Noncovalent Interactions in Metal Complexes. VIII.[1] Syntheses, Properties, and Stereoselectivities of Lanthanoid Complexes with 1-*l*-Menthyloxy-3-benzoylacetone

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Lanthanoid complexes with 1-*l*-menthyloxy-3-benzoylacetone, $[Ln(l\text{-moba})_3(H_2O)_n]$ (Ln=La, Pr, Nd, Eu, Dy, Ho, Tm; n=0, 1, or 2), have been synthesized and characterized by elemental analyses, molecular weight determinations, and electronic, circular dichroism, and luminescence spectra. The molecular weight determinations suggest that the complexes are in a monomer-dimer equilibrium in nondonating solvents while they are monomeric in donating solvents. The complexes exhibit fairly intense circular dichroisms at the f-f band region, demonstrating the stereoselective formation of an enantiomer. The stereoselectivities have been discussed in terms of the intramolecular interligand CH/π-interaction operating between the phenyl and the menthyl groups of the ligands. $[Eu(l\text{-moba})_3(H_2O)]$ shows luminescence at the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions in benzene. Based on the concentration dependence of the luminescence, it is demonstrated that dimerization facilitates nonradiative relaxation and greatly reduces the quantum efficiency of luminescence.

Lanthanoid complexes with 1,3-diketones have been the subject of current studies because of the utility in NMR spectroscopy as shift reagents[2] and the interest in photoluminescence.[3,4] Recently much attention has been paid to the lanthanoid complexes with chiral 1,3-diketones in connection with the chirality recognition of enantiomers[5,6] and stereoselectivity of the complexes.[7] It is known, however, that the lanthanoid complexes with 1,3-diketones derived from *d*-camphor exhibit no optical activity in the f-f transition region.[8] This is probably due to the absence of the interligand interaction within a molecule because of the larger ionic radius of the lanthanoid ions.

In the previous paper of this series,[9] we reported that tris(1-*l*-menthyloxy-3-benzoylacetonato)M(III) complexes, $[M(l\text{-moba})_3]$ (M=Co, Cr, Mn) (Fig. 1), prefer a *cis*-Δ-configuration. The stereoselectivity was attributed to an intramolecular interligand CH/π-interaction between the *l*-menthyl and the phenyl residues of the ligand (Fig. 2). Similar stereoselectivities were also observed for tris(1-*l*-menthyloxy-3-acetylacetonato)M(III) $[M(l\text{-moac})_3]$ (M=Co, Cr)[10] and tris{1-*l*-methyloxy-3-(2-naphthoxyl)acetonato}M(III) $[M(l\text{-mona})_3]$ (M=Co, Cr, Mn).[11] It is particularly noteworthy that $[Mn(l\text{-moba})_3]$ and $[Mn(l\text{-mona})_3]$ are readily obtained as an optically active form without any effort to resolution, though tris(1,3-diketonato)manganese(III) complexes have been believed to be hardly resolved owing to the lability of manganese(III) for ligand substitution.[12] These findings prompted us to synthesize the lanthanoid complexes with $l\text{-moba}^-$ and study their property and stereochemistry to see the effect of the intramolecular interligand CH/π-interaction.

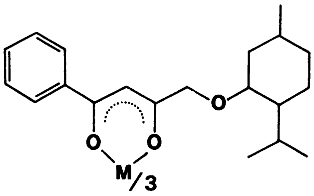

Fig. 1. Chemical structure of $[M(l\text{-moba})_3]$.

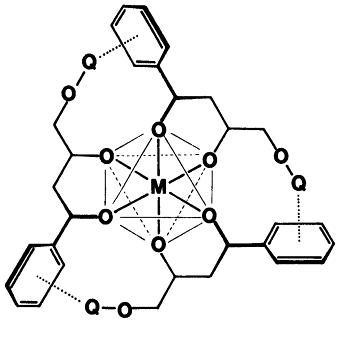

Fig. 2. Schematical representation of interligand CH/π-interaction supposed for $[M(l\text{-moba})_3]$ (Q=*l*-menthyl).

Experimental

Syntheses. Synthetic method of H(*l*-moba) was described in the preceding paper.[9] The lanthanoid complexes were obtained in a similar way. The procedure is exemplified by Eu^{III} complex. H(*l*-moba) (1.0 g) and NaOH (0.133 g) were dissolved in ethanol (10 cm^3). To this solution was added an ethanolic solution of $EuCl_3 \cdot 6H_2O$ (0.40 g), and the mixture was stirred for a few minutes and filtered. To the filtrate were added water (50 cm^3) and ether (100 cm^3), and the mixture was vigorously shaken. The ether layer was separated, shaken three times with water, and dried over sodium sulfate. On evaporating the solvent at room temperature, a yellow precipitate was obtained. It was collected and dried *in vacuo* over phosphorus pentaoxide.

Elemental analyses of the complexes thus prepared are given in Table 1.

Physical Measurements. Molecular weights were determined with a Hitachi Perkin-Elmer 115 Molecular Weight Apparatus in benzene and in ethanol. Electronic spectra were measured on a Shimadzu UV-visible Recording Spectrometer Model UV-240 in benzene. Circular dichroism spectra were recorded on a JASCO J-500C Spectropolarimeter in benzene. Luminescence spectra were recorded on a Hitachi Fluorescence Spectrophotometer in benzene with the excitation at 392.5 nm. The elemental analyses were carried out at

TABLE 1. ELEMENTAL ANALYSES OF COMPLEXES

Complex	Found (Calcd)/%		Color
	C	H	
La(l-moba)$_3$·H$_2$O	65.16(65.32)	7.78(7.58)	Cream yellow
Pr(l-moba)$_3$·H$_2$O	64.79(65.20)	7.63(7.57)	Greenish yellow
Nd(l-moba)$_3$·(H$_2$O)$_2$	64.13(63.97)	7.37(7.57)	Brick red
Eu(l-moba)$_3$·H$_2$O	64.08(64.56)	7.43(7.49)	Yellow
Dy(l-moba)$_3$	65.39(65.00)	7.79(7.54)	Cream yellow
Ho(l-moba)$_3$	64.78(64.85)	7.69(7.34)	Cream yellow
Tm(l-moba)$_3$	64.16(64.62)	7.71(7.32)	Cream yellow

the Service Center of Elemental Analysis, Kyushu University.

Results and Discussion

The lanthanoid(III) complexes of l-moba$^-$ were isolated as anhydrates, monohydrates, or dihydrate. The complexes of the first half of the lanthanoid series formed hydrates while the complexes of the latter half of the series formed anhydrates. This trend may be rationalized in terms of the lanthanoid contraction. That is, it is likely that in the complexes of the smaller metal ions the crowding of the hydrophobic residues of the ligand around the metal acts as an insulating sheath which interferes with the hydration, while such a steric effect is not so large as to hinder the hydration in the complexes with the large metal ions.

In donating solvents tris(1,3-diketonato) lanthanoid(III) complexes readily expand their coordination number from six to seven, eight, or nine by linking solvent molecules. In nondonating solvents, the complexes tend to dimerize (or polymerize) to achieve a higher coordination number than six by sharing the oxygen atoms of the ligand.[13] Hence, lanthanoid complexes with 1,3-diketones are in a monomer-dimer equilibrium in nondonating solvents.[6,7] In order to obtain an evidence for the equilibrium, molecular weights were determined in benzene over the concentration range 0.1—1.0 wt%. The results are shown in Fig. 3. Since each molecular weight increases with the increase of the concentration, the complexes evidently exist in a monomer-dimer equilibrium in benzene: $2[\mathrm{Ln}(l\text{-moba})_3] \rightleftarrows [\mathrm{Ln}_2(l\text{-moba})_6]$.[14]

As seen from Fig. 3, the dependency of molecular weight on concentration varies with the metal ions. The $\mathrm{La^{III}}$, $\mathrm{Pr^{III}}$, and $\mathrm{Eu^{III}}$ complexes show a large dependency on concentration, and almost all the molecules are dimerized at 1.0 wt%. It is likely that these complexes readily dimerize to achieve a higher coordination number owing to a relatively small interligand repulsion associated with the larger metal ions. Thus, the dimerization of these complexes is in line with their tendency to form hydrates. On the other hand, the molecular weights of the $\mathrm{Dy^{III}}$, $\mathrm{Ho^{III}}$, and $\mathrm{Tm^{III}}$ complexes show little dependency on concentration, and they are all monomeric in the concentration range examined. Since the size of the metal ion is relatively small, the bulky hydrophobic residues of the ligands

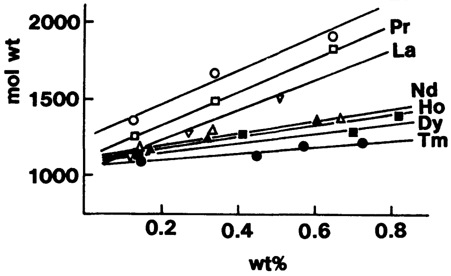

Fig. 3. Dependencies of molecular weights of the lanthanoid complexes on concentration in benzene: (▽): La, (□): Pr, (○): Eu, (△): Nd, (■): Dy, (▲): Ho, and (●): Tm complexes. The lines represent the trends of the molecular weight changes.

TABLE 2. ELECTRONIC AND CD SPECTRAL DATA OF COMPLEXES

Ln(III)	AB (ε)	CD ($\Delta\varepsilon \times 10^3$)
Pr	444 (7.59)	445 (−3.71)
	472 (3.91)	471 (−1.93)
	485 (1.95)	486 (−1.56)
	580 (sh)	583 (−1.19)
Nd		528 (−2.87)
		532 (+2.16)
		537 (−1.96)
		541 (+0.98)
	571 (11.7)	568 (−3.04)
	587 (18.6)	577 (−3.27)
		585 (−3.51)
	682 (−)	680 (−0.61)
	736 (2.36)	730 (−0.91)
	742 (2.54)	740 (−0.61)
	753 (2.76)	755 (−0.61)
	784 (sh)	790 (−1.63)
	802 (4.12)	795 (+1.52)
Eu		464 (−0.93)
	525 (−)	524 (−1.48)
Dy	450 (−)	450 (+4.00)
		455 (−3.30)
Ho	468 (−)	463 (−4.17)
		467 (+1.69)
		473 (+1.36)
Tm	684 (2.61)	683 (−1.69)
	660 (0.41)	660 (−0.31)

would cover the metal center and interfere with the dimerization. The $\mathrm{Nd^{III}}$ complex showed a concentration-dependence of molecular weight similar to those of the $\mathrm{Dy^{III}}$ and $\mathrm{Ho^{III}}$ complexes, though $\mathrm{Nd^{III}}$ is rather similar to $\mathrm{Pr^{III}}$ and $\mathrm{Eu^{III}}$ in ionic size. It is likely that the $\mathrm{Nd^{III}}$ complex is of eight-coordination with two water molecules and thence exhibits a low tendency to dimerize.

In donating solvents tris(1,3-diketonato) lanthanoid(III) complexes form solvent adducts to achieve a higher coordination number.[15] Such adducts formation would interfere with the dimerization of tris(1,3-diketonato)lanthanoid(III). Thus, we have measured the molecular weights of the *l*-moba complexes in ethanol, a donating solvent. The results indicate that the molecular weights are almost independent of concentration and fall in the range 1100—1200. It is obvious that the complexes forms adducts with one or two molecules of ethanol.

Difference spectral data of the complexes determined in benzene are given in Table 2. Each spectrum can be interpreted by means of free ionic terms. CD spectral data are also included in Table 2, and some of the spectra are shown in Figs. 4—6 as examples.

According to Richardson,[16] the interaction mechanisms between a metal ion and dissymmetric environment are classified into three: *i.e.,* (1) vicinal effect (chirality induced at the metal by the mere presence of asymmetric atom in the ligand), (2) conformational effect (chilarity arising from the asymmetric atom in a chelate ring), and (3) the configurational effect (chirality due to an asymmetric disposition of chelate rings about the metal). In general, optical activity arising from the vicinal effect is at least one order of magnitude smaller than that from the conformational effect[17] and two orders of magnitude smaller than that from the configurational effect.[18]

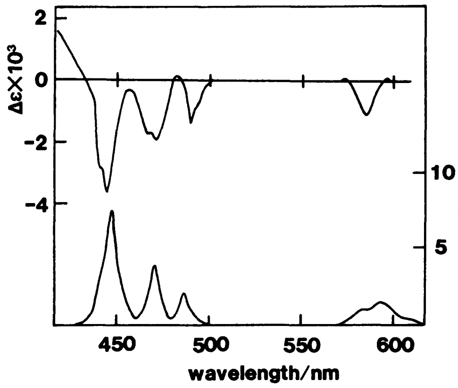

Fig. 4. Electronic and CD spectra of $[\mathrm{Pr}(l\text{-moba})_3(\mathrm{H_2O})]$ in benzene.

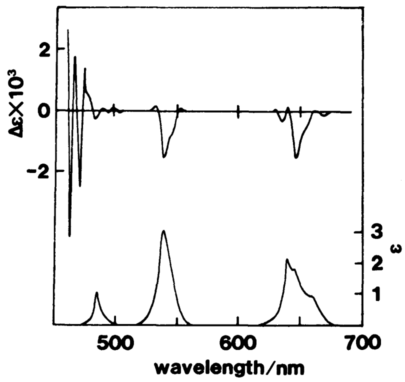

Fig. 5. Electronic and CD spectra of $[\mathrm{Ho}(l\text{-moba})_3]$ in benzene.

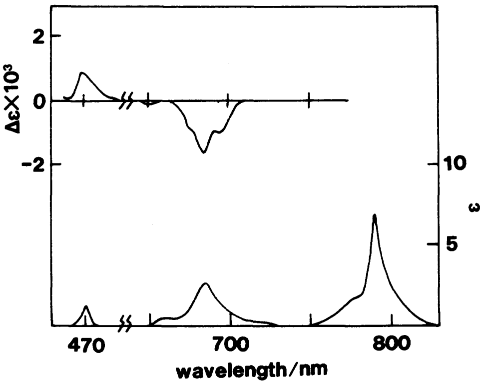

Fig. 6. Electronic and CD spectra of $[\mathrm{Tm}(l\text{-moba})_3]$ in benzene.

In the present complexes the chiral group is out of the chelate ring and far apart from the metal ion. Hence, the optical activity induced at the f-f transition region by its vicinal effect would be supposed to be very small on this ground. However, the CD intensities observed for the present complexes are considerably high and comparable to those of the complexes with L-amino acidate ions.[19,20] This clearly indicates that the optical activities of the complexes are caused by the configurational effect. Therefore the present study has revealed that the interligand noncovalent interaction can bring about a stereoselectivity of lanthanoid complexes in spite of the lability of lanthanoid ions for ligand substitutions. In the cases of the $\mathrm{Dy^{III}}$, $\mathrm{Ho^{III}}$, and $\mathrm{Tm^{III}}$ complexes, the main species present in benzene is monomeric anhydrate at the concentration ($\approx 10^{-2}$M 1M=1 mol dm^{-3}) for the CD measurements. Thus, it is quite reasonable to assume that the interligand CH/π-interaction operating between the *l*-menthyl and phenyl residues of *l*-moba$^-$ (Fig. 2) causes the stereoselectivity producing the *cis-Δ* isomer, by analogy with the cases of the 3d-transition metal complexes with *l*-moba.[9,11]

On the other hand, the $\mathrm{Pr^{III}}$ and $\mathrm{Eu^{III}}$ complexes are substantially dimeric in benzene solution at the concentration for the CD measurements. Observations of considerably intense CD bands in the f-f transition region for these complexes indicate the existence of a stereoselectivity in the dimers. The stereoselectivities in the dimers can also be attributed to the interligand noncovalent interaction, though the detail of the interaction in the dimers is not clear at present because of the lack of crystallographic data.

It is expected that the stereoselectivity effected by the interligand noncovalent interactions also takes place in the solvent adducts of the *l*-moba complexes. We measured CD spectrum of $[\mathrm{Dy}(l\text{-moba})_3]$ as a representative example in ethanol and compared it with the spectrum in benzene (Fig. 7). The CD spectrum in ethanol markedly differs from that of the monomeric [Dy(*l*-moba)$_3$] in benzene, implying the configurational change by the adduct formation. The considerably intense CD's in ethanol are indicative of a stereoselectivity in [Ln(*l*-moba)$_3$(EtOH)$_n$]. A similar stereoselectivity in the solvent adducts has been recognized for the lanthanoid complexes with the chiral 1,3-diketones derived from *d*-camphor.[4,15]

It is well known that Eu^{III} complexes with 1,3-diketones exhibit luminescence at the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions.[15,21–23] [Eu(*l*-moba)$_3$(H$_2$O)] also emits luminescence at 586 and 609 nm corresponding to the above transitions, respectively (Fig. 8). Interestingly, the intensity of the luminescence in benzene dramatically increases with the decrease of the concentration. Taking into account the monomer-dimer equilibrium of the complex, it is evident that the luminescence occurs only on the monomer. In relation to this, it should be noted that the Eu^{III} complexes with 1,3-diketones generally show only weak luminescence in nondonating solvents but its intensity is much enhanced on the addition of dimethyl sulfoxide to the solution.[15] Further, the adduct formations with "synergic agents" such as trioctylphosphine, tributyl phosphate, or dihexyl sulfoxide have been used to improve the quantum efficiency of luminescence[21]. Such enhancement of luminescence in these complexes can also be rationalized in terms of the shift of the monomer-dimer equilibrium to the monomeric species caused by the adduct formation with the solvent molecules or the synergic agents. It is generally accepted that the quantum efficiency of luminescence of lanthanoid complexes decreases when radiationless energy loss occurs in the excited state through the contact with other molecules, quenching impurities, or undesirable solvent molecules.[21] Therefore, the present results suggest that dimerization also facilitates nonradiative relaxation and thence greatly reduces the quantum efficiency of luminescence.

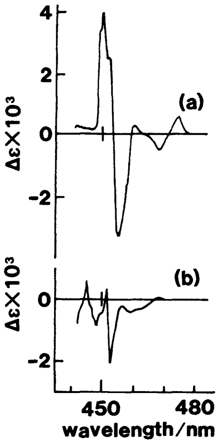

Fig. 7. CD spectra of [Dy(*l*-moba)$_3$]; (a) in benzene and (b) in ethanol.

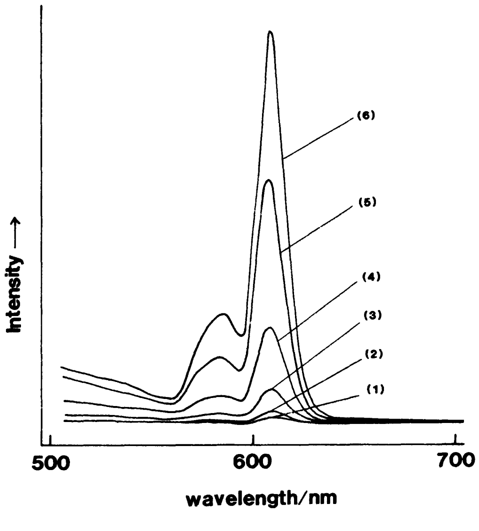

Fig. 8. Relative intensities of luminescence of [Eu(*l*-moba)$_3$(H$_2$O)] at various concentrations: (1): 3.681 $\times 10^{-2}$, (2): 1.841 $\times 10^{-2}$, (3): 1.104 $\times 10^{-2}$, (4): 7.362 $\times 10^{-3}$, (5): 3.681 $\times 10^{-3}$, and (6): 1.472 $\times 10^{-3}$ M.

In conclusion the present study has shown that the interligand CH/π-interaction causes the stereoselectivity in the monomers, dimers, and solvent-adducts of the lanthanoid complexes. Further, it is suggested that the interligand CH/π-interaction forms an insulating sheath to protect the complexes from dimerization and solvation, especially in the cases of smaller lanthanoid ions and in dilute solutions.

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