November, 1985] © 1985 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 58, 3377—3378 (1985) 3377

Substituent Effect on Stereoselectivity for Cobalt(III), Chromium(III), and Manganese(III) Complexes of Ring-substituted 1-*l*-Menthyloxy-3-benzoylacetones[1)]

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(Received June 14, 1985)

Synopsis. Stereoselectivities of tris(1-*l*-menthyloxy-3-benzoylacetonato)M(III) ([M(*l*-moba)$_3$] (M=Co^{III}, Cr^{III}, Mn^{III})) and its homologs [M(*l*-moba-Br)$_3$] and [M(*l*-moba-Me)$_3$] (possessing bromo and methyl substituents at the 4-position of the aromatic ring, respectively) were examined by CD spectra. The stereoselectivity increased in the order [Co(*l*-moba-Br)$_3$]<[Co(*l*-moba)$_3$]<[Co(*l*-moba-Me)$_3$], and this trend was explained in terms of the electronic effect of the substituents on the interligand CH/π-interaction.

In the previous paper we showed that tris(1-*l*-menthyloxy-3-benzoylacetonato)M(III) complexes, [M(*l*-moba)$_3$] (M=Co^{III}, Cr^{III}, Mn^{III}), were obtained predominantly in one isomer, *cis-Δ*, probably because of the intramolecular, interligand CH/π-interactions operating between the phenyl and the *l*-menthyl groups (Fig. 1, R=H).[2)] The interligand CH/π-interaction was supported by the enhanced selectivities in tris{1-*l*-menthyloxy-3-(2-naphthoyl)acetonato}M(III) complexes[3)], [M(*l*-mona)$_3$], compared with those in [M(*l*-moba)$_3$] because the π-system of the naphthyl group which is larger than the phenyl group give rise to a more efficient interaction with the *l*-menthyl group.

In order to obtain further evidences for the CH/π-interaction, we prepared in this study H(*l*-moba) homologs with bromo and methyl substituents at the 4-position of the aromatic ring (abbreviated as H(*l*-moba-Br) and H(*l*-moba-Me), respectively), and the stereoselectivities of their cobalt(III), chromium(III), and manganese(III) complexes were examined in comparison with those of [M(*l*-moba)$_3$].

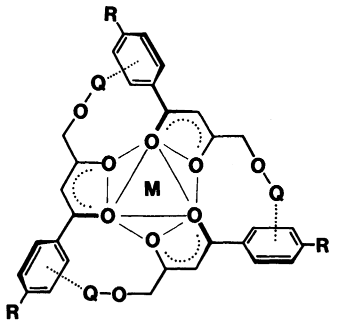

Fig. 1. Schematical representation of interligand CH/π-interaction supposed for [M(*l*-moba-R)$_3$] (Q=*l*-menthyl)

Table 1. Elemental analyses of the complexes

Complex	Found(%)		Calcd(%)	
	C	H	C	H
Co(*l*-moba-Br)$_3$·H$_2$O	57.63	6.37	57.20	6.40
Cr(*l*-moba-Br)$_3$·3H$_2$O	55.79	6.50	55.91	6.51
Co(*l*-moba-Me)$_3$	72.28	8.50	72.25	8.37
Cr(*l*-moba-Me)$_3$	72.60	8.51	72.73	8.45
Mn(*l*-moba-Me)$_3$	71.37	8.38	71.29	8.45

Experimental

H(*l*-moba-Br) and H(*l*-moba-Me) were synthesized in a way similar to that for H(*l*-moba), using *p*-bromoacetophenone and *p*-methylacetophenone instead of acetophenone, respectively.[2)]

The metal complexes, [M(*l*-moba-Br)$_3$] and [M(*l*-moba-Me)$_3$] (M=Co^{III}, Cr^{III}, Mn^{III}), were prepared in the same way as that of [M(*l*-moba)$_3$].[2)] The elemental analyses for the complexes are given in Table 1.

The electronic and circular dichroism (CD) spectra were measured in carbon tetrachloride on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 and a JASCO J-500C Spectropolarimeter, respectively.

Results and Discussion

The spectral data are listed in Table 2. The electronic spectra of the cobalt complexes closely resemble those of previously reported tris(1,3-diketonato)cobalt(III) complexes.[2–5)] In Fig. 2 the spectrum of [Co(*l*-moba-Me)$_3$] is shown with the CD spectrum as an example. [Co(*l*-moba-Me)$_3$] exhibits intense circular dichroism in the d-d band region, a positive CD at 15.2×10^3 cm^{-1}($\Delta\varepsilon$=+2.27) and a negative CD at 17.3×10^3 cm^{-1}($\Delta\varepsilon$=−10.00), demonstrating that the chirality is configurational in

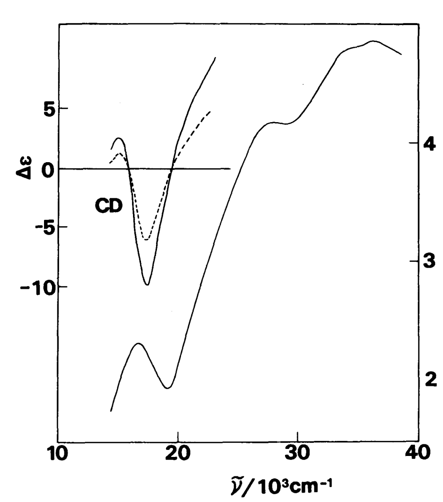

Fig. 2. Electronic and CD spectra of [Co(*l*-moba-Me)$_3$] (——) and [Co(*l*-moba)$_3$] (----) in carbon tetrachloride.

TABLE 2. ELECTRONIC AND CD SPECTRAL DATA IN CARBON TETRACHLORIDE

	CD[a] $\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1} ($\tilde{\nu}$/10^3 cm^{-1})		Absorption $\tilde{\nu}$/10^3 cm^{-1} (log ε)
[Co(*l*-moba-Br)$_3$]	+0.32(15.1)	− 1.73(17.3)	16.6(2.24), 27.4(sh), 35.1(sh), 36.8(4.80)
[Co(*l*-moba-Me)$_3$]	+2.36(15.2)	−10.00(17.3)	16.6(2.28), 27.5(4.16), 35.4(sh), 36.8(4.82)
[Cr(*l*-moba-Br)$_3$]	+0.17(15.9)	− 0.74(18.3)	17.1(2.03), 21.7(4.41), 32.0(4.42) 37.3(4.57)
[Cr(*l*-moba-Me)$_3$]	+0.79(16.2)	− 3.90(18.4)	17.6(2.02), 27.5(4.46), 32.3 (sh) 34.7(sh), 37.0(4.51)
[Mn(*l*-moba-Me)$_3$]	+0.15(18.2)	− 0.33(21.9)	8.0(2.18), 16.7(sh), 22.2(sh), 26.3(sh), 32.3(4.63), 38.5(4.42)

a) CD spectral data for [M(*l*-moba)$_3$]: +1.6(15.2) −6.1(17.4) for [Co(*l*-moba)$_3$], +0.56(15.9) −1.60(18.5) for [Cr(*l*-moba)$_3$], and +0.10(18.0) −0.24(22.0) for [Mn(*l*-moba)$_3$].

origin. The CD pattern is the same as that of [Co(*l*-moba)$_3$], but the intensity is much higher than that of [Co(*l*-moba)$_3$] as seen in Fig. 2. In comparison with the CD spectra of *Λ*-[Co(acac)$_3$][5] and [Co(*l*-moba)$_3$],[2] the preferred configuration of [Co(*l*-moba-Me)$_3$] was shown to be of *cis*-*Δ*. Similarly, the circular dichroism of [Co(*l*-moba-Br)$_3$] exhibited the same pattern as that of [Co(*l*-moba)$_3$][2] and [Co(*l*-mona)$_3$][3] in the d-d band region. However, its CD intensity was weaker than that of [Co(*l*-moba)$_3$] (See Table 2).

The electronic spectra of [Cr(*l*-moba-Br)$_3$] and [Cr(*l*-moba-Me)$_3$] resemble those of tris(1,3-diketonato)chromium(III) complexes previously reported.[2,6,7] Their CD spectral pattern in the visible region indicated the predominant formation of the *cis*-*Δ* isomer.[2]

The manganese complex [Mn(*l*-moba-Me)$_3$] also showed fairly intense CD at 18.2×10^3 and 21.9×10^3 cm^{-1}. It is presumed that the *cis*-*Δ* isomer also predominates in this case by analogy with the case of the cobalt(III) and chromium(III) complexes.

Thus, all the complexes showed a stereoselectivity which led to the formation of the *cis*-*Δ* isomer. From Table 2, it is seen that the CD intensity induced at the d-d band region increases generally in the order, [M(*l*-moba-Br)$_3$]<[M(*l*-moba)$_3$]<[M(*l*-moba-Me)$_3$], for each metal ion, suggesting the stereoselectivity enhanced in this order provided that the CD intensity of the *cis*-*Δ* isomer is not significantly affected by the substituents on the ring. The trend can be reasonably explained in terms of the electronic effect of the substituents on the ring. That is, the π-electron density of the ring should increase in the order 4-BrC$_6$H$_4$<C$_6$H$_5$<4-CH$_3$C$_6$H$_5$, and thence the interligand CH/π-interaction (Fig. 1) becomes more effective in this order.

The authors are grateful to Mr. Y. Hisaeda for measuring CD spectra.

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