

Noncovalent Interactions in Metal Complexes. VII [1]. High Stereoselectivity in Tris{1-l-menthyloxy-3-(2-naphthoyl)acetonato}-M(III) (M = Co, Cr, Mn) Effected by Interligand CH/ π -interaction

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Abstract

Tris-{1-l-menthyloxy-3-(2-naphthoyl)acetonato}-M(III) complexes (M = Co, Cr, Mn) were synthesized and the stereoselectivities of the complexes were examined. The complexes exhibit intense circular dichroisms in the d-d band region, demonstrating the stereoselective formation of one of the enantiomers. The preferred configuration is shown to be *cis*- Δ in all the complexes. High stereoselectivities in the present complexes compared with those in tris(1-l-menthyloxy-3-benzoylacetono)M(III) complexes are discussed in terms of the intramolecular interligand CH/ π -interaction occurring between the aromatic and the l-menthyl residues.

Introduction

Noncovalent interactions are known to operate in some metal complexes and to play significant roles in the structure, stability, and other properties of the complexes [2]. Previously we have shown that tris(1-l-menthyloxy-3-benzoylacetono)M(III) complexes, [M(l-moba)₃] (M = Co, Cr, Mn), show a stereoselectivity to produce the *cis*- Δ isomer predominantly [3]. This was presumed to be due to the intramolecular interligand CH/ π -interactions operating between the phenyl group and the l-menthyl group. Since noncovalent interactions are generally enhanced when the π -system of an aromatic residue as an interacting counter-part becomes larger [4, 5], it is interesting to investigate the stereoselectivity of tris(1,3-diketono)M(III) complexes to determine the effect of the change in the aromatic residue of the ligand.

Thus, in this study we synthesized a new 1,3-diketone ligand, 1-l-menthyloxy-3-(2-naphthoyl)acetone (abbreviated as H(l-mona), Fig. 1), where the phenyl group of H(l-moba) is replaced with a naphthyl group, and its metal complexes [M(l-mona)₃] with cobalt(III), chromium(III), and manganese(III) ions.

The stereoselectivities of the complexes were

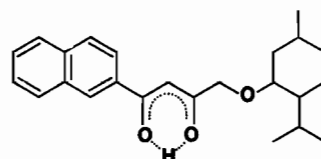


Fig. 1. Chemical structure of H(l-mona).

examined by means of circular dichroism (CD) spectra in comparison with those of [M(l-moba)₃], and are discussed in terms of the size of the aromatic residue in the interligand CH/ π -interaction.

Experimental

Syntheses

H(l-mona)

To a stirred mixture of ethyl l-menthyloxyacetate (10 g) and NaH (1.7 g) in dry ether (50 cm³) was added dropwise a solution of 2-acetylnaphthalene (7.2 g) in ether (80 cm³) at 45–50 °C. After the addition was completed, the stirring was continued at this temperature for additional 3 hrs. Then the reaction mixture was cooled with an ice-bath, and 30 cm³ of ethanol was added to decompose the reaction mixture. The mixture was made acidic by adding hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with ether (100 cm³). The combined ethereal solution was shaken with a saturated sodium bicarbonate solution and then with water. To the ether solution was added a solution of copper(II) acetate monohydrate (6 g) in aqueous ammonia (10%, 100 cm³), and the mixture was stirred vigorously to give a deep green mass of [Cu(l-mona)₂], recrystallized from chloroform–methanol. The yield was about 14 g.

Found: C, 64.66; H, 6.66%. Calcd for C₁₈H₂₈O₆·Cu·CHCl₃: C, 64.40; H, 6.51%.

The copper complex was dissolved in ether (200 cm³), and this solution was shaken vigorously with dilute sulfuric acid (20%, 100 cm³). The ether layer was separated, washed with a saturated sodium bicar-

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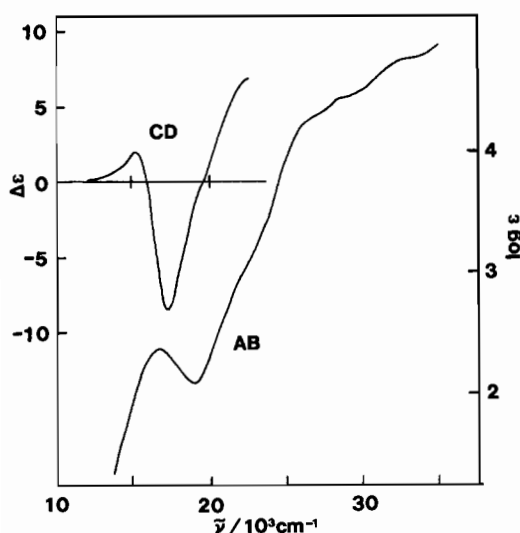


Fig. 2. Absorption (AB) and CD spectra of $[\text{Co}(\text{l-mona})_3]$.

bonate solution and then with water, and dried over anhydrous sodium sulfate. H(l-mona) was obtained as a pale yellow, oily substance on evaporating the solvent; it was used for the preparation of complexes without further purification.

$[\text{Co}(\text{l-mona})_3]$

To a stirred mixture of cobalt(II) hydroxycarbonate (0.10 g) and H(l-mona) (1.0 g) was added dropwise H_2O_2 (30%, 10 cm^3) at 90 °C. A crude product obtained as green oily substance was extracted with ether and submitted to column chromatography on alumina (2 × 10 cm) with ethanol as the eluent. When petroleum ether was added to the concentrated eluate, the complex precipitated as a green crystalline solid.

Found: C, 74.95; H, 7.82%. Calcd. for $\text{C}_{72}\text{H}_{87}\text{O}_9\text{Co}$: C, 74.85; H, 7.59%.

$[\text{Cr}(\text{l-mona})_3]$

A mixture of chromium(III) chloride hexahydrate (0.24 g), H(l-mona) (0.1 g), triethylamine (0.3 g), and active charcoal (0.1 g) in ethanol (20 cm^3) was refluxed for 12 hrs. The reaction mixture was filtered while hot, and chromatographed over alumina. On adding petroleum ether to the concentrated eluate, the complex was obtained as greenish brown solid.

Found: C, 74.28; H, 7.58%. Calcd for $\text{C}_{72}\text{H}_{87}\text{O}_9\text{Cr}\cdot\text{H}_2\text{O}$: C, 74.14; H, 7.69%.

$[\text{Mn}(\text{l-mona})_3]$

To a solution of manganese(II) chloride tetrahydrate (0.15 g) and H(l-mona) (1.0 g) in ether (30 cm^3) were added an aqueous solution (7 cm^3) of sodium acetate (0.12 g) and then an aqueous solu-

tion (5 cm^3) of potassium permanganate (0.03 g) with stirring. To the dark green solution thus formed was added sodium acetate (0.12 g), and the mixture refluxed for 10 min. On cooling the manganese(III) complex was obtained as a brown solid; it was recrystallized from a benzene-petroleum ether mixture to form brown plates.

Found: C, 75.00; H, 7.62%. Calcd for $\text{C}_{72}\text{H}_{87}\text{O}_9\text{Mn}$: C, 75.11; H, 7.62%.

Measurements

Electronic spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 in carbon tetrachloride. Circular dichroism spectra were recorded on a JASCO J-500C Spectropolarimeter, using the same solvent.

Results and Discussion

Electronic and CD spectra of $[\text{Co}(\text{l-mona})_3]$ are shown in Fig. 2. The electronic spectrum resembles the spectra of other *tis*(1,3-diketonato)cobalt(III) complexes [6–8]. Intense circular dichroisms were observed at 15.2×10^3 and 17.2×10^3 cm^{-1} , which are the ${}^1\text{A}_1 \rightarrow {}^1\text{A}_2$ and ${}^1\text{A}_1 \rightarrow {}^1\text{E}$ components of the octahedral ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ transition under D_3 symmetry [8].

It is known that a metal ion interacts with an asymmetric environment through three major mechanisms [9]: (1) vicinal effect (chirality induced at the metal by the simple presence of an asymmetric atom of the ligand), (2) conformational effect (chirality 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 [10] and two orders of magnitude smaller than that from the configurational effect [11].

In $[\text{Co}(\text{l-mona})_3]$ the chiral group is far apart from the chelate ring. Hence the optical activity induced at the d–d band region by its vicinal effect should be very small. However, the circular dichroisms observed at 15.2×10^3 and 17.2×10^3 cm^{-1} are so intense as to attribute the chirality to the configurational origin. Indeed, its CD is higher than that of optically pure $[\text{Co}(\text{acac})_3]$ [12, 13]. In comparison with the spectrum of $\Delta\text{-}[\text{Co}(\text{acac})_3]$ [13] (a positive CD at 15.9×10^3 cm^{-1} and a negative CD at 17.6×10^3 cm^{-1}), the configuration of the present complex can be determined to be Δ . In analogy with the case of the l-moba complexes [3], it is likely that the stereoselectivity of the complex is brought about by the interligand CH/ π -interaction between the naphthyl group and the l-menthyl group, as shown schematically in Fig. 3. Such CH/ π -interaction should stabilize

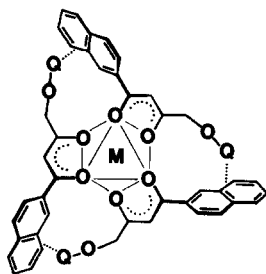


Fig. 3. Schematic representation of interligand CH/ π -interaction in $[M(l-mona)_3]$ (Q = 1-menthyl).

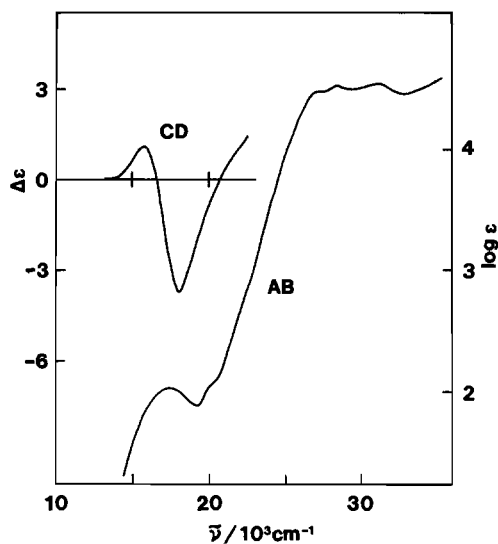


Fig. 4. Absorption and CD spectra of $[Cr(l-mona)_3]$.

the *cis*- Δ isomer in more than a few kilocalories per mole relative to other isomers.

Electronic and CD spectra of $[Cr(l-mona)_3]$ are shown in Fig. 4. The electronic spectrum resembles the spectra of other tris(1,3-diketonato)chromium(III) complexes [14, 15]. $[Cr(l-mona)_3]$ exhibits a positive CD at $15.8 \times 10^3 \text{ cm}^{-1}$ and a negative CD at $18.1 \times 10^3 \text{ cm}^{-1}$, which correspond to the ${}^4A_2 \rightarrow {}^4A_2$ and ${}^4A_2 \rightarrow {}^4E$ components of the octahedral ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition under D_3 symmetry [14]. The CD intensities are very high and are comparable to the CD intensities of optically pure Δ - $[Cr(acac)_3]$ [16]. This clearly demonstrates the chirality of the complex to be configurational in origin. The preferred configuration of this complex is determined to be Δ , based on the identical CD pattern with that of Δ - $[Cr(acac)_3]$ [16] in the visible region. It is natural to suppose that the interligand CH/ π -interaction (Fig. 3) produces the *cis*- Δ isomer predominantly, though the resolution of the enantiomers seems to be incomplete in this case (judging from the CD intensities, lower than those of pure Δ - $[Cr(acac)_3]$).

Electronic and CD spectra of $[Mn(l-mona)_3]$ are shown in Fig. 5. The electronic spectrum exhi-

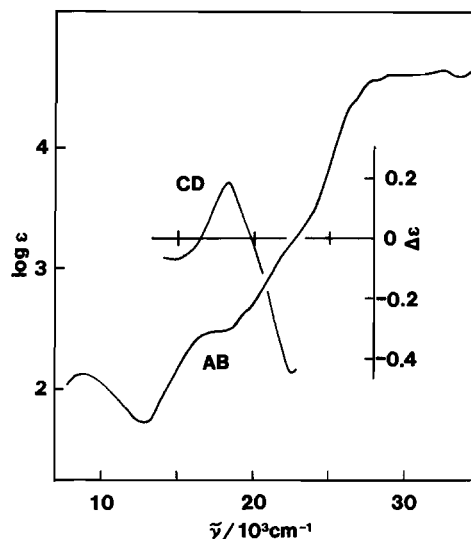


Fig. 5. Absorption and CD spectra of $[Mn(l-mona)_3]$.

bits d-d bands at 8.6×10^3 , 16.5×10^3 , and $\sim 22 \times 10^3 \text{ cm}^{-1}$, which are usually observed for $[Mn^{III}O_6]$ chromophore with a distorted configuration from Oh symmetry [17]. Contrary to the general observation that tris(1,3-diketonato)manganese(III) complexes are hardly resolved because of their lability for ligand substitution [18], $[Mn(l-mona)_3]$ shows fairly intense circular dichroisms at 18.3×10^3 and $22.2 \times 10^3 \text{ cm}^{-1}$. Again we presume that the interligand CH/ π -interaction brings about the stereoselectivity leading to the predominant formation of the *cis*- Δ isomer. However, the optical purity of this complex is not known because the manganese(III) complexes with 1,3-diketones have not yet been resolved.

Thus, it is established that the interligand CH/ π -interaction brings about a high stereoselectivity in $[M(l-mona)_3]$ to produce the *cis*- Δ isomer. CD spectral results of the complexes are given in Table I, together with those of $[M(l-moba)_3]$ for comparison. Since the extinction coefficient of the d-d band under consideration is essentially the same between $[M(l-mona)_3]$ and $[M(l-moba)_3]$, we adopt the ratio of the CD intensity of a l-mona complex to that of the corresponding l-moba complex, $\bar{r} = \Delta\epsilon(l-mona)/\Delta\epsilon(l-moba)$ (average value for two CD bands), as a measure of stereoselectivity. The \bar{r} value is larger than unity in all the cases. It is evident that the stereoselectivity is enhanced by replacing the phenyl group with the naphthyl group, especially in the cases of the chromium(III) and manganese(III) complexes. The higher stereoselectivities in $[M(l-mona)_3]$ may be rationalized by the strengthened CH/ π -interaction in the naphthyl/menthyl pair compared with the phenyl/menthyl pair, because of the larger π -system of the naphthyl group when compared with the phenyl group.

TABLE I. CD Spectral Data for [M(l-mona)₃] and [M(l-moba)₃].

M(III)	$\Delta\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ($\bar{\nu}/10^3 \text{ cm}^{-1}$)				$\bar{\Gamma}^a$
	[M(l-mona) ₃]		[M(l-moba) ₃]		
Co(III)	+2.0 (15.2)	-8.5 (17.2)	+1.6 (15.2)	-6.1 (17.4)	1.3
Cr(III)	+1.16(15.8)	-3.73(18.1)	+0.56(15.5)	-1.60(18.5)	2.2
Mn(III)	+0.18(18.3)	-0.44(22.2)	+0.10(18.0)	-0.24(22.0)	1.8

^a $\bar{\Gamma} = \Delta\epsilon(\text{l-mona})/\Delta\epsilon(\text{l-moba})$; average value for two CD bands.

In the previous paper [3] we pointed out that the optical activity of [Co(l-moba)₃] is higher than that of optically pure [Co(acac)₃]. From the present study the following order in the optical activity is deduced for the cobalt(III) complexes: [Co(l-mona)₃] > [Co(l-moba)₃] > optically pure [Co(acac)₃]. This suggests the operation of a secondary effect to the optical activity in addition to the configurational effect. Though a detailed interpretation is difficult at present because of the lack of structural information, it is plausible that the interligand CH/ π -interaction (Fig. 3) more or less enhances the distortion from Oh toward D₃ symmetry in the coordination geometry, relative to the case of the simple Δ configuration such as Δ -[Co(acac)₃].

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