

Table XI. Net Atomic Charges on Cations and Ligands in Cation-Clay-Hydration Complexes

	M	O <sub>W</sub> <sup>a</sup>	O <sub>W</sub> <sup>b</sup>	O <sub>P</sub> <sup>-c</sup>	N <sub>7</sub>
Zn <sup>2+</sup>	2.0+				
5'-AMP				0.68-	0.28-
Zn·6H <sub>2</sub> O	0.90+		0.56-		
Zn·5'-AMP					
type I	0.53+		0.47-	0.47-	0.41-
type II	0.59+	0.59-	0.50-	0.55-	0.26-
type III	0.61+		0.47-	0.48-	0.25-
Mg <sup>2+</sup>	2.0+				
5'-AMP				0.68-	0.28-
Mg·6H <sub>2</sub> O	1.53+		0.63-		
Mg·5'-AMP					
type II	0.90+	0.70-	0.54-	0.55-	0.38-
type III	0.91+		0.51-	0.61-	0.26-

<sup>a</sup> H<sub>2</sub>O bound to cation and to phosphate oxygen. <sup>b</sup> H<sub>2</sub>O bound to cation. <sup>c</sup> Phosphate oxygen bound to cation.

mation. Thus, steric considerations appear to favor the formation of 4-coordinated, rather than 6-coordinated, metal-nucleotide-water complexes in the clay, consistent with the model of complex formation (eq 1) used in this study.

### Conclusion

In this study we have characterized the binding of 5'-AMP, 5'-IMP, 5'-GMP, 2'-AMP, and 3'-AMP to hydrated Zn<sup>2+</sup> and Mg<sup>2+</sup>, a process presumed to occur when they are adsorbed

in the interlamellar space of ion-exchanged homionic bentonite clays. The energetics of complex formation and modes of cation-nucleotide binding obtained appear to account for the three types of specificities observed: the preference (1) of Zn<sup>2+</sup>-exchanged clays for 5'-AMP > 5'-IMP ≥ 5'-GMP, (2) of Zn<sup>2+</sup>-exchanged clays for 5'-AMP > 2'-AMP > 3'-AMP, and (3) of 5'-AMP for Zn<sup>2+</sup>- rather than Mg<sup>2+</sup>-exchanged clays. In addition, Zn<sup>2+</sup> has been shown to bind to the clay more strongly than Mg<sup>2+</sup>, in keeping with the observed ability of Zn<sup>2+</sup> to displace Mg<sup>2+</sup> from bentonite clay. Also, the preference of Mg<sup>2+</sup> for phosphate-site binding and of Zn<sup>2+</sup> for N<sub>7</sub>-phosphate bridge binding has been clearly demonstrated for 5'-nucleotides. Finally, differences in mode of binding of Zn<sup>2+</sup> to different nucleotides and of Mg<sup>2+</sup> and Zn<sup>2+</sup> for 5'-AMP could account for some, but not all, of the differences in availability of exchangeable sites of nucleotide binding. These results strongly implicate direct cation-nucleotide complex formation in the adsorption of nucleotides on homionic clays and imply that such complexes could then be involved in subsequent polymerizations.

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**Registry No.** 5'-AMP, 61-19-8; 5'-IMP, 131-99-7; 5'-GMP, 85-32-5; 2'-AMP, 130-49-4; 3'-AMP, 84-21-9; Zn, 7440-66-6; Mg, 7439-95-4.

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## Noncovalent Interactions in Metal Complexes. 3.<sup>1</sup> Stereoselectivity Caused by Interligand, Hydrophobic CH...π Interaction in 1-*l*-Menthoxo-3-benzoylacetato Complexes

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Bivalent and trivalent metal complexes of 1-*l*-menthoxy-3-benzoylacetone (H(*l*-moba)) have been synthesized and characterized by means of NMR, electronic absorption, and circular dichroism spectra. On the basis of the NMR spectrum, it was demonstrated that the *cis* isomer was preferentially formed in the case of [Co(*l*-moba)<sub>3</sub>]. CD spectra revealed that [Co(*l*-moba)<sub>3</sub>] was almost optically pure without any effort for resolution, while [Cr(*l*-moba)<sub>3</sub>] was partly resolved. [Mn(*l*-moba)<sub>3</sub>] was also shown to be optically active. The absolute configurations of [Co(*l*-moba)<sub>3</sub>] and [Cr(*l*-moba)<sub>3</sub>] were determined to be of the Δ form, the same configuration being supposed for [Mn(*l*-moba)<sub>3</sub>]. Selective syntheses of the *cis*-Δ isomer for [M(*l*-moba)<sub>3</sub>] have been interpreted in terms of the interligand, hydrophobic CH...π interaction operating between the phenyl and the chiral *l*-menthyl groups.

### Introduction

Hydrophobic interactions are known to occur in biomolecules and to contribute to forming a distinct structural conformation, which provides the specificity required in most biological processes.<sup>2</sup> Such hydrophobic interactions occur between two aliphatic (or alicyclic) groups, between two aromatic groups, and between aliphatic and aromatic groups. In the cases of metal complexes of low molecular weight, interligand hydrophobic interactions may provide distinct features in stability, structure, and reactivity.<sup>1,3,4</sup> Stability enhancement of ternary complexes owing to hydrophobic ring-ring stacking has been well documented by Sigel and co-workers.<sup>3</sup> Recently, Fisher and Sigel showed that the interligand interaction operating between aromatic and aliphatic

groups increases the stability of the ternary complexes containing an amino acid and bipyridyl or *o*-phenanthroline.<sup>4</sup> However, recognition of interligand, hydrophobic interaction in metal complexes has been restricted mostly to stability, and there has been very few applications of this effect to selective syntheses and reactions.<sup>5</sup>

In the preceding papers<sup>1,5</sup> we have shown that in the cobalt(III) complexes with Schiff bases derived from *l*-menthyl β-(2-hydroxybenzoyl)propionate and amino acids, the hydrophobic CH...π interaction between the aromatic ring and the chiral *l*-menthyl group induces an asymmetry around the metal ion (the term "hydrophobic CH...π interaction" will be adopted to describe the interaction operating between an aromatic ring and an alkyl or an alicyclic group). By the use of these optically active complexes, partial asymmetric transformations of racemic amino acids to give one optical isomer were achieved.<sup>5</sup> Thus, interligand, hydrophobic interactions can be applicable for selective syntheses of geo-

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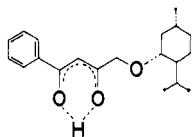


Figure 1. Structure of H(*l*-moba).

metrical isomers and for stereospecific reactions of complexes.

In order to demonstrate further this interligand, hydrophobic CH $\cdots\pi$  interaction in the selective syntheses of geometrical and optical isomers of complexes, we have synthesized some bivalent and trivalent metal complexes of a new 1,3-diketone, 1-*l*-menthoxy-3-benzoylacetone (abbreviated as H(*l*-moba), Figure 1), which contains phenyl and chiral *l*-menthyl groups in the molecule. Although these two groups are much separated from each other in the ligand molecule, hydrophobic CH $\cdots\pi$  interaction must be possible between the phenyl group of one ligand and the *l*-menthyl group of the other ligand within a complex if two or three *l*-moba $^-$  ions appropriately coordinate to a metal ion. Thus, the structures of the complexes have been examined and discussed in relation to the stereoselectivity induced by the interligand, hydrophobic CH $\cdots\pi$  interaction.

### Experimental Section

**Syntheses. Ethyl *l*-Menthoxycetate.** This was readily prepared by the reaction of *l*-menthoxyacetyl chloride<sup>6</sup> and absolute ethanol. Excess ethanol was removed by vacuum distillation, and the remaining pale yellow, oily substance was used for preparing the ligand without further purification.

**H(*l*-moba).** To a stirred mixture of ethyl *l*-menthoxyacetate (10.0 g) and NaH (1.6 g) in dry ether (100 mL) was added dropwise a solution of acetophenone (5.0 g) in ether (30 mL) at 45 °C over a period of 30 min. After the addition was complete, stirring at this temperature was continued for additional 2 h. The reaction mixture was cooled with ice water, and unreacted NaH was decomposed by adding ethanol (50 mL). Then, acetic acid (10 mL) was added, and the mixture was stirred for 1 h to form two layers. The upper ethereal layer was separated and the lower layer was extracted twice with 50-mL portions of ether. The combined ethereal solution was shaken with saturated sodium bicarbonate solution and then with water. To this solution was added a solution of copper(II) acetate hydrate (2.0 g) in ammonia water (10%, 100 mL), and the mixture was vigorously stirred to give deep green mass of [Cu(*l*-moba)<sub>2</sub>]. It was collected and recrystallized from ether. The yield was about 4 g.

The copper complex was dissolved in ether (200 mL), and this solution was vigorously shaken with sulfuric acid (20%, 100 mL). The ether layer was separated, washed with saturated sodium bicarbonate solution and then with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent left H(*l*-moba) as a pale yellow, oily substance. The yield was 3.1 g. Anal. Calcd for C<sub>20</sub>H<sub>27</sub>O<sub>3</sub>: C, 76.16; H, 8.63. Found: C, 76.52; H, 8.74.

**[Cu(*l*-moba)<sub>2</sub>].** This complex was obtained as deep green prisms as described above. It was also obtained by the reaction of H(*l*-moba) (1.6 g) and ammoniacal solution of copper(II) acetate hydrate (0.5 g). Anal. Calcd for C<sub>40</sub>H<sub>52</sub>O<sub>6</sub>Cu: C, 69.16; H, 7.84. Found: C, 69.52; H, 8.08.

**[Ni(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].** To an ammoniacal solution of nickel(II) acetate tetrahydrate (0.6 g) was added H(*l*-moba) (1.6 g), and the mixture was stirred for 1 h to give pale green mass. It was collected and recrystallized from a chloroform-methanol mixture to give pale green crystals. Anal. Calcd for C<sub>40</sub>H<sub>56</sub>O<sub>8</sub>Ni: C, 66.21; H, 8.05. Found: C, 66.17; H, 8.02.

**[Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].** The synthetic method for the preparation of this complex is nearly the same as that for [Ni(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]. It forms pink prisms. Anal. Calcd for C<sub>40</sub>H<sub>56</sub>O<sub>8</sub>Co: C, 66.19; H, 8.05. Found: C, 65.94; H, 7.95.

**[Mn(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].** This complex was obtained by the reaction of manganese(II) acetate tetrahydrate (0.6 g) and the ligand (1.6 g) in water (70 mL). The yellow mass thus obtained was collected and

recrystallized from a chloroform-methanol mixture. Anal. Calcd for C<sub>40</sub>H<sub>56</sub>O<sub>8</sub>Mn: C, 66.55; H, 8.09. Found: C, 66.48; H, 8.15.

**[Co(*l*-moba)<sub>3</sub>].** Cobalt(II) hydroxycarbonate (0.15 g) and the ligand (1.0 g) were placed in a 200-mL beaker and warmed at 90 °C on a water bath. When hydrogen peroxide (10%, 30 mL) was slowly added on this mixture with vigorous stirring, the reaction mixture assumed an intense green color. After being cooled to room temperature, the complex was extracted with ether. Evaporation of ether left a green, oily substance. It was dissolved in benzene, and the benzene solution was passed through an alumina column (15 × 100 mm). The eluent was concentrated to ca. 5 mL, diluted with dry ether (5 mL), and left to stand overnight in a refrigerator to give green prisms.

This complex was also obtained by the air oxidation of [Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] in the presence of the free ligand as follows. To a solution of H(*l*-moba) (0.3 g) and [Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (0.7 g) in a chloroform-ethanol mixture (1:1, 100 mL) was added charcoal (0.3 g), and air was bubbled through this solution for 10 h. The reaction mixture, which assumed a green color, was passed through an alumina column (10 × 100 mm), and the eluent was slowly concentrated to give green prisms.

The same complex was also obtainable by the reaction of the ligand and K<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>]·3H<sub>2</sub>O, in nearly the same way as that for preparing tris(benzoylacetato)cobalt(III), [Co(bzac)<sub>3</sub>].<sup>7</sup> Anal. Calcd for C<sub>60</sub>H<sub>78</sub>O<sub>9</sub>Co: C, 71.69; H, 8.12. Found: C, 71.75; H, 8.34.

**[Cr(*l*-moba)<sub>3</sub>].** To a solution of chromium(III) chloride tetrahydrate (0.23 g) and the ligand (1.0 g) in ethanol (150 mL) were added charcoal (0.3 g) and triethylamine (0.1 g). The mixture was refluxed for 12 h. The charcoal was separated by filtration. The filtrate was concentrated to ca. 30 mL and left to stand overnight in a refrigerator. The green crystals which separated were collected and recrystallized from benzene. Anal. Calcd for C<sub>60</sub>H<sub>78</sub>O<sub>9</sub>Cr: C, 72.19; H, 8.18. Found: C, 71.71; H, 8.19.

**[Mn(*l*-moba)<sub>3</sub>].** Manganese(II) chloride tetrahydrate (0.12 g) and H(*l*-moba) (2.0 g) were dissolved in ethanol (70 mL). To this was added an aqueous solution (15 mL) of sodium acetate (0.4 g) and then an aqueous solution (10 mL) of potassium permanganate (0.013 g) with stirring. The solution became dark green. Additional sodium acetate (0.4 g) was added to the solution, and the mixture was heated at 70 °C for 10 min. When the reaction mixture was cooled by means of ice water, a dark green mass was obtained. It was dissolved in benzene, and the solution was passed through an alumina column (15 × 100 mm). The eluent was concentrated to 10 mL, diluted with petroleum ether (10 mL), and kept in a refrigerator to give dark green plates. Anal. Calcd for C<sub>60</sub>H<sub>78</sub>O<sub>9</sub>Mn: C, 71.97; H, 8.15. Found: C, 72.14; H, 8.28.

**[Fe(*l*-moba)<sub>3</sub>]·2C<sub>6</sub>H<sub>14</sub>.** To an ethanolic solution (50 mL) of anhydrous iron(III) chloride (0.16 g) and H(*l*-moba) (0.9 g) was added an aqueous solution (10 mL) of sodium acetate (0.15 g). The mixture was left to stand overnight at room temperature to give a brick red solid. It was collected by filtration and recrystallized from hexane as red crystals, which contain 2 molecules of hexane/iron atom. Anal. Calcd for C<sub>72</sub>H<sub>106</sub>O<sub>9</sub>Fe: C, 73.63; H, 9.31. Found: C, 74.14; H, 9.31.

**Physical Measurements.** The NMR spectra were measured on a Hitachi NMR spectrometer Model R-20-B in carbon tetrachloride using tetramethylsilane as an internal standard. The electronic and CD spectra were measured in carbon tetrachloride or in benzene on a Shimadzu multipurpose spectrophotometer Model MSP-5000 and a JASCO ORD/CD optical dispersion recorder, respectively. The infrared spectra were measured with a Hitachi infrared spectrometer Model 215 on KBr disks or with Nujol mulls. The magnetic susceptibilities were measured by the Faraday method. The elemental analyses were carried out by the Elemental Analysis Service Center, Kyushu University.

### Results and Discussion

The proton NMR spectrum of H(*l*-moba) is given in Figure 2a. A broad signal around 15.8 ppm can be assigned to the enol proton.<sup>8,9</sup> Aromatic proton signals were found in the region of 7.3–8.0 ppm. On the basis of the intensity ratio and the shielding effect of the chelate ring, signals at 7.85–7.95

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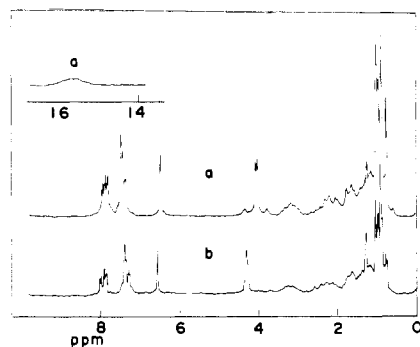


Figure 2. NMR spectra of (a) H(*l*-moba) and (b) [Co(*l*-moba)<sub>3</sub>].

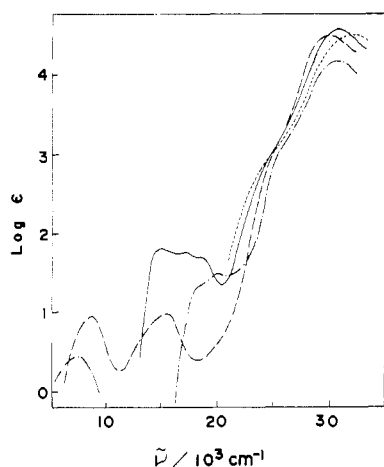


Figure 3. Electronic absorption spectra in chloroform of (—) [Cu(*l*-moba)<sub>2</sub>], (---) [Ni(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (---) [Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], and (---) [Mn(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].

ppm are assigned to the ortho protons and the signals at 7.33–7.45 ppm to the meta and para protons.<sup>9</sup> The signal from the methine proton on the chelate ring appeared at 6.47 ppm. The AB quartet around 4 ppm can be assigned to the methylene proton adjacent to the *l*-menthoxy group. This spectral feature clearly indicates that H(*l*-moba) exists as the keto–enol form in carbon tetrachloride, as do other 1,3-diketones.<sup>8,9</sup> In the liquid state, however, H(*l*-moba) showed IR bands at 1680 and 1600 cm<sup>-1</sup>, revealing the existence of both the diketo and the keto–enol forms.<sup>8</sup> The band at 1680 cm<sup>-1</sup> disappeared on complexation, and new bands appeared in the region 1500–1600 cm<sup>-1</sup>.

The magnetic moments of [Cu(*l*-moba)<sub>2</sub>], [Ni(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], and [Mn(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] are 1.84, 2.81, 4.93, and 5.97 μ<sub>B</sub>, respectively, at room temperature. The absorption spectra of these complexes are shown in Figure 3. The strong band near 32 000 cm<sup>-1</sup> is tentatively assigned to the π–π\* transition in the ligand. The ligand field band of [Cu(*l*-moba)<sub>2</sub>] splits into three components (15 200, 17 700, and 18 900 cm<sup>-1</sup>). This spectrum resembles the spectra of other copper(II) complexes with 1,3-diketones.<sup>10–12</sup> The absorption spectrum of [Ni(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] shows two bands at 8800 and 15 600 cm<sup>-1</sup>, indicating a nearly octahedral symmetry around the metal ion.<sup>13,14</sup> The absorption spectrum of [Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] can also be interpreted in terms of the O<sub>h</sub> symmetry around the metal ion with the bands at 7700 and 19 000 cm<sup>-1</sup> being assigned to the <sup>4</sup>T<sub>2g</sub> ← <sup>4</sup>T<sub>1g</sub> and <sup>1</sup>T<sub>1g</sub>(P)

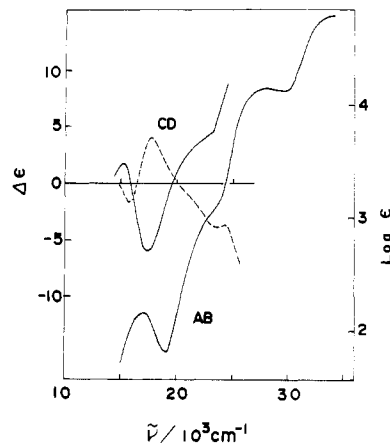


Figure 4. Absorption and CD spectra of (—) [Co(*l*-moba)<sub>3</sub>] and CD spectrum of (---) Δ-[Co(acac)<sub>3</sub>].

← <sup>4</sup>T<sub>1g</sub> transitions, respectively.<sup>14–16</sup> The electronic spectrum of [Mn(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] showed no strong absorption in the region below 20 000 cm<sup>-1</sup>. This can reasonably be explained by the fact that a high-spin manganese(II) ion has no spin-allowed d–d band. A solution of [Mn(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] in carbon tetrachloride gradually assumed a red color upon long exposure to air. It is likely that the manganese complex was oxidized by molecular oxygen to a manganese(III) species.

All of the complexes showed no CD band in the visible region. This appears natural because there exists an approximate inversion center at the metal atom, if a planar or a trans-octahedral structure is supposed for these complexes. Further, the vicinal effect of the chiral *l*-menthyl group is negligibly small in these complexes. On the basis of a consideration of Dreiding models, the distance between the phenyl group of the ligand and the *l*-menthyl group of the neighboring ligand is too large to cause the interligand, hydrophobic CH...π interaction, as long as two *l*-moba<sup>-</sup> ions coordinate to the metal ion in a planar fashion. From these facts, we have concluded that [Ni(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], and [Mn(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] possess a trans-octahedral configuration.

[Co(*l*-moba)<sub>3</sub>] is diamagnetic. Its proton NMR spectrum is given in Figure 2b. The methine proton on the chelate ring and the methylene proton adjacent to the *l*-menthoxy group appear at 6.55 and 4.31 ppm as singlets, respectively. In general, cobalt(III) complexes of asymmetric 1,3-diketones are obtained as a mixture of *cis* and *trans* isomers.<sup>17</sup> In the case of *trans*-[Co(bzac)<sub>3</sub>], unequivocal methyl proton signals appeared at 2.12, 2.13, and 2.17 ppm in chlorobenzene.<sup>17</sup> The singlet at 4.31 ppm of [Co(*l*-moba)<sub>3</sub>] clearly indicates that only the *cis* isomer is preferentially formed. This is particularly interesting because the *trans* isomer is predominantly formed in the case of [Co(bzac)<sub>3</sub>].<sup>17</sup>

The electronic and CD spectra of [Co(*l*-moba)<sub>3</sub>] in carbon tetrachloride are given in Figure 4. The synthetic routes did not affect the spectra obtained (cf. Experimental Section). The electronic spectrum resembles those of other tris(1,3-diketonato)cobalt(III) complexes.<sup>17–20</sup> [Co(*l*-moba)<sub>3</sub>] bears a marked CD spectral resemblance to optically active [Co(acac)<sub>3</sub>]<sup>21</sup> rather than to [Co(bzac)<sub>3</sub>]<sup>17</sup> in the visible region. Figure 3 also includes the CD spectrum of Δ-[Co(acac)<sub>3</sub>], whose absolute configuration has been determined by X-ray

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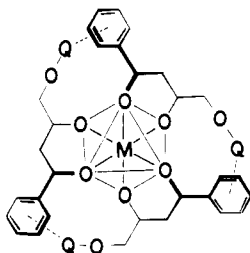


Figure 5. Schematic representation of interligand, hydrophobic CH... $\pi$  interaction in *cis*- $\Delta$ -[M(*l*-moba)<sub>3</sub>] (Q = *l*-menthyl).

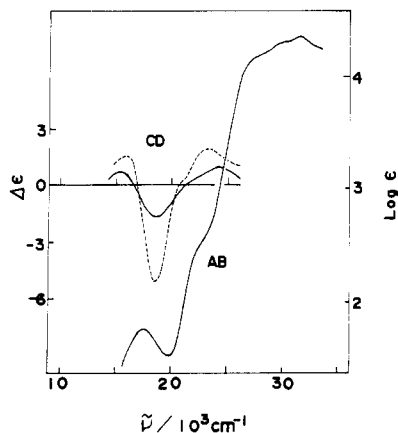


Figure 6. Absorption and CD spectra of (—) [Cr(*l*-moba)<sub>3</sub>] and CD spectrum of (---)  $\Delta$ -[Cr(acac)<sub>3</sub>].

methods.<sup>21</sup> The CD spectra of [Co(*l*-moba)<sub>3</sub>] and  $\Delta$ -[Co(acac)<sub>3</sub>] are nearly symmetric. Hence, the  $\Delta$  configuration around the metal may be assigned to [Co(*l*-moba)<sub>3</sub>] (the complex is diastereomeric with respect to the central metal and the *l*-menthyl group). Further, it is to be noted that the CD intensity in the visible region is very high and almost comparable to the intensity of optically pure [Co(acac)<sub>3</sub>].<sup>22</sup> This implies that [Co(*l*-moba)<sub>3</sub>] is almost completely resolved. The selective formation of the *cis*- $\Delta$  isomer of [Co(*l*-moba)<sub>3</sub>] may be attributed to the interligand, hydrophobic CH... $\pi$  interaction operating between the phenyl and the *l*-menthyl groups. This is visually shown in Figure 5. The interligand, hydrophobic CH... $\pi$  interaction might stabilize the *cis*- $\Delta$  isomer rather than the *cis*- $\Lambda$  isomer as well as the *trans*- $\Delta$  and *trans*- $\Lambda$  isomers. At present it is difficult to clarify which part of the *l*-menthyl group interacts with the aromatic ring.

The electronic and CD spectra of [Cr(*l*-moba)<sub>3</sub>] in carbon tetrachloride are given in Figure 6. Corresponding to the first d-d band at 17 400 cm<sup>-1</sup>, positive and negative CD bands were observed at 15 500 and 18 500 cm<sup>-1</sup>, respectively. These can be assigned to the <sup>4</sup>A<sub>2</sub> ← <sup>4</sup>A<sub>2</sub> and <sup>4</sup>E<sub>g</sub> ← <sup>4</sup>A<sub>2</sub> components of the <sup>4</sup>T<sub>2g</sub> ← <sup>4</sup>A<sub>2g</sub> transition (of O<sub>h</sub>) under a lowered symmetry D<sub>3</sub>.<sup>23</sup> A complete resolution of [Cr(acac)<sub>3</sub>] has been performed by Mason et al.<sup>24</sup> The absolute configuration of optically active [Cr(acac)<sub>3</sub>] can be determined by comparing its CD spectrum with the spectrum of [Cr((+)atc)<sub>3</sub>] ((+)atc = (+)-3-acetylcamphorate ion), whose absolute configuration has been determined by X-ray methods.<sup>25</sup> Figure 6 also includes the CD spectrum of  $\Delta$ -[Cr(acac)<sub>3</sub>]. As seen in the figure, the CD spectra of [Cr(*l*-moba)<sub>3</sub>] and  $\Delta$ -[Cr(acac)<sub>3</sub>] are similar to each other. Hence, the  $\Delta$  configuration may

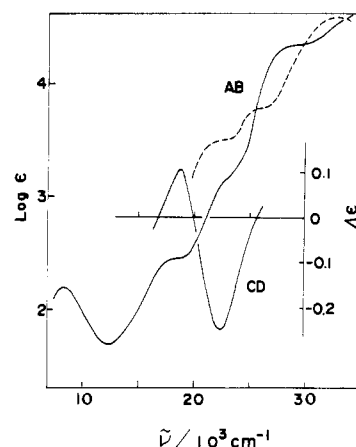


Figure 7. Absorption and CD spectra of (—) [Mn(*l*-moba)<sub>3</sub>] and absorption spectrum of (---) [Fe(*l*-moba)<sub>3</sub>].

be assigned to [Cr(*l*-moba)<sub>3</sub>]. However, the CD intensity of [Cr(*l*-moba)<sub>3</sub>] is about one-third of that of  $\Delta$ -[Cr(acac)<sub>3</sub>], implying only partial resolution of the [Cr(*l*-moba)<sub>3</sub>]. The  $\Delta$ -[Cr(*l*-moba)<sub>3</sub>]/ $\Lambda$ -[Cr(*l*-moba)<sub>3</sub>] ratio is estimated to be ca. 2 on the assumption that the CD intensity of  $\Delta$ -[Cr(*l*-moba)<sub>3</sub>] is the same as that of  $\Delta$ -[Cr(acac)<sub>3</sub>]. Again we presume that the interligand, hydrophobic CH... $\pi$  interaction brings about the stereoselectivity leading to the favorable formation of *cis*- $\Delta$  isomer (Figure 5).

The electronic and CD spectra of [Mn(*l*-moba)<sub>3</sub>] are given in Figure 7. The electronic spectrum resembles those of [Mn(acac)<sub>3</sub>] and [Mn(bzac)<sub>3</sub>].<sup>26-28</sup> Three absorption bands at 8000, 18 000, and 22 000 cm<sup>-1</sup> can be assigned to d-d transition bands.<sup>26-28</sup> A manganese(III) ion under an octahedral field should reveal only one spin-allowed d-d transition, <sup>5</sup>T<sub>2g</sub> ← <sup>5</sup>E<sub>g</sub>. The electronic spectrum of [Mn(*l*-moba)<sub>3</sub>], therefore, suggests a distortion of the [MnO<sub>6</sub>] chromophore from a rigid octahedron. The Jahn-Teller effect in the d<sup>4</sup> electronic configuration appears to be one of the reasons for this distortion.<sup>28</sup> A positive CD band was observed at 18 000 cm<sup>-1</sup> and a negative band at 22 000 cm<sup>-1</sup>. We believe that the interligand, hydrophobic CH... $\pi$  interaction selectively formed a stereoisomer, which is supposed to be the *cis*- $\Delta$  form by analogy to *cis*- $\Delta$ -[Co(*l*-moba)<sub>3</sub>] and *cis*- $\Delta$ -[Cr(*l*-moba)<sub>3</sub>] (Figure 5). This is particularly noteworthy since manganese(III) complexes are generally labile and are believed to be difficult to resolve. The optical purity of this complex cannot be determined because no manganese(III) complex of 1,3-diketone has been resolved thus far.

The electronic spectrum of [Fe(*l*-moba)<sub>3</sub>] revealed no strong absorption in the frequency region below 20 000 cm<sup>-1</sup>. This is due to the fact that [Fe(*l*-moba)<sub>3</sub>] is in the high-spin state (5.97  $\mu_B$  at room temperature) and hence has no spin-allowed d-d transition. The absorption bands in the region 20 000–26 000 cm<sup>-1</sup> can be attributed to the charge-transfer bands between the metal and the ligand.<sup>29</sup> This complex showed no CD bands in this region.

Thus, geometrical and optical selectivities have been recognized in [Co(*l*-moba)<sub>3</sub>], [Cr(*l*-moba)<sub>3</sub>], and [Mn(*l*-moba)<sub>3</sub>], and these selectivities are unambiguously attributed to the interligand, hydrophobic CH... $\pi$  interaction. The CD spectra of these complexes in benzene were practically the same as those in carbon tetrachloride. This implies that the interligand, hydrophobic CH... $\pi$  interaction is sufficiently strong to suppress

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the interaction between the *l*-menthyl group and solvent molecules. In general tris(1,3-diketono)cobalt(III) and -chromium(III) are known to undergo slow racemization in solution,<sup>21,30</sup> though it is recognized that cobalt(III) and chromium(III) complexes are generally inert. For example, racemization of optically active [Cr(acac)<sub>3</sub>] in 1:1 hexane-benzene is 50% complete at 25 °C in 8 days.<sup>30</sup> So that the racemization of [Co(*l*-moba)<sub>3</sub>] and [Cr(*l*-moba)<sub>3</sub>] could be examined, CD spectra were measured after the solutions were left to stand for 1 month. However, no substantial change was observed for the CD spectra of these solutions. Further, [Mn(*l*-moba)<sub>3</sub>] showed no CD spectral change after 10 days.

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All these facts suggest that the asymmetric field effected by the interligand, hydrophobic CH $\cdots\pi$  interaction preferentially stabilizes one stereoisomer (cis- $\Delta$  form) compared with other isomers.

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**Registry No.** Co(*l*-moba)<sub>3</sub>, 80630-19-9; Cr(*l*-moba)<sub>3</sub>, 80594-50-9; Mn(*l*-moba)<sub>3</sub>, 80594-51-0; Fe(*l*-moba)<sub>3</sub>, 80594-49-6; Ni(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, 80594-52-1; Co(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, 80594-53-2; Mn(*l*-moba)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, 80630-20-2; Cu(*l*-moba)<sub>2</sub>, 80594-54-3; H(*l*-moba), 80594-47-4; ethyl *l*-menthoxyacetate, 75410-31-0; K<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>], 15768-38-4.

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## Thermodynamic Origin of the Macrocyclic Effect in Crown Ether Complexes of Na<sup>+</sup>, K<sup>+</sup>, and Ba<sup>2+</sup>

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As compared to the noncyclic analogue pentaglyme, 18-crown-6 complexes of Na<sup>+</sup>, K<sup>+</sup>, and Ba<sup>2+</sup> have superior stabilities in methanol and methanol/water mixtures. This macrocyclic effect amounts to 3-4 orders of magnitude in the equilibrium formation constant and has been shown with use of calorimetric titrimetry to be primarily the result of more favorable enthalpic ( $\Delta H$ ) changes. The addition of water to the methanol solvent caused a decrease in the observed macrocyclic effects in all cases studied. These decreases were the result of less favorable enthalpic changes. As compared to K<sup>+</sup>, the macrocyclic effect for Na<sup>+</sup> is smaller, and again the decrease was the result of unfavorable enthalpic changes. Some stability constants were also measured with use of pentaethylene glycol for comparison to the corresponding glyme.

### Introduction

In earlier work describing the thermodynamics of cyclic polyether cation complexation reactions, Frensdorff<sup>1</sup> noted the higher stabilities of the complexes of cyclic polyethers over those of their linear glyme counterparts. He reported that the stability constants of complexes with the cyclic ligand 18-crown-6 (18C6) were several orders of magnitude larger than those with the corresponding open-chain compound pentaglyme (PG) (see Figure 1). Cabiness and Margerum<sup>2</sup> had also observed earlier that increased complex stability is found among transition-metal complexes of cyclic tetramine ligands over those of corresponding open-chain ligands. They suggested the term "macrocyclic effect" to describe this phenomenon which seemed to be a logical extension of the well-known chelate effect.

Just as some question arose over the thermodynamic origin of the chelate effect,<sup>3</sup> so different conclusions have been drawn concerning the macrocyclic effect; i.e., some investigators have ascribed the effect to enthalpic ( $\Delta H$ ) factors while others have implicated entropic ( $\Delta S$ ) factors as the most important in contributing to the enhanced stabilities ( $\Delta G$ ) of complexes containing macrocyclic ligands. Margerum and co-workers<sup>2,4,5</sup> found the enthalpy term to predominate in the observed macrocyclic effect when the formation of Ni(II) complexes of cyclam and those of 2,3,2-tet (Figure 1) are compared. Dei and Gori<sup>6</sup> reached a similar conclusion using the Cu(II) complexes of these two ligands. However, both Paoletti and co-workers<sup>7</sup> and Kodama and Kimura<sup>8</sup> found that the entropy

term was primarily responsible for the macrocyclic effect using Cu(II) complexes of cyclen and 2,2,2-tet. Paoletti and co-workers later concluded that the relative magnitude of the enthalpy contribution is critically dependent on the match between cation and ligand cavity sizes for transition metals.<sup>9</sup> In a study of Cu<sup>2+</sup> complexes of ligands containing S, N, and O donor atoms, Arnaud-Neu et al. concluded that the macrocyclic effect has both enthalpy and entropy contributions.<sup>10</sup>

One of the objectives of this study was to determine whether the macrocyclic effect found in polyether complexes of Na<sup>+</sup>, K<sup>+</sup>, and Ba<sup>2+</sup> was the result of either enthalpic or entropic factors or a combination of both factors. This was accomplished by comparing log *K*,  $\Delta H$ , and  $T\Delta S$  values for the reaction of these metal cations with cyclic 18C6 with corre-

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