated since it is evaluated primarily on the assumption that the splitting of the $^4T_1(^4F)$ band is entirely due to the spin-orbit coupling.

The $^4A_2\rightarrow{}^4T_1(^4P)$ band is too strong to be fully resolved.

A 26000-cm^{-1} band which perhaps corresponds to a 25910-cm^{-1} shoulder in the solution spectrum may be attributed to a charge-transfer transition between a ligand oxygen atom and a central Co(II) ion. This band is observed in higher wavenumbers than that of the Co(III) complex described above. The similar bands have been reported for the spectra of Co(II) in yttrium gallium garnet (26316 cm^{-1})[24] and of Ni(II) both in yttrium gallium garnet (23255 cm^{-1}) and in ZnO (22935 cm^{-1}).[25]

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