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Luminescence and Circularly Polarized Luminescence of Mononuclear and Binuclear Chromium(III) L-Alaninato Complexes

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Luminescence and circularly polarized luminescence (CPL) spectra were investigated at low temperatures in order to clarify the chiroptical and electronic structures of monomeric and dimeric chromium(III) alaninato complexes. In the monomeric complexes, [Cr(L-(or D-)ala)$_3$]$\cdot$H$_2$O, R$_1$ and R$_2$ lines of opposite spectral signs were found in the CPL spectra. The signs and relative intensities of the peaks were found to be comparable with circular dichroism (CD) spectra by employing theoretical arguments based on a strong crystal field theory. In the case of hydroxo-bridged dimeric complexes, [Cr$_2$(OH)$_2$(L-(or D-)ala)$_4$]$\cdot$3H$_2$O, although the luminescence spectra of exchange-coupled pair states were clearly observed with a deduction of reasonable exchange interaction parameters, the CPL spectral components were not discernible because of the *meso*-type structure.

The luminescence properties of a large number of chromium(III) complexes have been thoroughly investigated over several decades.1) A series of chromium complexes having amino acid ligands was carefully synthesized and the crystallographical as well as electronic structural data of the complexes were accumulated.2) We have synthesized various series of monomeric and dimeric chromium amino acid complexes, and have found that they show a wide variety of luminescence spectra, although the energy and the intensity of the spin-allowed transitions are quite similar.3)

We have been studying the chiroptical properties of chromium(III) complexes by using circularly polarized luminescence (CPL) spectroscopy.4) Recently, we have reported that complexes with L-(or D-)alaninato (ala) ligands showed very sharp and split-line spectra, from which much interesting chiroptical information can be obtained. In this paper we precisely describe the luminescence properties of some chromium alaninato complexes: namely, monomeric Λ-*fac*-[Cr(L-ala)$_3$],5) and dimeric [Cr$_2$(OH)$_2$(L-ala)$_4$],6) whose structures are shown in Fig. 1. The complexes of the enantiomer containing D-ala ligands were also used to confirm the results. Powdery samples of the chromium(III) complexes showed reproducible luminescence and CPL spectra at low temperatures. We would represent clearly resolved R$_1$ and R$_2$ lines of opposite signs for the circularly polarized luminescence (CPL) of the [Cr(L- (and D-) ala)$_3$]$\cdot$H$_2$O complex. A conventional crystal field theory regarding chirality is employed in order to explain some experimental foundations in the CPL spectra of the monomeric chromium(III) complexes. Then, fine structures due to exchange-coupled chromium pair are examined in the luminescence spectra of the binuclear complex.

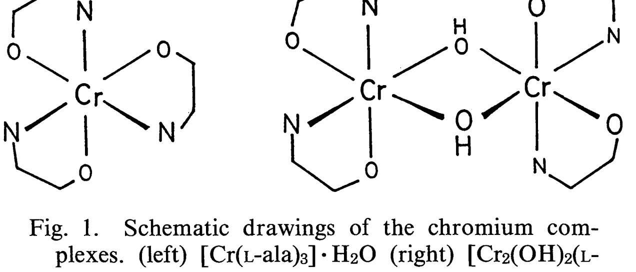

Fig. 1. Schematic drawings of the chromium complexes. (left) [Cr(L-ala)$_3$]$\cdot$H$_2$O (right) [Cr$_2$(OH)$_2$(L-ala)$_4$]$\cdot$3H$_2$O.

Experimental

Preparation of Mononuclear and Binuclear Chromium Complexes. The complexes were prepared by the reaction of [Cr(NH$_3$)$_6$](NO$_3$)$_3$ and L-alanine, according to Oki's method,7) but with a slight modification. The molar ratio of the hexaammine complex to the L-alanine ligand was intentionally varied in greater amounts in order to obtain good yields of mononuclear or binuclear chromium alaninato complexes separately.

[Cr(L-(or D-)ala)$_3$]$\cdot$H$_2$O. To a solution of [Cr(NH$_3$)$_6$](NO$_3$)$_3$ (6 mmol) in 70 mL of water was added 60 mmol of L- (or D-) alanine. This solution was heated to 70 °C for 90 min. Fine red needles of *fac*-Λ-[Cr(L-ala)$_3$]$\cdot$H$_2$O or *fac*-Δ-[Cr(D-ala)$_3$]$\cdot$H$_2$O were deposited and then separated and washed thoroughly with cold water. Anal. Calcd for CrC$_9$H$_{20}$N$_3$O$_7$: C, 33.51; H, 6.02; N, 12.66%. Found for L-ala complex: C, 33.84; H, 5.84; N, 13.06%. Found for D-ala complex: C, 33.48; H, 5.68; N, 13.09%.

[Cr$_2$(OH)$_2$(L-(or D-)ala)$_4$]$\cdot$3H$_2$O. To obtain the binuclear metal complex, 50 mL of an aqueous solution containing 6 mmol of [Cr(NH$_3$)$_6$](NO$_3$)$_3$ and 6 mmol of L- (or D-) alanine was heated to 70 °C for 90 min. The solution was kept for several days at room temperature. [Cr$_2$(OH)$_2$(L-(or D-)ala)$_4$]$\cdot$3H$_2$O was obtained as violet crystals. Anal. Calcd for Cr$_2$C$_4$H$_{32}$N$_4$O$_{13}$: C, 26.47; H, 5.92; N, 10.29%. Found for L-ala complex: C, 26.49; H, 6.05; N, 9.99%. Found for D-ala complex: C, 25.97, H, 5.56; N, 10.44%.

Spectroscopic Measurements. Since the obtained samples were almost insoluble in water, the absorption spectra were obtained using the complex (2—2.5 mg) in KBr (150 mg) pellets on a Hitachi U-3200 spectrophotometer. The magnitudes of the molar absorption coefficients ε in KBr pellets were estimated on the basis of Lambert-Beer's law. The CD spectra of the same sample were recorded on a JASCO J-40 spectropolarimeter.

The luminescence spectra were measured on an instrumental system constructed in this laboratory.8) Finely ground powder samples were excited by the 514.5 nm line of an argon-ion laser (Spectra Physics, model 2025-05). The luminescent light was analyzed by a Spex 1401 double monochrometer set at 0.5 nm spectral resolution, and detected by a cooled Hamamatsu R943-02 photomultiplier tube. The luminescence signal was monitored by a Keithley model 614 electrometer. These instruments were totally controlled by an Apple II GS microcomputer. The emission spectra were corrected for monochrometer and photomultiplier photoefficiency by using a standard tungsten lamp.

Several optical devices were inserted into this system in order to detect CPL signals. The excitation light was chopped by an optical chopper at 30 Hz, and the luminescent light was passed through a photoelastic modulator (Morvue PEM-1) operated at 50 kHz with a polarizer sheet. The output signal of the photomultiplier tube was fed to a PAR 181 current-sensitive preamplifier; the AC signals were processed simultaneously by a NF Circuit Design LI-573 lock-in amplifier for the total luminescent (TL) current at 30 Hz, and by a EG&G PAR 5206 lock-in amplifier for the CPL current at 50 kHz. The two output signals were digitized and sent to an Apple II GS computer.

Optical glass cryostats for liquid-nitrogen and liquid-helium temperatures were used for the low-temperature luminescence measurements. An Air Products "Displex" model 202 helium closed cycle refrigerator was used for the experiments between 12 and 77 K.

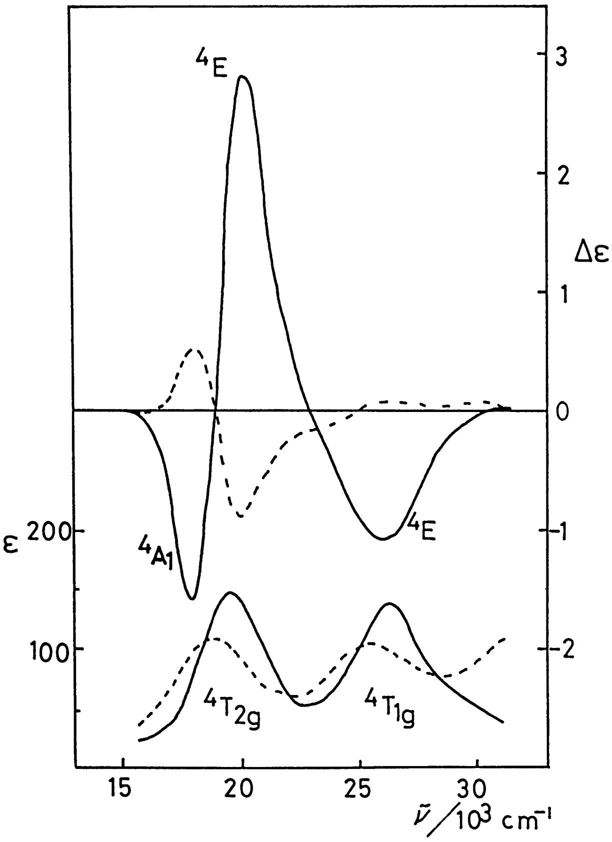

Fig. 2. Circular dichroism (upper part) and absorption spectra (lower part) of (——) [Cr(L-ala)$_3$]·H$_2$O and (----) [Cr$_2$(OH)$_2$(L-ala)$_4$]·3H$_2$O in KBr pellets at room temperature.

Results

Absorption and Luminescence Spectra of [Cr(L-ala)$_3$]·H$_2$O. The room-temperature absorption spectra are displayed in Fig. 2 to give the spin-allowed transitions of the monomeric and dimeric chromium L-alaninato complexes in KBr pellets. The two broad bands are indicated as corresponding to the $^4A_{2g}\rightarrow{}^4T_{2g}$, $^4T_{1g}$ transition, respectively.

The 77 K absorption spectrum in the 14400 cm^{-1} energy region in a KBr pellet is shown in Fig. 3. The two peaks separated by 40 cm^{-1} correspond to the R lines; these have been assigned to the transition from the $^4A_{2g}$ state to the trigonal components of the $^2E_g(O_h)$ level. Two other peaks were observed at 15108 cm^{-1} and 15051 cm^{-1} at 77 K (not shown in the figure) and assigned to the $^4A_{2g}\rightarrow{}^2T_{1g}$ transition.

The low-temperature luminescence spectrum of a powdered sample is shown in Fig. 4. At 77 K, two prominent peaks were observed at 14386 cm^{-1} (R$_1$) and 14424 cm^{-1} (R$_2$), separated by 38 cm^{-1} in energy. A strong peak was further observed at 14185 cm^{-1}. The luminescence spectrum of the enantiomer, [Cr(D-ala)$_3$]·H$_2$O, was confirmed to be identical in both shape and position with that of L-ala complex. The integrated relative R$_2$/R$_1$ intensity ratio of these peaks is 0.42 at 77 K. The highest-energy peak was found to lose its intensity at 4 K, though the spectral resolution at 4 K was not significantly improved at 4 K, as compared to 77 K.

Therefore, the two distinct peaks, R$_1$ and R$_2$, should be assigned to transitions which occur from the split states of $^2E_g(O_h)$ in a trigonal field.

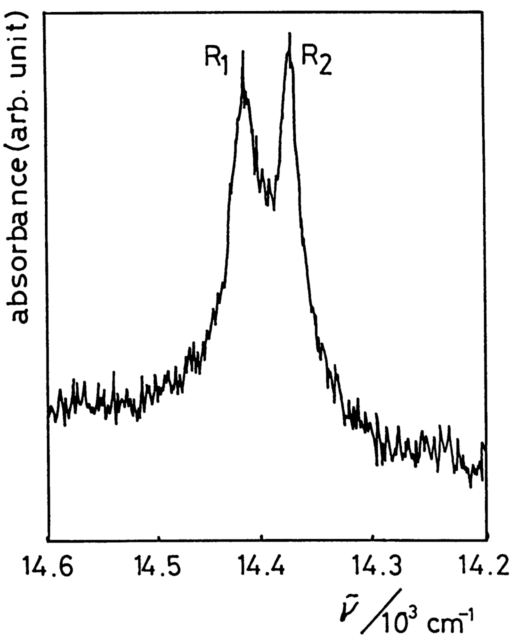

Fig. 3. Absorption spectrum of [Cr(L-ala)$_3$]·H$_2$O in KBr pellets at 77 K in the R line spectral region.

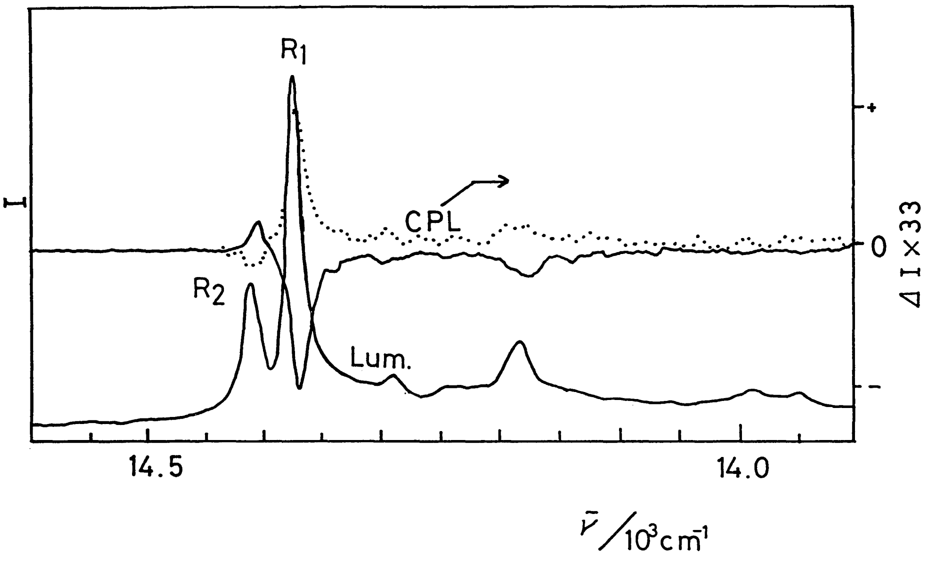

Fig. 4. Luminescence (I) and CPL (ΔI) spectra of tris alaninato chromium(III) complexes at 77 K. (——) [Cr(L-ala)$_3$]·H$_2$O, (——) [Cr(D-ala)$_3$]·H$_2$O. The intensity of ΔI is multipied by 33 compared to that of I.

CD and CPL Spectrum of [Cr(D-ala)$_3$]·H$_2$O. The room-temperature CD spectrum is also shown for the spin-allowed transition of [Cr(L-ala)$_3$]·H$_2$O in KBr pellets in Fig. 2. A similar spectrum pattern (but of opposite CD sign) was obtained for [Cr(D-ala)$_3$]·H$_2$O (but not displayed for clarity). The absolute values of $\Delta\varepsilon_{max}$ of a pair of enantiomers coincide with each others within 15% experimental discrepancies. In the CD spectrum of [Cr(L-ala)$_3$]·H$_2$O, a pair of bands of (+) and (−) signs was observed at 20,000 cm^{-1} in the $^4A_{2g}\rightarrow{}^4T_{2g}$ transition, and a single (−) band at 26,000 cm^{-1} in the $^4A_{2g}\rightarrow{}^4T_{1g}$ transition region.

Circularly polarized luminescence spectra of the powdered samples were recorded at 77 K. Figure 4 clearly shows two prominent R$_1$ and R$_2$ peaks of opposite CPL sign as well as some vibronic bands associated with the R$_1$ peak. The ordinate in the CPL spectrum indicates the (I_L—I_R) component of luminescence, where I_L and I_R refer to left-handed and right-handed circularly polarized luminescence, respectively. It is well-known that artificial CPL signals are often observed if the emitted light is partially linearly polarized under some conditions.[9] To reduce artifacts in the CPL measurement of a powdered sample, the following precautions were carefully taken. The exciting beam was aligned at 90° angle with respect to the emission direction, and the exciting Argon laser light was aligned so that its linearly polarized **E** vector was aligned in directions parallel to the detective direction of emission.[9] Furthermore, in order to examine the genuiness of the observed CPL spectra, both of the enantiomeric samples (i.e., [Cr(L-ala)$_3$]·H$_2$O and [Cr(D-ala)$_3$]·H$_2$O) were measured, and the luminescent dissymmetry factor g_{em} ($g_{em}=2\times(I_L-I_R)/(I_L+I_R)$) was evaluated for comparisons. The absolute values of g_{em} of the two enantiomers should, in principle, be equal. For the L-ala complex, the g_{em} value of the R$_1$ line was estimated to be −0.024 and that of R$_2$ line to be +0.0040. For the D-ala complex, the g_{em} of R$_1$ was +0.025, while that of R$_2$ line was −0.0038. These g values agreed in repeated experiments within ca. 10% errors. From these results it was confirmed that these CPL spectra were not caused by any artificial factors but were genuine.

A negative CPL peak was observed at 14185 cm^{-1} in [Cr(L-ala)$_3$]·H$_2$O, with $g_{em}=-0.021$. This peak may be a vibronic sideband of the R$_1$ line, since R$_1$ was found to have a negative sign. The vibrational progression was calculated to be 201 cm^{-1}.

Luminescence and Absorption Spectral Results of [Cr$_2$(OH)$_2$(L-ala)$_4$]·3H$_2$O. The luminescence spectra of the powdered sample of the binuclear complex are shown at low temperature in Fig. 5. At 43 K (solid curve), there are six peaks at around 14200 cm^{-1}. The peak locations are as follows: 14290, 14258, 14248, 14230, 14200, and 14164 in units of cm^{-1}. The luminescence intensity of these peaks was found to be very weak in comparison with the monomeric L-alaninato complex. A series of similar structures was also found in the 14000 cm^{-1} energy region. They were assigned to the vibronic peaks of 200 cm^{-1} energy relative to a group of 14200 cm^{-1} peaks. As the temperatures were lowered, the luminescence intensities of peaks **1** and **2** became reduced in intensity; at 4 K they completely disappeared.

The absorption spectrum of [Cr$_2$(OH)$_2$(L-ala)$_4$]·3H$_2$O is also shown in Fig. 2. Two spin-allowed bands, $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4T_{1g}$, are red-shifted in comparison with the monomeric complex. This corresponds to the fact that the dimeric complex (N$_2$O$_4$ coordination) has a weaker crystal field strength than the monomeric complex (N_3O_3 coordination).

CD and CPL Spectra of $[Cr_2(OH)_2(\text{L-ala})_4]\cdot 3H_2O$. The room-temperature CD spectrum of the dimeric complexes is also shown in Fig. 2. The CD intensity of the dimeric complex is considerably weak in contrast to the CD spectra of the monomeric complexes, and a higher energy CD band ($^4A_{2g}\rightarrow{}^4T_{1g}$) can scarcely be seen. This spectral result can be rationalized by the fact that the dimer has a "*meso*"-type structure, i.e. the absolute configuration around two chromium ions are opposite to each other. Some discussions are given later concerning these results.

Although we have attempted CPL measurements of this complex at 77 K several times, a reproducible CPL signal could not be obtained. The CPL intensity should be too small to be observed within our detection limits.

Discussion

I. Mononuclear Complex, *fac*-$[Cr(\text{L-ala})_3]\cdot H_2O$. The absolute configuration of this almost insoluble pink isomer was determined to be Λ by Gillard et al.[5] According to their report, this chromium complex was found to be isomorphous with *fac*-$[Co(\text{L-ala})_3]$ of the Λ structure.

Spin-Allowed Transitions. The broad bands (Fig. 2), assigned to the transitions $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4T_{1g}$ (in O_h notation) split in a trigonal crystal field, i.e., the $^4T_{2g}$ (O_h) electronic level must split into two components, ^4E and $^4A_1$. Actually, two CD bands of opposite signs are seen in the $^4T_{2g}$ absorption band in Fig. 2. According to a static crystal field model, Shinada[10] theoretically discussed the CD spectra of trigonally-distorted bidentate Cr(III) and Co(III) complexes in general. The Λ-$[Cr(ox)_3]^{3-}$ (ox=oxalato ion) complex is already known to show a positive CD band at higher energy, and a negative CD band at lower energy in the $^4A_{2g}\rightarrow{}^4T_{2g}$ transition regions. The CD data were reported to be as follows: ν ($\Delta\varepsilon$), 18.1×10^3 cm^{-1} (+2.83), 16.1×10^3 cm^{-1} (−0.12).[11] The higher- and lower-energy bands were assigned to transitions due to the ^4E and $^4A_1$ components. This analysis assumes, in turn, a positive trigonal splitting parameter, K. Considering the second-order rotatory strength, the net rotatory strength of the $^4A_{2g}\rightarrow{}^4T_{2g}$ band was estimated to have a positive value.[10] This theoretical result agrees with the observed spectrum.

A similar assignment can be made for the CD spectrum of $[Cr(\text{L-ala})_3]\cdot H_2O$. Although the actual point symmetry of this molecule is C_3, we analyzed the electronic levels of this complex by assuming a D_3 chromophore. Richardson has extended the static crystal field model[12] so that it can be applied to distorted octahedral complexes. As a result, he concluded theoretically that both the net rotatory strength of the $^4A_{2g}\rightarrow{}^4T_{2g}$ band and the trigonal splitting parameter K are positive for trigonally compressed and azimuthally contracted O_h chromium(III) complexes. This alaninato complex can be reasonably classified to have this type of structure. According to these considerations, it is concluded that the trigonal splitting parameter K of $[Cr(\text{L-ala})_3]\cdot H_2O$ is positive, i.e. the ^4E electronic level lies above the $^4A_1$ level. The observed fact that the net rotatory strength of the $^4A_{2g}\rightarrow{}^4T_{2g}$ transition is positive, i.e. (+) CD component is larger than the (−) CD component, is also consistent with his theory.

It is notable that a comparatively large CD band is observed in the $^4A_{2g}\rightarrow{}^4T_{1g}$ region (in O_h notation). This is attributed to the ^4E component of the $^4T_{1g}$ level, since the $^4A_{2g}\rightarrow{}^4E$ transition is magnetically allowed, but the other transition ($^4A_{2g}\rightarrow{}^4T_2$) is forbidden under D_3 symetry. According to another theory,[13] the $^4A_2\rightarrow{}^4E$ ($^4T_{1g}$) transition borrows CD intensity from $^4A_{2g}\rightarrow{}^4E$ ($^4T_{2g}$) by configuration interaction. The CD sign of this $^4A_{2g}\rightarrow{}^4E$ ($^4T_{1g}$) transition is opposite to that of $^4A_{2g}\rightarrow{}^4E$ ($^4T_{2g}$) if K is positive. The observation of a negative CD sign in the $^4T_{1g}$ band is in accordance with this prediction. However, the matrix element of the configuration interaction, which equals $3K/2$, is too small to interpret the CD intensity. Another mechanism[14] must contribute in addition to the configuration interaction with ^4E ($^4T_{2g}$).

Spin Forbidden Transitions. Two sharp peaks were detected in luminescence at 14424 and 14386 cm^{-1}. The peak locations and the energy separation (38 cm^{-1}) of these two luminescent peaks are in good agreement with the absorption peaks at 77 K. They have been assigned to the split components of the $^2E_g\rightarrow{}^4A_{2g}$ transition by a contribution of trigonal crystal field and spin-orbit coupling. According to Tanabe and Sugano's strong ligand field theory,[15] the splitting of Kramers doublet λ can be expressed as

$$\lambda = E(2\bar{A}) - E(\bar{E}) = 4K\zeta_{so}/(E(^2E_g) - E(^2T_{2g})), \qquad (1)$$

where ζ_{so} denotes the spin-orbit coupling constant. The denominator, $E(^2E_g)-E(^2T_{2g})$, must be negative, and the trigonal splitting parameter, K, being positive (as described in the previous section) is such that the splitting energy, λ, should be negative. The energy difference, $E(^2E_g)-E(^2T_{2g})$, in $[Cr(\text{L-ala})_3]$ was estimated to be −6900 cm^{-1} by considering the position of the $^4T_{2g}$ and $^4T_{1g}$ absorption bands using a conventional Tanabe and Sugano diagram with C/B=4.5. If the K parameter is assumed to be +300 cm^{-1}, we obtain a ζ_{so} parameter of 220 cm^{-1} in energy for λ=−38 cm^{-1}.

It is interesting to quote a large splitting of the ^2E_g state of other amino acid complexes, i.e., λ of *fac*-$[Cr(gly)_3]\cdot 3H_2O$ is 89 cm^{-1}, where gly=glycine.[16] The analysis of a large ^2E splitting is still controversial.[17] However, in the case of the L-alaninato complex, λ is comparable to 29 cm^{-1} in ruby. We conclude that λ should be negative in sign and that the 14424 (R_2) and 14386 (R_1) peaks should be assigned to the transition from the $\bar{E}$ and $2\bar{A}$ states, respectively.

CPL Spectrum of $[Cr(\text{L-ala})_3]\cdot H_2O$. Both positive and negative CPL peaks were detected in the R line region. For the $[Cr(\text{L-ala})_3]\cdot H_2O$ complex, the R_1 and R_2 peaks show a strong negative peak and a weak positive peak, respectively. Kaizaki et al. have presented theoretical arguments[18] to deduce the rotatory strength of the R lines based on Tanabe and Sugano's perturbation theory. The spin-forbidden transitions acquire both electric and magnetic dipole strengths through spin-orbit coupling from the spin-allowed transitions. In their calculation, only an electronic coupling between the ^2E_g and $^4T_{2g}$ states were taken into consideration, because, in trigonal symmetry, the $^4A_{2g}\rightarrow{}^4T_{2g}$ transitions are allowed in CD absorption, whereas the $^4A_{2g}\rightarrow{}^4T_{1g}$ transitions are forbidden. According to their theory, the rotatory strength of the R lines in trigonal symmetry can be calculated from the rotatory strength of the $^4A_{2g}\rightarrow{}^4E(^4T_{2g})$, $^4A_1(^4T_{2g})$ transitions, as follows:

$$R(\overline{E}) = 8R(^4A_1) + 20R(^4E) \qquad (2)$$

and

$$R(2\overline{A}) = 24R(^4A_1) + 12R(^4E), \qquad (3)$$

where $R(2\overline{A})$ and $R(\overline{E})$ are the rotatory strength of the R_1 and R_2 lines.

The low-temperature CD or CPL spectra of the R lines of $[Cr(en)_3]^{3+}$ (en=ethylenediamine) doped in a single crystal have already been reported.[19] Since only the axial spectra were measured, the R-line transitions borrow their intensity only from the ^4E component of the $^4T_{2g}(O_h)$ state. According to Eqs. 2 and 3, the axial rotatory strength ratio, $R_{ax}(\overline{E})/R_{ax}(2\overline{A})$, is estimated to be 5/3. Geiser and Güdel observed[19a] an axial circular dichroism of $[Cr(en)_3]^{3+}$ doped in a $2[Ir(en)_3]Cl_3\cdot KCl\cdot 6H_2O$ single crystal. They reported that the CD intensity of the $^4A_2\rightarrow\overline{E}$ transition is slightly larger than that of $^4A_2\rightarrow 2\overline{A}$ transition. The optical activity of single crystals of the spin-forbidden transitions of $[Cr(en)_3]^{3+}$ complex seems to be interpreted by Kaizaki's treatment.

In our case, the complex molecules are randomly dispersed in KBr pellets. We therefore have to take into account the contribution of the $^4A_1(^4T_{2g})$ components. From Eqs. 2 and 3, one can deduce that the signs and magnitudes of $R(\overline{E})$ and $R(2\overline{A})$ are mainly determined by the values of $R(^4E)$ and $R(^4A_1)$, respectively. In the observed spectra, indeed, the signs of the R_1 and R_2 lines in the CPL spectrum coincide with the signs of the $^4A_1$ and ^4E CD bands.

The relative CPL intensity ratios of the two peaks of ^2E are given by

$$\Delta I(\overline{E})/\Delta I(2\overline{A}) = (2+5\alpha)/(6+3\alpha)\times\exp(-\Delta E/k_BT), \qquad (4)$$

where $\Delta I(\overline{E})$ and $\Delta I(2\overline{A})$ are CPL intensities of the two peaks, and $\alpha=R(^4E)/R(^4A_1)$ is the rotatory strength ratio of the $^4T_{2g}$ transition, ΔE the splitting of the ^2E_g level, and the k_B the Boltzmann constant. The CPL intensity ratio, $I(\overline{E})/I(2\overline{A})$, was evaluated from the observed 77 K CPL spectra to be −0.15. By employing this value, the calculated α ratio is −0.63. The room-temperature CD spectrum (Fig. 2), however, gives an α ratio of −2.0. This quantity seems not to be agreeable with this treatment.

We now consider some reasons why the theoretical predictions differ from the observations. First of all, we must reconsider the validity of Eqs. 2 and 3, as follows. In the theoretical considerations described so far, only the spin-orbit coupling between the ^2E_g and $^4T_{2g}$ (O_h) levels were considered for calculations of the rotatory strength. Under strict octahedral symmetry, indeed, the ^2E_g level can only mix with the $^4T_{2g}$ level, not with the $^4T_{1g}$ level (theoretically) through a spin-orbit interaction. Furthermore, most chromium complexes have a very small rotatory strength in the $^4A_{2g}\rightarrow{}^4T_{1g}$ region, as compared with the $^4A_{2g}\rightarrow{}^4T_{2g}$ region, so that the contribution from the $^4A_{2g}\rightarrow{}^4T_{1g}$ transition to the CPL intensity in the R lines can be reasonably ignored for ordinary cases. However, for the $[Cr(\text{L-ala})_3]\cdot H_2O$ complex, a large negative CD band, the rotatory strength of which is comparable to that of $^4T_{2g}$, was observed at the $^4A_{2g}\rightarrow{}^4E(^4T_{1g})$ transition (as described before). It should therefore be quite reasonable that the CPL transition of the R lines in trigonal symmetry acquire an additional negative rotatory strength by an introduction of the ^4E component of the $^4T_{1g}$ state. However, in perturbation theory, mixing of the ^4E state with the ^2E state is in inverse proportion to the energy difference, $\Delta E(^4E\text{—}^2E)$, the contribution of $^4E(^4T_{1g})$ being about half that of $^4E(^4T_{2g})$. Such a comparatively small negative contribution of the $^4E(^4T_{1g})$ state to the CPL intensity reduces the α value substantially; the observed α value approaches the theoretical value, −0.64. This contribution, however, may not be sufficient to understand the entire CPL intensity.

Secondary, one more assumption concerning Eqs. 2 and 3 must be pointed out. Eqs. 2 and 3 were obtained on the assumption that the trigonal splitting of $^4T_{1g}$ is small. The apparent trigonal splitting of the state, however, is very large (about 20000 cm^{-1}) in the CD spectrum. The actual splitting parameter must be smaller than this (as described in the next paragraph) and the difference between $\Delta E(^2E\text{—}^4E(^4T_{2g}))$ and $\Delta E(^2E\text{—}^4A_1(^4T_{2g}))$ must be considered. For the alaninato complex, since the energy of the $^4A_1(^4T_{2g})$ state is lower than that of $^4E(^4T_{2g})$, the coefficients of $R(^4A_1)$ become larger and those of $R(^4E)$ become smaller for Eqs. 2 and 3. Consequently, the theoretical value approaches the experimental value.

Thirdly, we examine the experimental value of α obtained from CD data. Since the rotatory strength of the $^4A_1$ and ^4E components of the $^4T_2$ band should have different signs, it is very difficult to correctly resolve the $^4T_2$ band into two components. An apparent splitting of the $^4T_2$ band in Fig. 2 is estimated to be 2000 cm^{-1}; this gives a trigonal splitting parameter of K=1300 cm^{-1}. The obtained K value is too large in comparison with that of ordinary chromium(III) complexes. Clearly, an overlapping of two components of the $^4T_2$ band must occur; it is therefore difficult to estimate the correct α value from the spectrum.

No further quantitative discussion can be presented because of theoretical and experimental ambiguities. We think that the quantitative disagreement of the theoretical and experimental values results from a combination of the above-mentioned causes. However, it should be mentioned here that the signs of the CPL peaks of the R lines correspond to those of the CD bands. Therefore, Eqs. 2 and 3 are very useful expressions to qualitatively explain the CPL spectra of trigonal chromium(III) complexes.

We consider the g_{em} value of a vibronic peak. A single vibronic peak was clearly observed in the CPL spectrum. In general, it is hard to predict the rotatory strength of a vibronically induced transition which strongly depends on the nature of the vibration modes. According to the Herzberg–Teller mechanism, it is shown that if the vibronic band is coupled with e-mode vibrations, the dissymmetry factor, g, is smaller in vibronics than in their electronic origin.[19a)] Geiser and Güdel[19a)] have considered the vibronic CD intensity of $[Cr(en)_3]^{3+}$ at low temperatures. They obtained very small g_{abs} values for almost all of the peaks which are coupled with e-mode vibrations. Still, they found some interesting vibronic levels, the g_{abs} values of which are 0.5—4 times larger in magnitude with respect to their electronic origins. These prominent vibronic peaks are assigned to correspond to totally symmetric vibration. Peacock and Stewart[19b)] reported that the g_{em} values for the R lines are 0.19 in the CPL of $[Cr(en)_3]^{3+}$. The g_{em} values of the vibronic bands seemed not to be as large as those of the electronic origin.

In the CPL spectra of $[Cr(L\text{-}ala)_3]\cdot H_2O$, the g_{em} value of a peak seen at 14185 cm^{-1} was found to be -0.021, which is almost equal in magnitudes to -0.024 at the electronic origin. Considering the above-mentioned arguments, this peak is assigned to be a vibronic peak of R_1 coupled with a symmetric vibrational mode.

II. Binuclear Complex, $[Cr_2(OH)_2(L\text{-}ala)_4]\cdot 3H_2O$. Electronic Eenergy Levels of Chromium Pair States. A series of peaks observed at low temperature (Fig. 5) can be interpreted as being due to the luminescence of a pair of chromium(III) ions. The ground state $|^4A_{2g}{}^4A_{2g}\rangle$ are usually well described by the eigenvalues of the Hamiltonian,[20)]

$$H = JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2, \tag{5}$$

where J denotes an isotropic exchange parameter, j is the biquadratic contribution and S_1, S_2 are the spin quantum numbers of the Cr(1) and Cr(2) ions, respectively. The exchange interactions lead to a splitting of the ground state into four spin sub-levels, denoted by S_t=0, 1, 2, and 3, where S_t is total spin quantum number,

$$S_t = S_1 + S_2, \tag{6}$$

At 4.2 K, four peaks were detected in luminescence (peak number **3**, **4**, **5**, and **6** in Fig. 5). They have been assigned to a transition from the lowest excited electronic levels to the ground pair states. According to Eq. 5, the theoretical energy splitting between the neighboring pair levels are calculated to be $J+13j/2$, $2J+7j$, and $3J-9j/2$ for the S_t=0, 1, 2, and 3, respectively. From the observed peak separations (18, 30, and 36 cm^{-1}) the exchange parameters were calculated to be J=13.3 cm^{-1} and j=0.6 cm^{-1}. These energy levels are illustrated in Fig. 6. The J value of this complex is consistent with that of 17.1 cm^{-1}, which was deduced from magnetic susceptibility measurements while neglecting the j terms.[21)] At higher temperatures, some

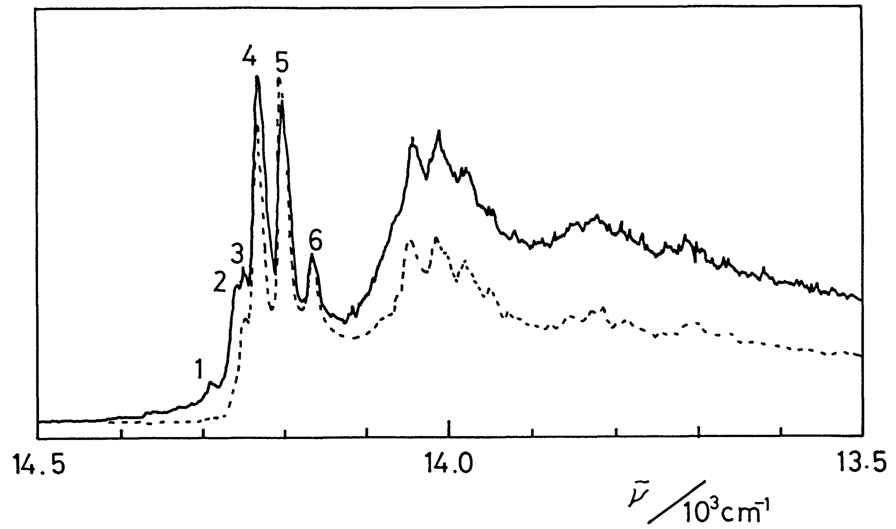

Fig. 5. Luminecsence spectra of $[Cr_2(OH)_2(L\text{-}ala)_4]\cdot 3H_2O$. (——) at 43 K and (-----) at 16 K.

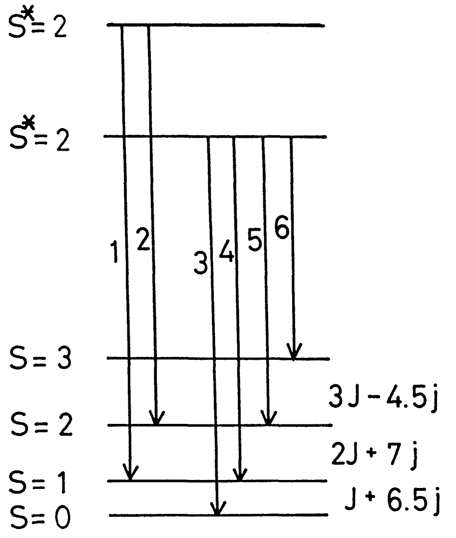

Fig. 6. Energy level diagram of exchange-coupled pair states in $[Cr_2(OH)_2(L\text{-}ala)_4]\cdot 3H_2O$.

high-energy peaks (peak number **1** and **2**) grow in intensity; these have been assigned to the transition from the next higher excited state. The interval between the lowest and the next-higher excited states was determined to be 42 cm^{-1}. The total spin numbers of the excited pair states were supposed from the peak intensity, as follows. The $|^4A_{2g}{}^2E_g\rangle$ pair state comprises four triplet ($S_t^*=1$) and four quintet ($S_t^*=2$) states. The observed transitions occur from these excited states and ground pair states ($S_t=0$, 1, 2, and 3). Two mechanisms[22] are possible to obtain the optical intensity in the pair system. They are a single ion mechanism and an exchange mechanism. The $\Delta S=0$ transition is allowed by both mechanisms; thus, this $\Delta S=0$ transition generally gives the most intense luminescence. Since the luminescence spectrum at 4 K (Fig. 5) shows that peak **5**, which is assigned to the $S_t=2$ state, is the most intense, the total spin number of the lowest excited state is determined to be 2 (see Fig. 6). A small peak, **3**, is assigned to the transition from $S_t^*=2$ to $S_t=0$. Although both mechanisms cannot explain a $\Delta S=2$ transition, a weak $\Delta S=2$ transition had already been reported for $\mu\text{-}(OH)_2\text{-}[Cr_2(OH)_2(en)_2]^{2+}$.[23] Since, no distinct peak assigned to the transition from the next lower excited state to the $S_t=0$ ground state could be observed, the next excited state may also be assigned to $S_t^*=2$.

Optical Activity of $[Cr_2(L\text{-}ala)_4(OH)_2]\cdot 3H_2O$. We were not successful in detecting the CPL spectra for this binuclear complex. It has already been shown[6] that the structure of this complex is of the "*meso*" type, i.e., one chromium moiety has a *Λ* configuration and the other has *Δ* (Fig. 1). Accordingly, the entire optical activity was smaller than that of the monomeric complex, $[Cr(L\text{-}ala)_3]\cdot H_2O$. The CD intensity of the dimeric complex is, indeed, one third of the monomer (see Fig. 4). Furthermore, the total luminescence intensity of this dimer was found to be considerably lower than that of the corresponding monomer. It is reasonable to think that no CPL spectrum could be obtained at the present stage.

Conclusion. We have obtained the following results from the luminescence and CPL spectra of chromium alaninato complexes:

(1) Sharp luminescence and CPL spectra were obtained at low temperatures in the R-line energy regions for $[Cr(L\text{-}(\text{or } D\text{-})ala)_3]\cdot H_2O$. The CPL spectral features are qualitatively well explained if we assume that the rotatory strength of the R lines are mainly determined by contributions from the trigonally split components of the allowed $^4A_{2g}\rightarrow{}^4T_{2g}$ transitions. However, both theoretical and experimental difficulties prevent us from obtaining any quantitative discussion regarding the limit of crystal-field theory.

(2) Highly structured luminescence spectra of $[Cr_2(OH)_2(L\text{-}ala)_4]\cdot 3H_2O$ were observed and interpreted by a Heisenberg-type of an exchange-coupled system. The exchange parameters were determined as being $J=13.3$ cm^{-1} and $j=0.6$ cm^{-1}. The CPL spectrum, however, was not observed, since this complex is considered to be a *meso*-type dimer complex.

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