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Effect of pH on the Circular Dichroism(CD)-sensitive Transitions of Some Lanthanoid(III) Complexes and "Pseudo CD-sensitive Transitions" of Europium(III) and Terbium(III) Complexes

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The effect of pH on the CD-sensitive transitions of lanthanoid(III) complexes with *l*-propylenediaminetetraacetic acid(*l*-PDTA) and L-ethylenediaminedisuccinic acid(L-EDDS) was studied. The relation between the cross-over pH where the CD pattern changes or sign of CD reverses and the number of 4f-electrons in lanthanoid(III) complexes with L-EDDS showed a tetrad curve. A strong evidence for coordination of hydroxide ions was suggested. "Pseudo CD-sensitive bands" in the spectra of the complexes of europium(III) and terbium(III) which do not obey the selection rule $\Delta J \leq 1$ were found, and the mechanisms of these transitions were elucidated.

The circular dichroism (CD)-sensitive band has been observed on the J'-band of magnetic dipole character for some lanthanoid(III) complexes with optically active ligands. The experimental result was in accordance with the theory proposed previously.[1,2] It was observed that intensities and patterns of CD-sensitive bands of lanthanoid(III) complexes vary remarkably with pH of solutions, especially with high pH's. This phenomenon in the lanthanoid(III) complexes with *l*-PDTA or L-EDDS was studied in detail. The work has revealed some new information on the coordination bonds of the lanthanoid(III) complexes.

The pseudo CD-sensitive bands in the spectra of europium(III) and terbium(III) complexes were found and the mechanism of these bands which do not obey the selection rule $\Delta J \leq 1$, was discussed.

Experimental

Materials. All lanthanoid(III) perchlorates were prepared by dissolving lanthanoid oxides of 99.9% purity in perchloric acid and their concentrations were standardized by EDTA titration using xylenol orange as an indicator. *l*-PDTA was synthesized by Dwyer's method[3] and L-EDDS by the method of Neal and Rose[4] from 1,2-dibromoethane and L-aspartic acid, respectively. The sample solution was prepared by mixing lanthanoid(III) perchlorate with the ligand at 1 : 1 mole ratio (practically 10% excess of the ligand for *l*-PDTA and 5% excess for L-EDDS). The final concentration of lanthanoid(III) in complex was made to be 0.1 mol/l. The pH of the solution of *l*-PDTA complex was adjusted by 5 M NaOH and that of L-EDDS complex by aqueous ammonia. H[Pr(L-EDDS)]·2H_2O and H[Dy(L-EDDS)]·2H_2O were prepared by Moeller's method[5] and CD spectra of these complexes were measured at various pH values.

Measurements. Absorption and CD spectra of the complexes were measured with a JASCO model ORD/UV-5 optical rotatory dispersion recorder with a CD attachment, a 10 mm cell, at room temperature. It was found more convenient to use a 50 mm cell for H[Pr(L-EDDS)]·2H_2O and H[Dy(L-EDDS)]·2H_2O at various pH values in aqueous solutions. A Hitachi-Horiba model F-5 pH meter was used for pH measurements.

Results

The CD spectra of lanthanoid(III) complexes with *l*-PDTA and L-EDDS were measured at various pH values in aqueous solutions. In a strongly alkaline region, it was found that the patterns of CD-sensitive bands of these complexes vary remarkably with increasing pH value. The changes in the patterns and

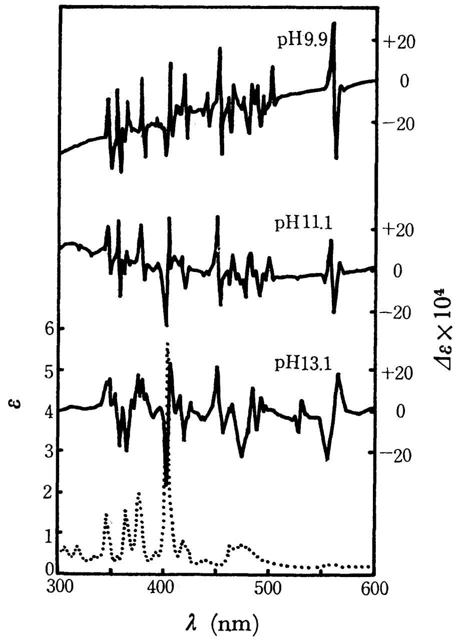


Fig. 1. Alterations of CD spectra for Sm(III)-*l*-PDTA complex: ——, CD spectra ($\Delta\varepsilon$); ……, absorption spectrum.

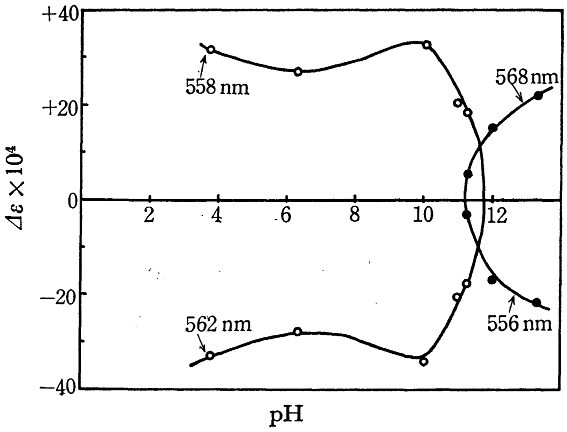


Fig. 2. Plot of $\Delta\varepsilon$ for CD components of the ${}^4G_{5/2} \leftarrow {}^6H_{5/2}$ transition of Sm(III)-*l*-PDTA complex *vs.* pH.

intensities of the CD spectra of samarium(III) complexes with *l*-PDTA are shown in Fig. 1. The pH values plotted against $\Delta\varepsilon(=\varepsilon_l-\varepsilon_r)$ for CD components of $^4G_{5/2}\leftarrow{}^6H_{5/2}$ transition are shown in Fig. 2. The same features were observed also in the case of the Eu(III), Dy(III), Ho(III), Er(III), and Tm(III) complexes with *l*-PDTA. In order to confirm the phenomena observed for lanthanoid(III) complexes with *l*-PDTA, the CD spectra of Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), and Tm (III) complexes with L-EDDS were recorded more precisely by using the chart scales of 4 or 2 nm /cm. The following CD-sensitive and other transitions of the lanthanoid(III) complexes with L-EDDS were studied: Pr(III) complex, $^3P_2\leftarrow{}^3H_4$; Nd(III) complex, $^4G_{9/2}\leftarrow{}^4I_{9/2}$; Sm(III) complex, $^4H_{5/2}\leftarrow{}^6H_{5/2}$; Eu(III) complex, $^5D_0\leftarrow{}^7F_1$ and $^5G_2\leftarrow{}^7F_1$; Gd(III) complex, hardly any change observed in CD spectra in the pH range 9~11.5; Tb(III) complex, $^5G_6\leftarrow{}^7F_6$; Dy(III) complex, $^4I_{15/2}\leftarrow{}^6H_{15/2}$; Ho(III) complex, $^3K_8\leftarrow{}^5I_8$; Er(III) complex, $^2K_{15/2}\leftarrow{}^4I_{15/2}$; and Tm(III) complex, ($^3F_3$, $^3F_2$)$\leftarrow{}^3H_6$. A few examples are shown in Figs. 3(a) and 3(b). Similar features were observed for the other lanthanoid(III) complexes with L-EDDS. The cross-over pH values, where intensity of CD spectrum of L-EDDS complex changes suddenly, are plotted against the number of 4f-electrons (Fig. 4).

The CD spectra of H[Pr(L-EDDS)]·2H$_2$O and H[Dy(L-EDDS)]·2H$_2$O in aqueous solutions coin-

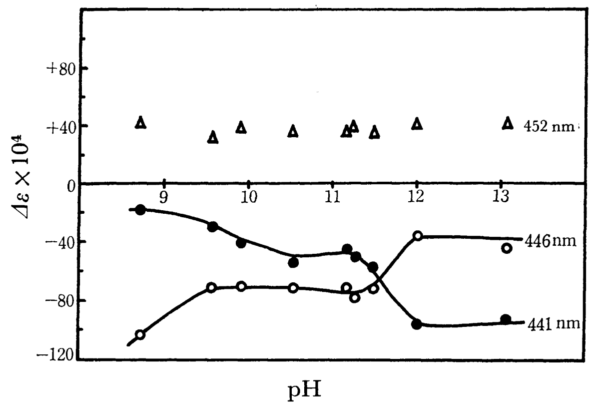


Fig. 3(a). Plot of $\Delta\varepsilon$ for CD components of the $^3P_2\leftarrow{}^3H_4$ transition of Pr(III)-L-EDDS complex *vs.* pH.

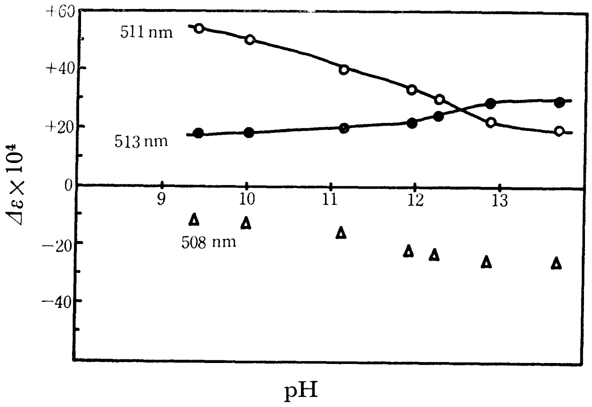
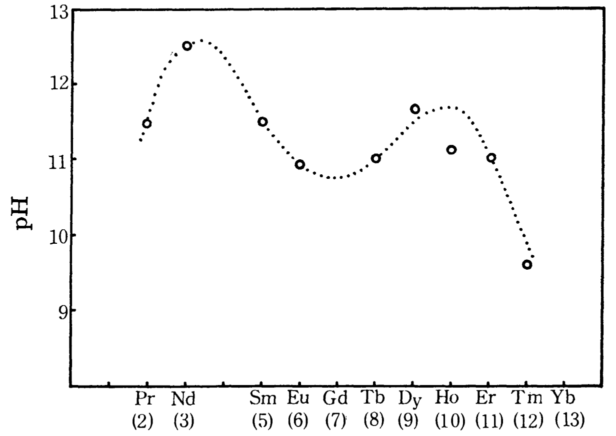


Fig. 3(b). Plot of $\Delta\varepsilon$ for CD components of the $^4G_{9/2}\leftarrow{}^4I_{9/2}$ transition of Nd(III)-L-EDDS complex *vs.* pH.



Number in parentheses: No. of 4f-electrons

Fig. 4. Relation between the cross-over pH and the number of 4f-electrons for L-EDDS complexes of lanthanoids(III).

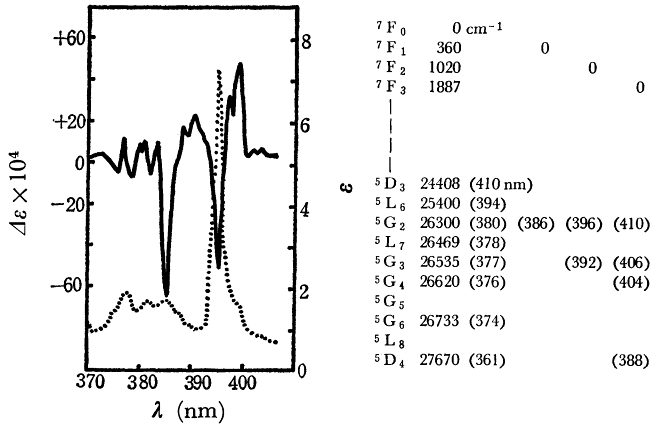


Fig. 5. Absorption and CD spectra of Eu(III)-L-EDDS complex at pH 11.02, 370—400 nm spectral region, and diagrams of the tentatively assigned energy levels: ——, CD spectrum ($\Delta\varepsilon$); ……, absorption spectrum.

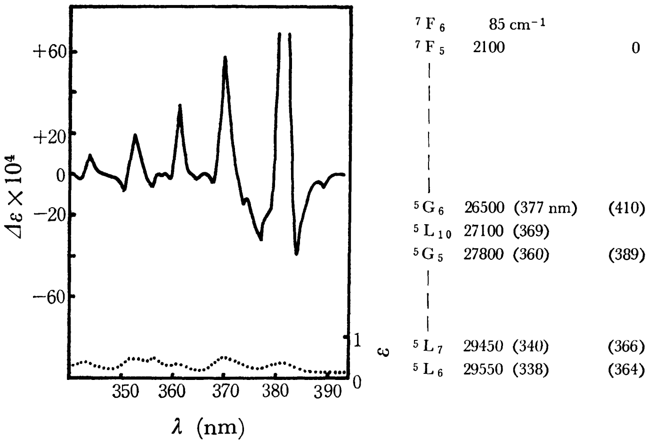


Fig. 6. Absorption and CD spectra of Tb(III)-L-EDDS complex at pH 11.3, 350—390 nm spectral region, and diagrams of the tentatively assigned energy levels: ——, CD spectrum ($\Delta\varepsilon$); ……, absorption spectrum.

cide with those at neutral pH region in the mixed solutions of the lanthanoids(III) and L-EDDS. By increasing the pH of these solutions, similar changes of patterns took place, but they were not so remarkable as those of a mixed solution of lanthanoids(III) and L-EDDS.

Similar to the band (660 nm) of Tm(III) complex with *l*-PDTA,[2] other bands of the same kind which do not obey the selection rule $\Delta J \leq 1$, were also observed in europium(III) and terbium(III) complexes with L-EDDS. We will call these bands "pseudo CD-sensitive bands". The excited levels of such newly located "pseudo CD-sensitive transitions" are the group of bands at 386, 388, 392, and 410 nm of Eu(III) complex and a band at ~370 nm of Tb(III) complex (Figs. 5 and 6).

Discussion

We have reconfirmed that the "CD-sensitive bands",[2] where magnetic dipole transitions are allowed, always show marked intense bands. In Fig. 4, the cross-over pH values where CD pattern changes or sign of CD reverses, are plotted against the number of 4f-electrons. The curve shows a tetrad-type curve. In view of the coordination number of the lanthanoid(III) ion, *l*-PDTA or L-EDDS chelates may be possibly coordinated by hydroxide ions in strongly alkaline solutions.

According to Condon,[6] the rotational strength $\mathbf{R}_{ab}$ is determined by $\mathbf{R}_{ab}=(e^2/2mC)\mathbf{I}_m\langle a\mathbf{Q}b\rangle\langle b\mathbf{L}a\rangle$, where a and b are the wave functions of states a and b of the molecule or ion, $e\langle a\mathbf{Q}b\rangle$ and $e/2mC\cdot\langle b\mathbf{L}a\rangle$ are the induced electric and magnetic moments, respectively, of an electronic transition $b\leftarrow a$, and $\mathbf{I}_m$ is the imaginary part of the scalar product of these two moments. In general, a more simplified and practical expression of the rotational strength is $\mathbf{R}_{ab}=\rho\mu\cos\theta$, where ρ and μ are the real electric and magnetic dipole moments of the transition, respectively, and θ is the angle between the directions of the two moments. Thus, the following interpretation is acceptable for the changes of CD spectra. Coordination of hydroxide ions at the innersphere might perturb the surroundings of the lanthanoid(III) ion, and the magnitude and direction of induced electric dipole moment are forced to change, the intensity and sign of CD changing remarkably at a certain high pH. However, other methods such as pH titration and absorption spectrum could not detect the variation owing to low sensitivity. This was successfully found by means of the "CD-sensitive band". Thus, the variation was examined all over the bands again and "pseudo CD-sensitive bands" in the spectra of the complexes of Eu(III) and Tb(III), not obeying the selection rule $\Delta J \leq 1$, were found. The α $(=\Delta\varepsilon/\varepsilon)$ values of their dissymmetry ratio were estimated to be in the order of 10^{-2}. The phenomena could be elucidated by taking into consideration, transitions not only from the ground state, but also those from some higher excited states (Figs. 5 and 6). For Eu(III) complex, transitions from the first excited state $^7F_1$ and the second excited state $^7F_2$ have been reported.[7] The corresponding "pseudo CD-sensitive transition" of $^5G_2\leftarrow{}^6F_1$ and $^5G_2\leftarrow{}^7F_2$ of Eu(III) complex could be observed at 386 and 396 nm, respectively. The former band could immediately be assigned to the transition $^5G_2\leftarrow{}^7F_1$ on the basis of CD intensity and dissymmetry ratio. However, for the latter band, by overlapping of the band of a transition of $^5L_6\leftarrow{}^7F_0$ at 394 nm, the value of α remains in the order of 10^{-3}. A similar consideration accounted for the intensity of the CD band at 392 nm, superimposed on a band arising from the transition of $^5G_3\leftarrow{}^7F_2$.

By assuming that a transition from the third excited state $^7F_3$ takes place, the intensities of the CD components of the transition $^5G_2\leftarrow{}^7F_3$ for 410 nm and the transition $^5D_4\leftarrow{}^7F_3$ for 388 nm could be explained as due to the "pseudo CD-sensitive transition".

The unexpected intense CD bands at 370 nm of Tb(III) complex could be explained similarly by assuming the corresponding transition from the first excited state, ~2.1 kK higher than the ground level, *i.e.* the transition $^5L_6\leftarrow{}^7F_5$. It is impossible to do more accurate work on account of lack of detailed information on these mechanisms in atomic spectroscopy. However, the CD-sensitivity seems to be easily contained in the formal mechanism already developed for CD intensity of the lanthanoid(III) complex with optically active ligand in solution. It is difficult to study this phenomenon in aqueous solution at a low temperature. Though there is no experimental evidence of this mechanism, it is supposed that the origin of the "pseudo CD-sensitivity" in some europium(III) and terbium(III) complexes lies in the transition from some higher excited levels, satisfying the selection rule $\Delta J \leq 1$.

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