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Noncovalent Interactions in Metal Complexes. 15*. Stereoselectivity of Cobalt(III) Mixed Chelates with Bis(1-l-menthyloxy-3-benzoylacetone)ethylenediimine and a Diamine

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Abstract

Cobalt(III) mixed chelates, [Co(l-mobaen)(DA)]-PF_6 (l-moba = bis(1-l-menthyloxy-3-benzoylacetone)-ethylenediiminate ion; DA = en, tn, bpy, phen), have been synthesized and their stereoselectivities have been examined by means of electronic, ^1H NMR, and circular dichroism spectra. The complexes with bpy or phen (A-type complexes) showed a stereoselectivity giving rise to the Δ-*cis*-β isomer predominantly, together with the Λ-*cis*-β isomer; the Δ/Λ ratios for [Co(l-mobaen)(bpy)]PF_6 and [Co(l-mobaen)(phen)]PF_6 were estimated at *ca.* 2.5 and 2.0, respectively. The complexes with en or tn (B-type complexes) showed a high stereoselectivity giving rise to the Λ-*cis*-α isomer. The stereoselectivity observed for the present complexes has been discussed in terms of noncovalent interactions operating within complex molecule.

Introduction

We have shown that noncovalent interactions occur between organic residues within a complex molecule [2] and give rise to a stereoselectivity producing one of the possible geometrical isomers or diastereomers of metal complexes predominantly [2–5]. We have extensively investigated noncovalent interactions affecting stereoselectivities of binary complexes such as tris(1-l-menthyloxy-3-benzoylacetonato)M(III) and its homologs [3]. Noncovalent interactions in ternary complexes are also of interest, particularly in view of stereospecificity in enzyme/metal/substrate or enzyme/metal/inhibitor complexes [6–8]. As a continuation of this series, we have examined in this study the stereoselectivity of cobalt(III) mixed chelates [Co(l-mobaen)(DA)]PF_6, which are constituted of bis(1-l-menthyloxy-3-benzoylacetone)ethylenediiminate ion (l-mobaen^{2-}, see Fig. 1) and a diamine (DA = en, tn, bpy, phen)*. These complexes may adopt either the *cis*-α or *cis*-β configuration. For these configurations the complexes are diastereomeric (Δ(l) and Λ(l)) with respect to the metal and the menthyl residue (Fig. 2). If noncov-

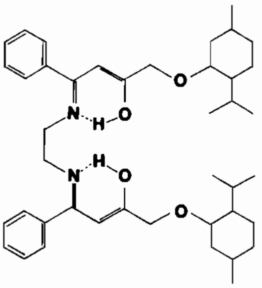
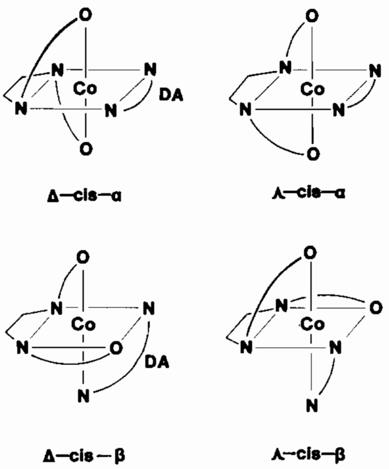


Fig. 1. Chemical structure of H(l-mobaen).



Δ–cis–α

Λ–cis–α

Δ–cis–β

Λ–cis–β

Fig. 2. Possible configurations of [Co(l-mobaen)(DA)]$^+$.

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*The following abbreviations are adopted: en, ethylenediamine; tn, 1,3-diaminopropane; bip, 2,2′-bipyridyl; phen, 1,10-phenanthroline.

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alent interactions occur within a complex molecule, the equilibrium between the diastereomers may shift to one direction resulting in the predominant formation of one of the diastereomers. The structure and the preferred configuration of [Co(l-mobaen)(DA)]PF_6 have been investigated in order to reveal intramolecular noncovalent interactions affecting the stereoselectivity of the complexes.

Experimental

Preparations

1-l-Menthyloxy-3-benzoylacetone was prepared by the method [3b] previously reported.

H_2(l-mobaen)

A mixture of 1-l-menthyloxy-3-benzoylacetone (3.0 g), ethylenediamine (0.3 g), and a small amount of *p*-toluenesulfonic acid in dry benzene (30 cm^3) was refluxed for 3 h, and the water formed by condensation was eliminated as the benzene azeotrope. The reaction mixture was cooled to room temperature and *p*-toluenesulfonic acid was removed by filtration. On evaporating the solvent, H_2(l-mobaen) was obtained as an oily substance. It was used for the synthesis of complexes without further purification.

[Co(l-mobaen)]

This complex was obtained as red crystals by the reaction of cobalt(II) acetate tetrahydrate (1.2 g) and the ligand (3.1 g) in the presence of NaOH (0.4 g) in methanol (30 cm^3). A precaution was taken for protecting the reaction from oxidation with molecular oxygen.

[Co(l-mobaen)(DA)]PF_6 (DA = en, tn, bpy, phen)

These mixed chelates were obtained in nearly the same way. The synthetic way is exemplified by that for [Co(l-mobaen)(bpy)]PF_6. A mixture of [Co(l-mobaen)] (0.2 g) and 2,2'-bipyridyl (0.1 g) in methanol (10 cm^3) was stirred for 6 h in an open atmosphere to give a brown solution. Then an aqueous solution of KPF_6 (0.1 g) was added to the solution to give brown crystals. After the solution was allowed to stand overnight, the crystals were collected, washed with water, and dried over P_2O_5 in a vacuum desiccator.

A portion of each complex was recrystallized from acetonitrile and submitted to elemental analysis. The yields and the elemental analyses for the cobalt(II) and cobalt(III) complexes prepared in this study are given in Table I.

Measurements

^1H NMR spectra (90 MHz) were recorded on a Hitachi R-20B Spectrometer in $CDCl_3$ or CD_3CN. Tetramethylsilane was used as an internal standard. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 in chloroform. Circular dichroism spectra were obtained with a JASCO J-500C Spectropolarimeter in chloroform. Elemental analyses were obtained at the Elemental Analysis Service Center, Kyushu University.

Results and Discussion

The cobalt(III) mixed chelates are classified into two type based on their electronic spectral features, *i.e.*, A-type ([Co(l-mobaen)(bpy)]PF_6 and [Co(l-mobaen)(phen)]PF_6) and B-type ([Co(l-mobaen)(en)]PF_6 and [Co(l-mobaen)(tn)]PF_6). As exemplified by the spectrum of [Co(l-mobaen)(bpy)]PF_6 in Fig. 3, the A-type complexes each shows distinct absorptions at 16.5×10^3 and 20×10^3 cm^{-1}. These may be assigned to d–d transition bands split under a symmetry lower than O_h. On the other hand, the B-type complexes do not show any distinct absorption but an unresolved shoulder around 18×10^3 cm^{-1}, as seen in the spectrum of [Co(l-mobaen)(en)]PF_6 (Fig. 4). The intense band near 26×10^3 cm^{-1}, which is seen for both A-type and B-type complexes, may be attributed to an intraligand transition, presumably to a π–π^* transition involving π-function of the azomethine group [9, 10].

It is assumed that the A type complexes have the *cis-β* configuration, because their electronic spectra resemble those of [Co(acacen)(acac)] [11] and related complexes [4, 12–14] whose *cis-β* configura-

TABLE I. Yields and Elemental Analyses of [Co(l-mobaen)] and [Co(l-mobaen)(DA)]PF_6

	Yield (%)	Found (%)			Calc. (%)		
		C	H	N	C	H	N
[Co(l-mobaen)]	85	70.50	8.11	3.79	70.67	8.19	3.92
[Co(l-mobaen)(bpy)]PF_6	92	61.52	6.59	5.44	61.53	6.55	5.52
[Co(l-mobaen)(phen)]PF_6	90	62.54	6.60	5.29	62.42	6.40	5.39
[Co(l-mobaen)(en)]$PF_6 \cdot CH_3CN$	80	58.12	7.67	7.44	57.55	7.24	7.30
[Co(l-mobaen)(tn)]$PF_6 \cdot \frac{1}{2}CH_3CN$	80	58.18	7.24	6.50	57.95	7.35	6.61

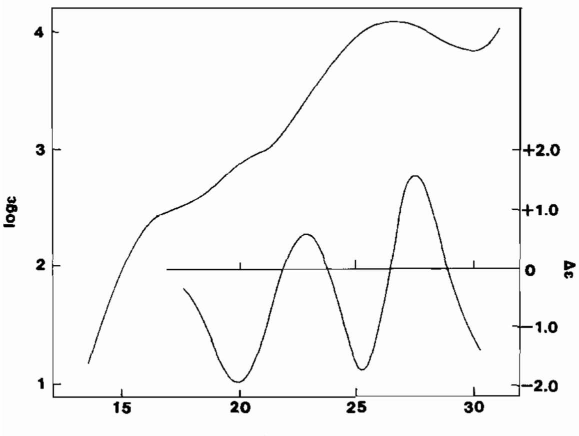

Fig. 3. Electronic and circular dichroism spectra of [Co(l-mobaen)(bpy)]PF_6 in $CHCl_3$.

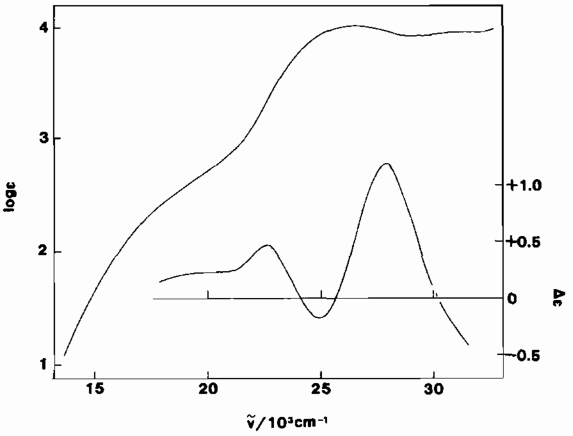

Fig. 4. Electronic and circular dichroism spectra of [Co(l-mobaen)(en)]PF_6 in $CHCl_3$.

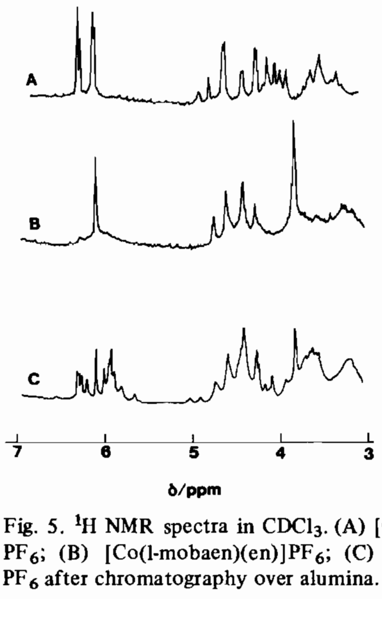

Fig. 5. ^{1}H NMR spectra in $CDCl_3$. (A) [Co(l-mobaen)(bpy)]PF_6; (B) [Co(l-mobaen)(en)]PF_6; (C) [Co(l-mobaen)(en)]PF_6 after chromatography over alumina.

tions have been demonstrated by single-crystal X-ray analysis [15, 16] or ^{1}H NMR [4, 11, 14, 17]. This is confirmed by NMR spectral investigations. Typical spectra in the 4–7 ppm region are shown in Fig. 5. In the spectrum of [Co(l-mobaen)(bpy)]PF_6 (trace A of Fig. 5) two signals due to the methine proton on the chelate ring appear at 6.13 and 6.30 ppm, as expected for the *cis*-β configuration. Further, it is seen that each methine signal is constituted of two components, probably attributable to the diastereomers (Δ(l) and Λ(l)) for this configuration. The signal for the methylene proton adjacent to the l-menthyloxy group appears as multiplet in the region 4–5 ppm. This multiplet may result from the inequivalence of the two methylene groups, consistent with the *cis*-β configuration.

The B-type complexes differ from the A-type complexes in ^{1}H NMR spectral feature also. The spectrum of [Co(l-mobaen)(en)]PF_6 (trace B of Fig. 5) shows one singlet at 6.09 ppm for the methine proton on the chelate ring and a distinct AB quartet at 4.7 ppm for the methylene proton adjacent to the l-menthyloxy group. A similar NMR spectral feature (one singlet for the methine proton and an AB quartet for the methylene proton) is seen for [Co(l-mobaen)(tn)]PF_6. Further, the ethylene proton of the en of [Co(l-mobaen)(en)]PF_6 appears as a singlet at 3.84 ppm. All these facts suggest that the B-type complexes have either the *cis*-α configuration or *trans* configuration. If the complexes are *trans*-octahedral, the en or tn should act as a bridging group to form an infinite chain. However, the B-type complexes are found to be highly soluble in most organic solvents such as chloroform. Hence, the complexes are presumed to be of *cis*-α configuration.

In order to gain further evidence for their configurations and to see if noncovalent interactions occur within each complex molecule, circular dichroism (CD) spectra of the cobalt(III) mixed chelates have been investigated. The CD spectrum of [Co(l-mobaen)(bpy)]PF_6 is included in Fig. 3, and the numerical data are given in Table II. The CD spectra of the A-type complexes are similar to each other and show significant CD at 19.5×10^3 (negative), 22.5×10^3 (positive), 25×10^3 (negative), and 27.5×10^3 cm^{-1} (positive). The optical activity observed is attributable to the configurational effect but not to the vicinal effect, since the optical activity due to the latter is generally weak [18]. The absolute configuration for these complexes is determined as Δ, in the light of the CD spectral results for *cis*-β cobalt(III) mixed chelates whose absolute configuration is known [4, 14, 19].

As mentioned above, the methine proton signals for the A-type complexes are constituted of two components of unequal intensity. This is presumably due to the coexistence of the diastereomers, Δ(l) and Λ(l), which are equilibrated in solution. We may

TABLE II. Electronic and CD Spectral Data for Cobalt(III) Mixed Chelates

	Absorption $\tilde{\nu}$ (10^3 cm^{-1}) (log ϵ (dm^3 mol^{-1} cm^{-1}))		CD $\tilde{\nu}$ (10^3 cm^{-1}) ($\Delta\epsilon$ (dm^3 mol^{-1} cm^{-1}))	
[Co(l-mobaen)(bpy)]PF$_6$	16.8(2.46)	20.7(2.94)	19.7(−1.96)	22.8(+0.60)
	26.5(4.10)		25.2(−1.72)	27.5(+1.60)
[Co(l-mobaen)(phen)]PF$_6$	16.1(2.35)	20.0(2.90)	19.6(−1.16)	22.5(+0.88)
	26.7(4.14)		25.0(−1.86)	27.6(+0.76)
[Co(l-mobaen)(en)]PF$_6$	18sh[a]	26.3(4.02)	19.0(+0.18)	22.4(+0.44)
			24.8(−0.19)	27.7(+1.18)
[Co(l-mobaen)(tn)]PF$_6$	18sh	26.5(3.95)	17.0(+0.27)	21.4(+0.27)
			25.0(−0.74)	27.7(+0.95)

[a] sh = shoulder.

assign the pair of the more intense component of each methine signal to the Δ-isomer and the pair of the weaker component to the Λ-isomer. The components for the methine signal at the lower field are well resolved. Based on the relative intensities of the components for the methine signal, the Δ/Λ ratio is estimated at *ca.* 2.5 for [Co(l-mobaen)(bpy)]PF$_6$ and *ca.* 2.0 for [Co(l-mobaen)(phen)]PF$_6$.

Each of the B-type complexes shows significant CD at 22.5×10^3 (positive), $\sim 25 \times 10^3$ (negative), and 27.5×10^3 cm^{-1} (positive), together with a weak band below 20×10^3 cm^{-1} (positive). The optical activity observed adds a strong support for the *cis-α* (but not *trans*) configuration of the B-type complexes. The preferred absolute configuration for these complexes may be determined to be Λ, as discussed later. The selectivity of the B-type complexes is presumably very high, judging from the fact that the methine proton signal appears as one sharp singlet.

It has been shown that cobalt(III) mixed chelates of this type are considerably labile and often undergo structural changes in solution [4, 11, 14, 20, 21]. It is found that the B-type complexes show very complicated NMR spectra as seen in trace C of Fig. 5 when chromatographed over neutral alumina. This suggests that the *cis-α* configuration for the complexes is unstable and the complexes undergo a structural change or decomposition on alumina. On the other hand, NMR and CD spectra (and hence the Δ/Λ ratio) of the A-type complexes were not affected by chromatography over alumina, indicating that the *cis-β* configuration is thermodynamically stable.

Fujii *et al.* [17] have reported that [Co(bzacen)(en)]ClO$_4$ (bzacen^{2-} = bis(benzoylacetone)ethylenediiminate ion), which bears a structural resemblance to [Co(l-mobaen)(en)]PF$_6$, prefers the *cis-β* configuration. Indeed, the *cis-α* configuration was unknown for cobalt(III) mixed chelates of the present type. It is likely that some intramolecular noncovalent interactions occurring within the complex molecule stabilize the hitherto unknown *cis-α* configuration. Our preliminary study has revealed that [M(l-mobaen)] (M = Co^{II}, Cu^{II}, Ni^{II}) are essentially planar but exhibit significant CD at the ligand field band region, suggesting a distortion of the coordination plane. The negative CD observed at $\sim 18 \times 10^3$ cm^{-1} for [Cu(l-mobaen)] and [Ni(l-mobaen)] indicates the dextral chirole (Δ) [9, 10] for these complexes. It should be noted that the deformation mode of the l-mobaen in these complexes is the same as that in Λ-*cis-α*-[Co(l-mobaen)(DA)]PF$_6$. This fact may be regarded as an indication of the Λ absolute configuration of the B-type complexes. A similar distortion was found for [Cu(l-moba)$_2$] and [Ni(l-moba)$_2$(H$_2$O)$_2$] (l-moba$^-$ = 1-l-menthyloxy-3-benzoylacetonate ion), and this distortion was attributed to an intramolecular noncovalent interaction occurring between the l-menthyl group and the chelate π-system [5]. Thus, we believe that the l-menthyl/chelate-π interaction operating within l-mobaen^{2-} causes a dextral distortion in [Co(l-mobaen)] and leads to the stereoselective formation of Λ-*cis-α* isomer for the B-type complexes.

The preferred configuration (Δ-*cis-β*) for the A-type complexes differs from that for the B-type complexes. We presume that an interligand noncovalent interaction occurring between l-mobaen^{2-} and bpy or phen plays the major role in giving rise to the stereoselectivity of the A-type complexes.

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