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Non-covalent Interactions in Metal Complexes. V.[1] Stereoselectivity in Cobalt(III) Mixed-chelates with a Salen-like Schiff Base and 1-*l*-Menthyloxy-3-benzoylacetone

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Cobalt(III) mixed-chelates, Co(SB)(*l*-moba), containing a salen-type Schiff base (SB) and 1-*l*-menthyloxy-3-benzoylacetone (H(*l*-moba)) have been synthesized, where H_2salen stands for *N,N′*-disalicylideneethylenediamine. These complexes were shown to have a *cis*-β-octahedral structure, based on electronic and infrared spectra. They showed circular dichroism in the visible region, demonstrating an induction of an asymmetry around the metal ion. On the basis of NMR and CD spectra and in comparison with the CD spectrum of Λ-Co(sal-(*S*, *S*)-ch)(bazc), it was shown that the Co(SB) (*l*-moba) complexes prefer the Λ-*cis*-β_1-configuration. The reaction of racemic *N,N′*-disalicylidene-*trans*-1,2-cyclohexanediaminatocobalt(II) (Co(salch)) and racemic *N,N′*-disalicylidene-1,2-propanediaminatocobalt(II) (Co(salpn)) with H(*l*-moba) in a 2 : 1 mole ratio yielded Λ-*cis*-β_1-Co(sal-(*S*, *S*)-ch)(*l*-moba) and Λ-*cis*-β_1-Co(sal-(*R*)-pn)(*l*-moba), respectively, as a main species. The stereoselectivity in the present complexes has been discussed in terms of the inter-ligand, hydrophobic CH/π-interaction which may occur between the *l*-menthyl group and an aromatic ring of the Schiff bases.

Recently, there has been an increasing interest in inter-ligand, hydrophobic interactions which bring about stereoselectivity and stereospecificity in metal complexes.[1–3] In the preceding paper of this series,[2] we have shown that tris(1-*l*-menthyloxy-3-benzoylacetonato)M(III), [M(*l*-moba)$_3$] (M=Co, Cr, Mn), prefers the *cis*-Δ-configuration. This stereoselectivity was attributed to the inter-ligand, hydrophobic CH/π-interaction[4] operating between an *l*-mentyl group of one ligand and the phenyl group of the adjacent ligand in the complex. In this study, we have prepared the cobalt(III) mixed-chelates, Co(SB)(*l*-moba), containing a salen-like Schiff base (SB) and *l*-moba$^-$, where H_2salen denotes *N,N′*-disalicylideneethylenediamine, and examined their configuration on the basis of ^{1}H-NMR and circular dichroism (CD) spectra. The purpose of this study is to investigate the stereoselectivity in Co(SB)(*l*-moba) in terms of the hydrophobic CH/π-interaction, which may occur between an aromatic ring of the Schiff base and the *l*-methyl group of *l*-moba$^-$. Schiff bases used in this study are *N,N′*-disalicylideneethylenediamine (H_2salen), its ring-substituted homologs (H_2(R-salen); R=3-MeO, 4-OH, 5-Me, 5-Br), (1*S*,2*S*)-*N,N′*-disalicylidene-1,2-cyclohexanediamine (H_2sal-(*S,S*)-ch), and (*R*)-*N,N′*-disalicylidene-1,2-propanediamine (H_2sal-(*R*)-pn). Further, in order to examine if *l*-moba$^-$ selectively reacts with one of the optical isomers of the racemic cobalt(II) complexes, cobalt(III) mixed-chelates, Co(salch)(*l*-moba), and Co(salpn)(*l*-moba), were prepared by reacting racemic *N,N′*-disalicylidene-*trans*-1,2-cyclohexanediaminatocobalt(II) (Co(salch)) and racemic *N,N′*-disalicylidene-1,2-propylenediaminatocobalt(II) (Co(salpn)) with H(*l*-moba) in a 2 : 1 mole ratio, respectively, and their configura tions were studied.

Experimental

Syntheses. Synthetic method of H(*l*-moba) is described in the previous paper.[2] Syntheses of Co(salen) and its homologs were carried out by the usual method in the literatures.[5,6] (*R*)-1,2-Propanediamine[7] and (1*S*,2*S*)-1,2-cyclohexanediamine[8] were obtained by resolving racemic diamines.

*Co(SB)(*l*-moba).* Cobalt(III) mixed-chelates were obtained in nearly the same way. Synthesis of Co(salen)-(*l*-moba) is exemplified. A mixture of Co(salen) (0.2 g) and H(*l*-moba) (0.2 g) in methanol (30 cm^3) were refluxed for 3 h in an open atmosphere. Color of the solution turned from red to green. The reaction mixture was concentrated to 5 cm^3 and to this was added peroleum ether to give a green precipitate. It was dissolved in a benzene–ethanol mixture (5 : 3 in volume) and the solution was passed through an alumina column (1.5 cm×20 cm). The eluent was concentrated to *ca.* 10 cm^3 and allowed to stand overnight in a refrigerator to give Co(salen)(*l*-moba) as green crystals.

Co(sal-(*S,S*)-ch)(bzac) was also prepared by the reaction of Co(sal-(*S,S*)-ch) and benzoylacetone (Hbzac).

Table 1. Elemental analyses of cobalt(III) mixed-chelates

Complex	Found(%)			Calcd(%)		
	C	H	N	C	H	N
Co(salen)(*l*-moba)	67.39	6.30	4.40	67.49	6.45	4.37
Co(5-Me-salen)(*l*-moba)	68.02	6.89	4.19	68.25	6.78	4.19
Co(5-Br-salen)(*l*-moba)	53.92	5.08	3.48	54.15	4.92	3.51
Co(4-OH-salen)(*l*-moba)	64.19	6.52	4.18	64.28	6.14	4.16
Co(3-MeO-salen)(*l*-moba)	63.98	6.40	4.31	64.13	6.47	4.00
Co(sal-(*S,S*)-ch)(*l*-moba)	68.80	6.81	4.02	69.15	6.82	4.03
Co(sal-(*S,S*)-ch(bzac)	66.49	5.54	5.25	66.66	5.41	5.18
Co(sal-(*R*)-pn)(*l*-moba)	68.40	6.66	4.32	68.09	6.33	4.29

Elemental analyses of the cobalt(III) mixed-chelates are given in Table 1.

Measurements. Electronic spectra were recorded on a Shimadzu MPS-5000 spectrophotometer in methanol. NMR spectra were recorded on JEOL Fourier Transform NMR Spectrometer Model FX90Q in $CDCl_3$, tetramethylsilane being used as an internal standard. CD spectra were recorded on a JASCO ORD/SP spectrometer in methanol.

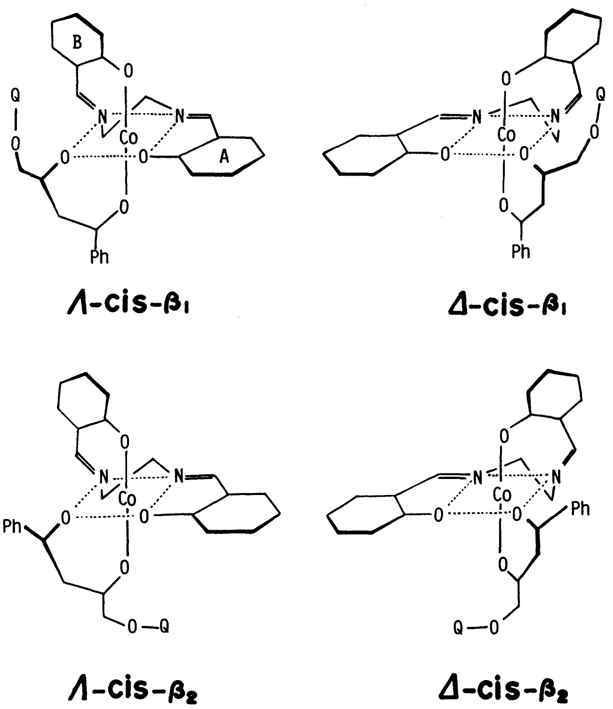
Results and Discussion

It is known that cobalt(III) mixed-chelates of the Co(salen)(ab) type are obtainable by the reaction of Co(salen) and a bidentate ligand (ab) in the presence of molecular oxygen.[9–11] X-Ray analyses of Co(salen)-(acac) ($acac^-$=2,4-pentanedionate anion)[12] and Co-(salen)(bzac)[13] have revealed that $salen^{2-}$ coordinates to the metal to form a *cis*-β-octahedral structure and the diketonate ion ($acac^-$ and $bzac^-$) coordinates to the metal with the oxygen atoms. The present complexes Co(SB)(*l*-moba) bear a marked similarity in infrared spectrum to Co(salen)(acac) and show the bands at 1590—1550 and 1540—1520 cm^{-1} characteristic of chelated 1,3-diketonate ion.[14,15] Electronic spectra of the complexes also resemble the spectra of Co(salen)-(acac)[10] and Co(salen)(bzac),[9] showing the bands around 16×10^3 ($\log\varepsilon\approx2.5$) and $26\times10^3\ cm^{-1}$ ($\log\varepsilon\approx3.9$) (Table 2). This spectral feature is quite comparable with those of pseudo-octahedral cobalt(III) complexes with a N_2O_4-donor set.[16,17] Based on these facts, we may conclude that the Co(SB)(*l*-moba) complexes possess a *cis*-β-octahedral structure.

There are two possible geometrical isomers for Co-(SB)(*l*-moba) due to the coordination attitude of *l*-$moba^-$. With respect to the imino nitrogens of the Schiff base and the carbonyl oxygen at the 2-position of *l*-$moba^-$, the geometrical isomers are described as *mer*(N,N,O) and *fac*(N,N,O). Hereafter, these isomers will be represented by *cis*-β_1 and *cis*-β_2, respectively. Each of these isomers is asymmetric about the central metal ion. Hence, four isomers are considered for Co(SB)(*l*-moba). They are exemplified by the isomers of Co(salen)(*l*-moba) in Fig. 1.

Table 2. Electronic spectral data for cobalt(III) mixed-chelates in methanol

Complex	$\tilde{\nu}/10^3cm^{-1}(\log\varepsilon)$	
Co(salen)(*l*-moba)	16.3(2.54)	26.6(3.90)
Co(5-Me-salen)(*l*-moba)	16.0(2.59)	26.0(3.88)
Co(5-Br-salen)(*l*-moba)	16.3(2.63)	25.6(3.85)
Co(4-OH-salen)(*l*-moba)	16.7(2.77)	27.4(4.03)
Co(3-MeO-salen)(*l*-moba)	16.1(2.62)	26.3(3.87)
Co(sal-(*S*,*S*)-ch)(*l*-moba)	16.3(2.48)	26.0(3.89)
Co(sal-(*R*)-pn)(*l*-moba)	16.2(2.52)	26.6(3.91)


Λ-cis-β₁ Δ-cis-β₁

Λ-cis-β₂ Δ-cis-β₂

Fig. 1. Four isomeric structures of Co(salen)(*l*-moba) (Q=*l*-menthyl).

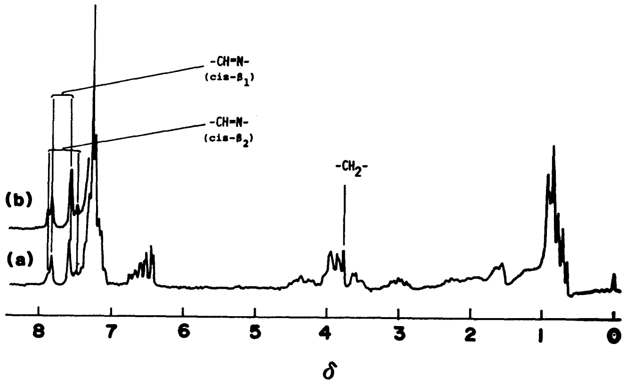


Fig. 2. NMR spectra of Co(salen)(*l*-moba) in $CDCl_3$. (a) Soon after dissolution and (b) at equilibrium.

In order to determine the geometrical structure for Co(SB)(*l*-moba), ^1H-NMR spectra were measured in $CDCl_3$. The spectrum of Co(salen)(*l*-moba) is shown in Fig. 2 as an example. The signal of relatively high intensity in the region 0.65—0.94 ppm can be assigned to the menthyl protons. The signal at 3.77 ppm is ascribed to the methylene proton adjacent to the *l*-menthyloxyl group. This is obscured by the signals attributable to the ethylene signals of the Schiff base. However, assignment of the methylene signal of *l*-$moba^-$ can be unambiguously performed by comparing the spectrum with those of Co(salen)(acac) and Co(salen)-(bzac). The signal due to the methine proton of *l*-$moba^-$ should exist around 6.6 ppm, but this is concealed or superposed by the complicated signals of the aromatic protons. The most characteristic feature in the NMR spectrum is the singlets at 7.57 and 7.82 ppm, which can be attributed to the azomethine protons. Unequivalence of the azomethine signals is consistent with the *cis*-β-configuration of the $salen^{2-}$ moiety. More careful examination of the NMR spectrum revealed that there are another pair of singlets at 7.47 and 7.84 ppm of weaker intensity. They are also assigned to the azomethine protons. Appearance of two pairs of azomethine signals implies that the two geometrical isomers, *cis*-β_1

TABLE 3. SELECTED ^{1}H-NMR SPECTRAL DATA OF COMPLEXES (ppm)

Complex	CH_2[a]	Menthyl	Azomethine			
			cis-β_1		*cis*-β_2	
H(*l*-moba)	4.05	0.77—1.03				
Co(salen)(*l*-moba)	3.77	0.65—0.94	7.57	7.82	7.47	7.84
Co(5-Me-salen)(*l*-moba)	3.78	0.66—0.94	7.50	7.74		7.78
Co(5-Br-salen(*l*-moba)	3.76	0.65—0.94	7.50	7.75	7.45	7.82
Co(3-MeO-salen)(*l*-moba)	3.8	0.76—0.93	7.49	7.81		7.88
Co(sal-(*S*,*S*-ch)(*l*-moba)	3.8	0.64—0.96	7.44	7.80		7.90
Co(sal-(*R*)-pn)(*l*-moba)	3.75	0.65—0.95	7.55	7.80		7.85

a) Methylene adjacent to *l*-methyloxyl group.

TABLE 4. CD SPECTRAL DATA OF Co(SB) (*l*-moba) AND RELATED COMPLEX IN METHANOL

Complex	$\tilde{\nu}/10^3cm^{-1}$ ($\Delta\varepsilon$)		
Co(salen)(*l*-moba)	15.9(0.32)	19.5(0.10)	23.0(−0.31)
Co(5-Me-salen)(*l*-moba)	16.3(0.85)	18.8(0.25)	22.2(−1.18)
Co(5-Br-salen)(*l*-moba)	16.4(0.88)	19.0(0.23)	22.6(−1.10)
Co(3-MeO-salen)(*l*-moba)	15.8(0.61)	18.2(0.23)	21.9(−0.61)
Co(4-OH-salen)(*l*-moba)	16.2(0.70)	19.4(0.26)	22.6(−0.67)
Co(sal-(*S*,*S*)-ch)(*l*-moba)	16.0(9.80)	19.5(2.00)	22.8(−15.80)
Co(sal-(*S*,*S*)-ch)(bzac)	16.0(10.00)	19.0(2.60)	22.7(−16.20)
Co(sal-(*R*)-pn)(*l*-moba)	16.1(1.60)	19.6(0.52)	
Co(salch)(*l*-moba)[a]	16.6(0.20)	19.4(0.08)	
Co(salpn)(*l*-moba)[b]	16.0(0.58)	19.4(0.16)	22.7(−0.84)

a) Complex obtained by the reaction of racemic Co(salch) and *l*-moba. b) Obtained by the reaction of racemic Co(salpn) and *l*-moba.

and *cis*-β_2, are present in solution.

The intensities of two pairs of the azomethine signals were shown to be time-dependent. The major pair decreased their intensity slightly with time, while the minor pair increased their intensity. This suggests that the *cis*-β_1- and *cis*-β_2-isomers are in equilibrium in solution. The equilibrium was attained within 2 d. A part of the NMR spectrum of Co(salen)(*l*-moba) at equilibrium is shown in Fig. 2. Judging from the intensities of the azomethine singlets at equilibrium, two geometrical isomers are assumed to exist in a *ca.* 1 : 5 mole ratio in the case of Co(salen)(*l*-moba). The ratio of two geometrical isomers for the other Co(SB)(*l*-moba) complexes is also estimated at 1 : 3—1 : 6. Some selected ^{1}H-NMR spectral data for Co(SB)(*l*-moba) at equilibrium are given in Table 3. Table 3 also includes the NMR spectral data for free H(*l*-moba).

When the NMR spectrum of Co(SB)(*l*-moba) is compared with that of H(*l*-moba), it is noted that the signal due to the methylene protons of *l*-moba$^-$ shifts upfield by complex formation. In the case of [Co(*l*-moba)$_3$], the methylene signal shifts downfield (4.31 ppm).[2] The downfield shift of the methylene signal relative to that of H(*l*-moba) is also observed for Pd-(*l*-moba)$_2$ (4.20 ppm) and for [Pd(bipy)(*l*-moba)]ClO_4 (4.20 ppm).[18] These facts suggest that the methylene group adjacent to the *l*-methyloxyl group is shielded by a ring current in a predominant species of Co(SB)-(*l*-moba). NMR spectrum of Co(salen)(acac) shows two methyl signals at 1.94 and 1.76 ppm. The latter has been assigned to the methyl group which is in a close proximity above the benzene ring (B benzene ring) (see Fig. 1).[12,19] Thus, upfield shift of the methylene signal in Co(SB) (*l*-moba) relative to that of H(*l*-moba) leads us to a conclusion that the *cis*-β_1-isomer is predominantly formed at the equilibrium.

Each Co(SB)(*l*-moba) complex showed CD bands around 16×10^3 (positive), 19×10^3 (positive shoulder), and 23×10^3 cm^{-1} (negative). This is a good indication for the occurence of an inter-ligand, hydrophobic CH/π-interaction between the B benzene ring of the Schiff base and the *l*-menthyl group of *l*-moba$^-$. Typical CD spectra are shown in Fig. 3, and the numerical data are given in Table 4.

In order to determine the absolute configuration of the present complexes, Co(sal-(*S*,*S*)-ch)(*l*-moba) and Co(sal-(*S*,*S*)-ch)(bzac) were prepared and their CD spectra were recorded (Fig. 3 and Table 4). CD spectra of these complexes bear a marked resemblance both in sign and in intensity. It is likely that the stereoselectivity in these complexes is mostly due to the steric requirement of the sal-(*S*,*S*)-ch^{2-} moiety and the weak hydrophobic CH/π-interaction is practically supressed in Co(sal-(*S*,*S*-ch)(*l*-moba). Fujii *et al.* have demonstrated that Co(sal-(*S*,*S*)-ch)(ab) preferentially takes the *Λ*-configuration because of the steric control of the (1*S*,2*S*)-1,2-cyclohexanediamine moiety.[20,21] Despite the low intensity of the CD bands, the similarity of the CD spectra of Co(SB)(*l*-moba) to those of Co(sal-(*S*,*S*)-ch)(*l*-moba) and Co(sal-(*S*,*S*)-ch)(bzac) leads us to the conclusion that the *Λ*-*cis*-β_1-isomer is predominantly formed in the present complexes. CD spectral pattern of Co(sal-(*R*)-pn)(*l*-moba) is also the same as those of Co(SB)(*l*-moba). This implies that the stereo-

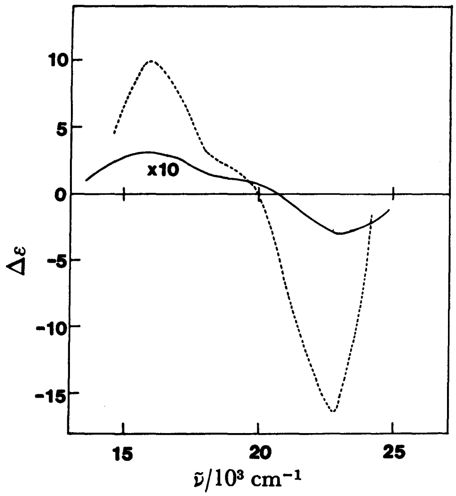


Fig. 3. CD spectra of (——) Co(salen)(*l*-moba) and (------) Co(sal-(*S*,*S*)-ch)(bzac).

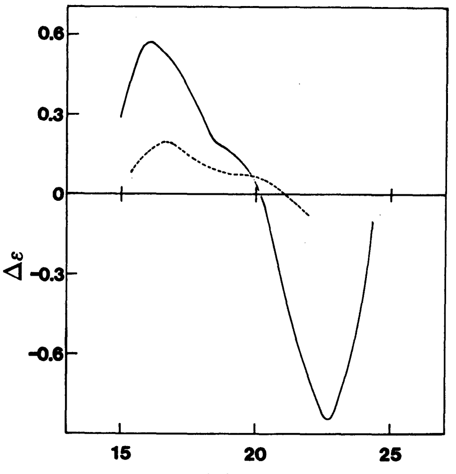


Fig. 4. CD spectra of (——) Co(salpn)(*l*-moba) and (------)Co(salch)(*l*-moba).

selectivity of sal-(*R*)-pn^{2-} is identical with that of sal-(*S*,*S*)-ch^{2-}.

In order to further demonstrate the potential contribution of the inter-ligand, hydrophobic CH/π-interaction to geometrical and optical selectivities in Co(SB)(*l*-moba), we have prepared Co(salch)(*l*-moba) and Co(salpn)(*l*-moba) by the reaction of racemic Co(salch- and racemic Co(salpn) with H(*l*-moba) in a 2 : 1 mole ratio, respectively. These complexes showed circular dichroism in the visible region (Fig. 4). For Co(salch)-(*l*-moba) eight isomers are considered: Δ-*cis*-β_1-Co(sal-(*S*,*S*)-ch)(*l*-moba), Λ-*cis*-β_1-Co(sal-(*S*,*S*)-ch)(*l*-moba), Δ-*cis*-β_1-Co(sal-(*R*,*R*)-ch)(*l*-moba), Λ-*cis*-β_1-Co(sal-(*R*,*R*)-ch)(*l*-moba), Δ-*cis*-β_2-Co(sal-(*S*,*S*)-ch)(*l*-moba), Λ-*cis*-β_2-Co(sal-(*S*,*S*)-ch)(*l*-moba), Δ-*cis*-β_2-Co(sal-(*R*,*R*)-ch)(*l*-moba), and Λ-*cis*-β_2-Co(sal-(*R*,*R*)-ch)(*l*-moba). Similarly eight isomers are considered for Co(salpn)-(*l*-moba). Although no informations are available at present on proportions of the isomers and on the sign and the intensity of circular dichroism of each isomer, a marked resemblance of the CD spectra of Co(salch)(*l*-moba) and Co(salpn)(*l*-moba) to those of Co(SB)(*l*-moba) suggests that *l*-moba$^-$ reacts selectively with one of the optical isomers, Co(sal-(*S*,*S*)-ch) and Co(sal-(*R*)-pn), respectively. This stereoselectivity may be interpreted in terms of the inter-ligand, hydrophobic CH/π-interaction between the *l*-menthyl group and the B benzene ring. Notably the CD intensity of Co(salch)(*l*-moba) is lower than that of Co(salpn)(*l*-moba) and the lowest among the complexes obtained in this study, although the CD intensity for Co(sal-(*S*,*S*)-ch)(*l*-moba) much exceeds that of Co(sal-(*R*)-pn)(*l*-moba). A strong stereoselectivity originated from the (1*S*,2*S*)-1,2-cyclohexanediamine moiety must diminish the contribution from the hydrophobic CH/π-interaction. It is likely that the stereoselectivity and the discrimination in metal complexes owing to the hydrophobic interactions are induced when a hydrophobic side chain attached to the ligand is flexible.

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