High Stereoselectivity of Tris[4-(*l*-menthyloxy)-1-(*p*-tolyl)-1,3-butandionato]lanthanoid(III)[1]

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Synopsis. Tris[4-(*l*-menthyloxy)-1-(*p*-tolyl)-1,3-butanedionato]lanthanoid(III), [Ln(*l*-moba-Me)$_3$](Ln=La, Pr, Nd, Eu, Gd, Dy, Ho, Er, Tm), showed a high stereoselectivity effected by intramolecular noncovalent interactions, giving rise to the cis-Δ form.

We have shown that interligand noncovalent interactions operate within a complex molecule and cause a high stereoselectivity of metal complexes to give rise to one of the possible stereoisomers.[2] In the case of tris[4-(*l*-menthyloxy)-1-phenyl-1,3-butanedionato]metal(III) [M(*l*-moba)$_3$] (M=Co, Cr, Mn, Ln-(lanthanoid ions)) the cis-Δ form is predominantly formed.[3,4] Further, it was found that tris[4-(*l*-menthyloxy)-1-(*p*-tolyl)-1,3-butanedionato]metal(III) [M(*l*-moba-Me)$_3$] (M=Co, Cr, Mn) showed a higher stereoselectivity compared with [M(*l*-moba)$_3$].[5] The configurational analysis for [Co(*l*-moba-Me)$_3$] by means of high resolution NMR spectroscopy has demonstrated that this complex is in pure cis-Δ form.[6] For our ultimate object to develope new stereoselective reactions by use of sterically-controlled lanthanoid complexes, it is desired to prepare new complexes of higher stereoselectivity. This paper deals with the synthesis and stereoselectivity of lanthanoid complexes with H(*l*-moba-Me).

Experimental

Preparations. H(*l*-moba-Me) was prepared by the method described previously.[5]

[Ln(*l*-moba-Me)$_3$]. H(*l*-moba-Me) (1×10^{-3} mole) and NaOH (1×10^{-3} mole) in ethanol (30 cm^3) were stirred for 30 min. To the resulted gelatinous solution was added lanthanoid(III) chloride (3.3×10^{-4} mole), and the mixture was stirred for 3 h. The reaction mixture was filtered, and the solvent was evaporated to dryness. The oily substance thus obtained was crystallized from ethanol.

Measurements. Electronic and circular dichroism spectra were recorded in benzene on a Shimadzu UV-215 Spectrophotometer and a JASCO J-500 Spectropolarimeter, respectively. Molecular weights were determined with a Hitachi Perkin-Elmer 115 Apparatus in benzene. The elemental analyses were obtained at the Elemental Analysis Service Center, Kyushu University.

Results and Discussion

The elemental analyses for the complexes (Table 1) suggest that all the complexes obtained can be described by the general formula [Ln(*l*-moba-Me)$_3$]. The molecular weight (1150) of [Eu(*l*-moba-Me)$_3$] determined at the 0.13 wt% concentration in benzene

Table 1. Elemental Analyses of Complexes

	Found(%)		Calcd(%)	
	C	H	C	H
[Pr(*l*-moba-Me)$_3$]	66.54	7.71	67.01	7.77
[Nd(*l*-moba-Me)$_3$]	66.97	7.87	66.81	7.74
[Eu(*l*-moba-Me)$_3$]	66.48	7.77	66.36	7.69
[Gd(*l*-moba-Me)$_3$]	65.80	7.70	66.05	7.65
[Dy(*l*-moba-Me)$_3$]	65.82	7.65	65.75	7.62
[Ho(*l*-moba-Me)$_3$]	65.49	7.69	65.61	7.60
[Er(*l*-moba-Me)$_3$]	65.20	7.71	65.48	7.59
[Tm(*l*-moba-Me)$_3$]	65.17	7.63	65.38	7.57

Table 2. Electronic and Circular Dichroism Spectral Data for Complexes

	AB	CD	
	wavelength /nm (ε)	wavelength/nm ($\Delta\varepsilon\times10^3$)	
[Pr(*l*-moba-Me)$_3$]	444(5.81)	446(−6.46)	
	448(6.38)	447(−4.87)	
	472(5.18)	472(−4.87)	
	486(2.28)	489(−3.56)	
	580(0.87)	589(−1.32)	
	594(1.52)		
[Nd(*l*-moba-Me)$_3$]	512(3.19)		
	528(7.61)	525(−2.73)	
	572(27.3)	571(−5.46)	
	582(42.9)	577(−7.59)	587(+5.82)
		587(−8.50)	
	680(0.44)		
[Eu(*l*-moba-Me)$_3$]	463(3.20)		
	433(0.40)	438(−2.30)	
[Dy(*l*-moba-Me)$_3$]	452(0.77)	449(+4.10)	452(+3.28)
		455(−5.17)	
[Ho(*l*-moba-Me)$_3$]	451(89.5)	450(+35.1)	
	460(28.5)	458(+12.0)	464(−10.1)
	468(8.14)	467(+5.29)	
	473(6.78)	470(−6.74)	
	484(7.46)		
	537(20.3)	533(+1.69)	538(−2.41)
[Er(*l*-moba-Me)$_3$]	488(2.14)	485(−1.07)	
	520(33.0)	518(+10.1)	
	523(25.7)	522(+8.26)	528(+0.93)
	542(0.69)	542(+0.93)	
[Tm(*l*-moba-Me)$_3$]	685(2.26)	683(−1.93)	
	662(0.50)	660(−0.43)	

ε: Extinction coefficient given in the unit dm^3 mole^{-1} cm^{-1}

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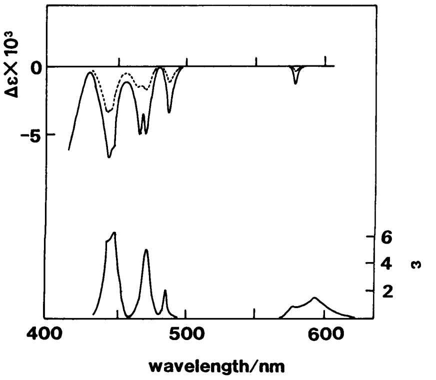

Fig. 1. Difference absorption and circular dichroism spectra of [Pr(*l*-moba-Me)$_3$] (——) and [Pr(*l*-moba)$_3$] (······). The absorption spectrum of [Pr(*l*-moba)$_3$] is essentially the same as that of [Pr(*l*-moba-Me)$_3$].

well agrees with the value (1140.4) for this composition, whereas the molecular weight (1260) at the 0.87 wt% is slightly larger. It is likely that [Ln(*l*-moba-Me)$_3$] dimerizes at a higher concentration, as demonstrated for the complexes with H(*l*-moba)[4] and other lanthanoid complexes with 1,3-diketones.[7] However, such a tendency to dimerize is much low compared with the *l*-moba complexes[4] as judged from the molecular weight measurements, and [Ln(*l*-moba-Me)$_3$] may be assumed to be practically monomeric in the concentration range ($\approx 10^{-2}$ M (1 mol dm^{-3})) for the electronic and circular dichroism spectral measurements.

In Table 2 are given spectral and circular dichroism spectral data in benzene. Electronic and circular dichroism spectra for [Pr(*l*-moba-Me)$_3$] are shown in Fig. 1 together with the circular dichroism spectrum of [Pr(*l*-moba)$_3$]. The Pr, Nd, Eu, Dy, Ho, Er, and Tm complexes show circular dichroism at the f–f transition bands. The CD intensities are significantly high and comparable to those of the L-amino acidato complexes.[8,9] This fact indicates that the optical activities observed are due to the configurational effect (disymmetry around the metal) but not the vicinal effect from the *l*-menthyl moiety. It is likely that the noncovalent interligand interaction occuring between the *l*-menthyl and *p*-tolyl groups leads to a controlled disposition of the *l*-moba-Me$^-$ molecules about the metal (Fig. 2). The preferred configuration of the complexes is assumed as cis-Δ by analogy with the case of [Co(*l*-moba-Me)$_3$] and [Cr(*l*-moba-Me)$_3$].[5]

As is seen in Fig. 1, the CD bands of f–f transitions of [Pr(*l*-moba-Me)$_3$] are more intense than those of

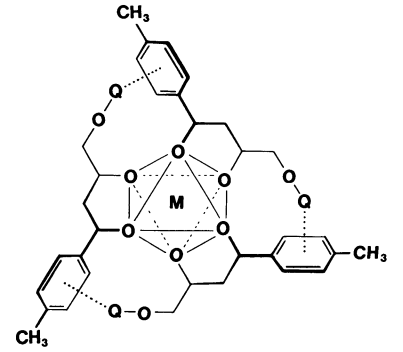

Fig. 2. Schematical representation of interligand interaction in [M(*l*-moba-Me)$_3$].

[Pr(*l*-moba)$_3$].[4] The same trend was observed for the Nd, Dy, Eu, Ho, and Tm complexes with *l*-moba and *l*-moba-Me (the comparison can not be made for the Gd and Er complexes because Gd complexes show no f–f band (and thence no CD) below 310 nm[10] and the Er complex of *l*-moba has not been obtained). This trend is the same as that found for the transition metal homologs.[5] Thus, it is revealed that the interligand *l*-menthyl/*p*-tolyl interaction is more effective than the *l*-menthyl/phenyl interaction also for lanthanoid complexes in causing the stereoselectivity of the complexes.

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