The Stereochemistry and Reactivity of Metal-Schiff Base Complexes. V. The Solvent Effect on the Stereoselectivity of Cobalt(III) Complexes Containing a sal_2en-type Schiff Base and L-Amino Acid

Yuki Fujii,* Yasuo Kuwana, Sozo Takahashi,†† Keiko Shimizu, and Kumiko Hiroi

Department of Chemistry, Faculty of Science, Ibaraki University, Bunkyo-cho, Mito, Ibaraki 310

††Department of Chemistry, Ibaraki Technical College, Nakane, Katsuta, Ibaraki 312

(Received December 12, 1981)

The solvent effect on the stereoselectivity between Λ- and Δ-β_2-diastereoisomers of cobalt(III) complexes with the general formula of [Co(Schiff base)(L-aa)], where Schiff base represents sal_2en^{2-}, α-Me-sal_2en^{2-}, and 5,6-benzo-sal_2en^{2-}, and where L-aa denotes L-alaninate, L-valinate, L-methioninate, and L-phenylalaninate, was studied. Generally, the Λ-β_2-isomer was more stable than the Δ-β_2-isomer in solution, and the stereoselectivity of all the L-ala-complexes and of the L-met-complex with 5,6-benzo-sal_2en increased in the following order of solvents : acetone=DMF$\leq$*t*-BuOH<*s*-BuOH<*i*-PrOH<*n*-BuOH<*n*-PrOH<EtOH<MeOH. On the other hand, the stereoselectivity of L-val- and L-phe-complexes with sal_2en and 5,6-benzo-sal_2en increased in the following order : acetone=DMF<MeOH<EtOH<*n*-PrOH<*n*-BuOH<*i*-PrOH<*s*-BuOH<*t*-BuOH. In the case of 5,6-benzo-sal_2en complexes with L-val and L-ile, the Δ-β_2-isomer was preferred rather than the Λ-β_2-isomer in acetone and DMF with 8—13% stereoselectivity. From the spectroscopic evidence, a hydrogen bonding between the OH group of alcoholic solvents and phenolic oxygen atoms of a Schiff base ligand was assummed, and the above phenomena were explained in terms of the steric difference between the Λ- and Δ-β_2-isomers for the solvation with the alcoholic solvents by means of the hydrogen bonding.

Detailed studies have been directed toward the thermodynamic stereoselectivity of $Co(N_4)$-complexes with a chiral amino acid. In these studies, the energy differences among the diastereoisomers have been explained mainly in terms of the intramolecular steric interaction (nonbonded interactions, bond deformations, angle deformations, and torsional strain) of the diastereoisomers.[1-3] However, the results of energy-minimization calculations have sometimes disagreed with the observed values. In such cases, an intermolecular interaction between the diastereoisomers and solvent molecules has been suggested.[2-4] In fact, it is well known that racemic *cis*-$[Co(en)_2Cl_2]^+$ and racemic α-$[Co(trien)Cl_2]^+$ antiracemize in an optically active solvent.[5] It has been pointed out recently for *trans*-$[Co((R)\text{-pn})_2X_2]^+$ (X=Cl^- and Br^-) that the conformation of the (*R*)-pn chelate ring changes depending on the nature of the solvents.[6] It has also reported that solvents affect the conformation of the 3,2,3-tet chelate ring of *trans*-$[Co(3,2,3\text{-tet})(N_3)_2]^+$ and the conformation of 1,3-diamine of *trans*-$[Co(1,3\text{-diamine})_2X_2]^{+n}$ (X=Cl^-, CN^-, and NH_3).[7,8] These facts suggest that solvents play an important role in the thermodynamic stereoselectivity of metal complexes.

In the course of our study of the stereoselectivity of Co(III)-Schiff base complexes with a chiral amino acid,[9] we found that the stereoselectivity of Co(III)-Schiff base complexes is much higher than that of $Co(N_4)$-complexes. In order to explain the high stereoselectivity, an X-ray study of $(-)_{435}$-Λ-β_2-[Co(α-Me-sal_2en)(L-ile)]·$1.5H_2O$ was carried out;[10] however, no steric factor stabilizing this configuration has been found. In this paper, the solvent effect on the stereoselectivity of a series of β_2-[Co(Schiff base)(L-aa)] complexes will be investigated in detail.[11]

Experimental

Preparation of Complexes. β_2-[Co(sal_2en)(L-aa)] and β_2-[Co(α-Me-sal_2en)(L-aa)] were prepared as previously repoted.[9] β_2-[Co(5,6-benzo-sal_2en)(L-aa)] was prepared as follows. (Since the preparation is similar for all the amino acids used here, the method for only the L-ala-complex is described.) L-Alanine (0.5 g, 5.5×10^{-3} mol) in a mixed solvent of water (20 cm^3) and methanol (100 cm^3) was added to a slurry of [Co(5,6-benzo-sal_2en)] (2.3 g, 5.4×10^{-3} mol) in 250 cm^3 of chloroform. The mixture was stirred vigorously in the open air for about 3 h to give a green solution. This solution was then filtered, and the filtrate was concentrated to a small volume at room temperature to give green crystals. In the cases of L-alanine, L-threonine, and L-isoleucine, the green crystals were recrystallized from methanol. In the cases of L-valine, L-leucine, L-methionine, and L-phenylalanine, the green crystals were washed with methanol. Yields, about 2.0 g (75%). The elemental analyses data are given in Table 1.

[Co(5,6-benzo-sal_2en)] was prepared as follows: 2-Hydroxy-1-naphthaldehyde (5.2 g, 3×10^{-2} mol) in 50 cm^3 of methanol was mixed with ethylenediamine (0.9 g, 1.5×10^{-2} mol); the Schiff base separated out as an yellow powder in about a 95% yield. $Co(CH_3COO)_2\cdot4H_2O$ (2.5 g, 1×10^{-2} mol), dissolved in methanol (100 cm^3), was added to a slurry of the ligand (3.7 g, 1×10^{-2} mol) in chloroform (200 cm^3). The mixture was heated at about 80 °C for 1 h to give a red complex, [Co(5,6-benzo-sal_2en)] in about an 80% yield. Found: C, 67.67; H, 6.74; N, 6.47%. Calcd for $CoC_{24}H_{18}N_2O_2$: C, 67.78; H, 6.62; N, 6.59%.

Preparation of Solutions. Extra-pure solvents were used after distillation. About 5×10^{-4} mol dm^{-3} solutions of the complexes were used for the AB and CD measurements. The establishment of equilibrium was confirmed from the mutarotation at 435 nm of the complex solutions. In acetone, the isomerization of the complexes was very slow. Therefore, activated charcoal was added to the acetone solutions, and the mixtures were warmed at about 50 °C until the solutions showed a constant rotation at 435 nm. The AB and CD measurements were carried out after the filtration of the activated charcoal. The concentration of the acetone solutions was calibrated by the use of the absorbance at 580 nm. No decomposition was found from the ^1H NMR spectra in the DMF-d_7 of the complexes recovered from acetone solutions. Also, the isomerization in DMF (*N*,*N*-dimethylformamide) was fairly slow; the solutions were warmed at about 40 °C to establish the isomerization equilibrium. No decomposition

TABLE 1. ELEMENTAL ANALYSES DATA

Complex	Found(%)			Calcd(%)		
	C	H	N	C	H	N
[Co(5,6-benzo-sal$_2$en)(L-ala)]·H_2O	61.03	4.87	8.13	61.02	4.93	7.91
[Co(5,6-benzo-sal$_2$en)(L-met)]	60.87	4.72	7.49	60.73	4.92	7.33
[Co(5,6-benzo-sal$_2$en)(L-val)]·H_2O	61.81	5.11	7.60	62.25	5.40	7.51
[Co(5,6-benzo-sal$_2$en)(L-thr)]·1.5H_2O	59.43	5.31	7.23	58.95	5.12	7.37
[Co(5,6-benzo-sal$_2$en)(L-leu)]·2H_2O	60.72	5.58	7.12	60.91	5.79	7.10
[Co(5,6-benzo-sal$_2$en)(L-ile)]·2H_2O	60.51	5.54	7.34	60.91	5.79	7.10
[Co(5,6-benzo-sal$_2$en)(L-phen)]·2H_2O	63.22	4.96	6.76	63.36	5.16	6.72

was found from the ^{1}H NMR spectra of the complexes in DMF-d_7 at 35 °C.

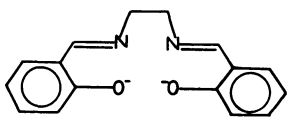
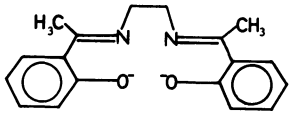
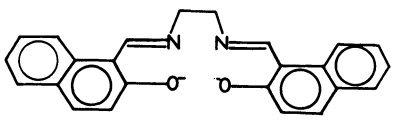
Measurements. The absorption (AB) and circular dichroism (CD) spectra were measured with a Hitachi 200-10 Spectrophotometer at 23 °C and with a JASCO J-20 Spectropolarimeter ar room temperature respectively. The optical rotation at 435 nm was measured with a JASCO DIP-140 Polarimeter. The ^{1}H NMR spectra were recorded with a Hitachi R-20 Spectrometer (60 MHz) or a Varian CFT-20 Spectrometer (80 MHz) at 35 °C.

Results and Discussion

Structure and Properties of Complexes. In a previous paper,[9] the *cis*-β_1-structure was assigned tentatively to [Co(sal$_2$en)(L-aa)] and [Co(α-Me-sal$_2$en)(L-aa)] (L-aa= L-ala, L-met, L-val, L-leu, L-ile, L-thr, L-phe, L-tyr, and L-trp). However, it has been found recently, in our X-ray study of $(-)_{435}$-[Co(α-Me-sal$_2$en)(L-ile)]·1.5H_2O, that the complex takes the *cis*-β_2-structure.[10] As is shown in Fig. 1, the AB and CD spectra of the L-ile-complex in methanol closely resemble those in the solid state (KBr disk), and the AB and CD spectra of Co(sal$_2$en)- and Co(α-Me-sal$_2$en)-complexes with various L-amino acidates in methanol are very similar to those of the L-ile-complex in methanol.[9] Accordingly, the *cis*-β_2-structure can be assigned to all the Co(sal$_2$en)- and Co(α-Me-sal$_2$en)-complexes with L-amino acidates in methanol.

As has been mentioned previously,[9] [Co(sal$_2$en)(L-aa)] and [Co(α-Me-sal$_2$en)(L-aa)] are isolated as a 1 : 1

TABLE 2. ABBREVIATIONS AND STRUCTURES OF SCHIFF-BASE LIGANDS

Structure	Abbreviation
	sal$_2$en
	α-Me-sal$_2$en
	5,6-Benzo-sal$_2$en

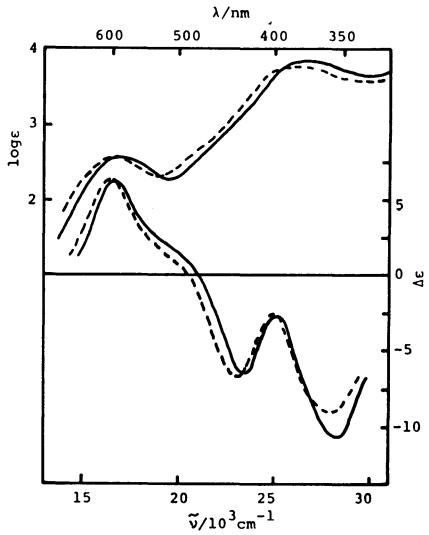


Fig. 1. AB and CD spectra of [Co(α-Me-sal$_2$en)(L-ile)].
——: In methanol under the equilibrium conditions,
------: in KBr disk (arbitrary scale).

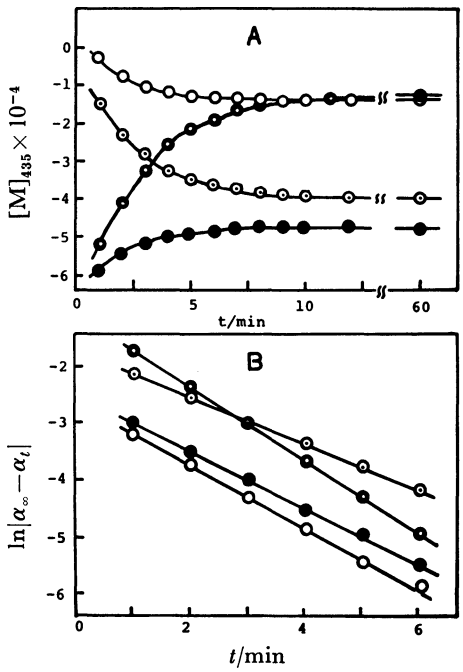


Fig. 2. Mutarotation at 435 nm of β_2-[Co(5,6-benzo-sal$_2$en) (L-aa)] in methanol at 23 °C (A) and the ln-plot (B).
—○—: L-ala-complex, —⊙—: L-thr-complex,
—○—: L-val-complex, —●—: L-phe-complex.

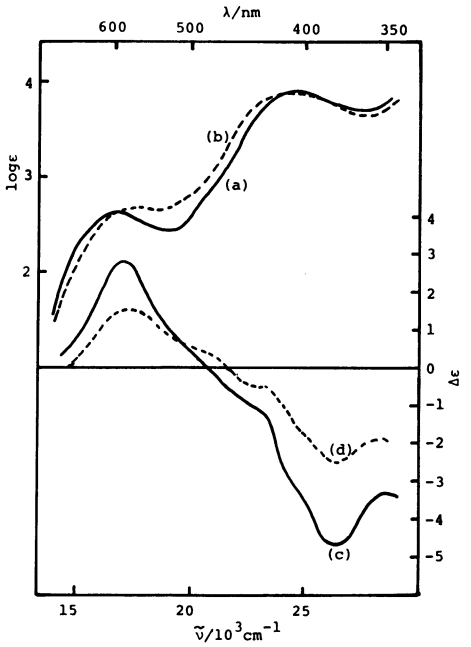


Fig. 3. AB and CD spectra of β_2-[Co(5,6-benzo-sal$_2$en)-(L-ala)] in methanol ((a) and (c)) and in DMF ((b) and (d)) under the equilibrium conditions.

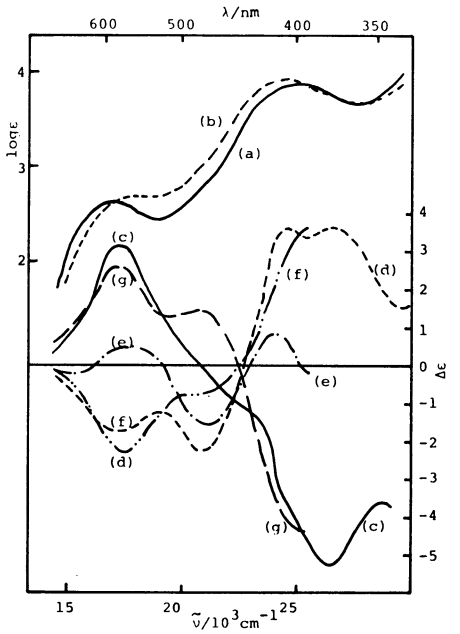


Fig. 4. AB and CD spectra of β_2-[Co(5,6-benzo-sal$_2$en)-(L-val)] in methanol ((a) and (c)) and in DMF ((b) and (d)) under the equilibrium conditions. (e): Vicinal CD of L-val of β_2-[Co(sal$_2$en)(L-val)], (f): CD curve rectified vicinal CD (e) for CD (d), (g): CD curve rectified vicinal CD (e) for CD (c).

mixture of Λ- and Δ-β_2-isomers or as a pure Λ-β_2-isomer. This difference in the isolated form comes from the solubility of the complexes. On the other hand, the isolated complexes exhibit mutarotation in methanol to show a minus rotation at 435 nm under equilibrium conditions.[9] These facts indicate that: 1) the complexes

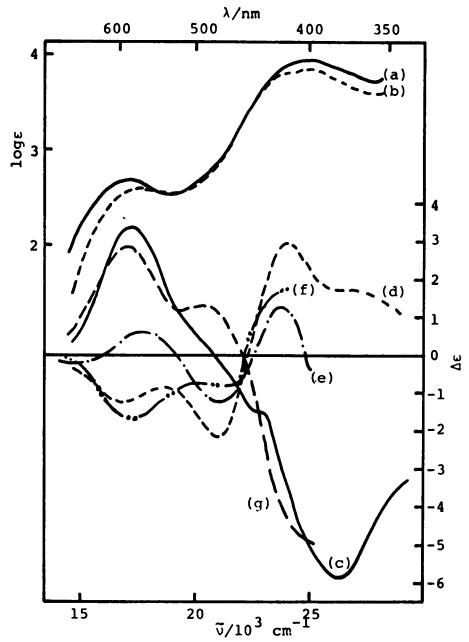


Fig. 5. AB and CD spectra of β_2-[Co(5,6-benzo-sal$_2$en)-L-ile)] in methanol ((a) and (c)) and in DMF ((b) and (d)) under the equilibrium conditions. (e): Vicinal CD of L-ile, (f): CD curve rectified vicinal CD (e) for CD (d), (g): CD curve rectified vicinal CD (e) for CD (c).

are labile in isomerization between Λ- and Δ-β_2-isomers in methanol, 2) the complexes exist as an equilibrium mixture of the two isomers in methanol, and 3) the Λ-β_2-isomer ($(-)_{435}$-isomer) is thermodynamically more stable than the Δ-β_2-isomer ($(+)_{435}$-isomer) in methanol. Also, in the cases of the [Co(5,6-benzo-sal$_2$en)(L-aa)] newly prepared here, they exhibit mutarotation in methanol to show a minus rotation at 435 nm under equilibrium conditions. Some representative mutarotations are shown in Fig. 2. The numerical data are given in Table 3. The plots of $\ln(\alpha_\infty - \alpha_t)$ *vs.* the time gave a straight line, indicating that two species of isomers, $(-)_{435}$- and $(+)_{435}$-isomers, are involved in each mutarotation. On the other hand, the AB spectra showed no clear change during the mutarotation. These facts suggest that: 1) [Co(5,6-benzo-sal$_2$en)(L-aa)] is also labile in isomerization and exists as an equilibrium mixture of $(-)_{435}$- and $(+)_{435}$-isomers in methanol; 2) the $(-)_{435}$-isomer is more stable than the $(+)_{435}$-isomer in methanol, and 3) both isomers have the same geometrical structure with respect to the coordinated atoms around the Co(III) ion.

Figures 3—5 show the AB and CD spectra of the representative 5,6-benzo-sal$_2$en complexes under the equilibrium conditions. The numerical data are listed in Table 4. The AB spectra and the CD spectral patterns of all the 5,6-benzo-sal$_2$en complexes in methanol closely resemble each other and are very similar to those of Λ-β_2-[Co(α-Me-sal$_2$en)(L-ile)] in methanol. Thus, it becomes clear that 1) all the 5,6-benzo-sal$_2$en complexes take the *cis*-β_2-structure, and 2) they favor the Λ-β_2-configuration over the Δ-β_2-configuration in methanol.

TABLE 3. MUTAROTATION DATA AND ISOLATION FORM OF β_2-[Co(5,6-BENZO-sal$_2$en)(L-aa)]

L-aa	Solvent	Temp °C	$[M]_{435}$ ° mol dm^{-3} m^{-1} (soon after dissolution)[a]	$[M]_{435}$ ° mol dm^{-3} m^{-1} (under equilibrium conditions)	Isomerization rate constant from Λ-β_2- to Λ-β_2- isomers k_{obsd}/s^{-1}, 23 °C	Isolation form Λ-β_2-isomer: Δ-β_2-isomer
L-ala	MeOH	23.5	−4000	−14000	$(9.3\pm0.2)\times10^{-3}$	
L-met	MeOH	23.5	−5500	−21000	$(7.6\pm0.2)\times10^{-3}$	
L-val	MeOH	23.5	−52000	−13000	$(6.2\pm0.1)\times10^{-3}$ [b]	
L-thr	MeOH	23.5	−15000	−40000	$(6.6\pm0.1)\times10^{-3}$	
L-leu	MeOH	23.5	−4000	−18000	$(8.5\pm0.2)\times10^{-3}$	
L-ile	MeOH	23.5	0	−12000	$(1.0\pm0.3)\times10^{-2}$	
L-phe	MeOH	23.5	−58800	−48000	$(8.4\pm0.2)\times10^{-3}$ [b]	
L-ala	DMF	36.0	+2000	−12000	$(1.3\pm0.1)\times10^{-5}$	1 : 1
L-met	DMF	36.0	+2600	−17000	$(2.1\pm0.1)\times10^{-5}$	1 : 1
L-val	DMF	36.0	−110000	+12000	$(2.1\pm0.1)\times10^{-5}$ [b]	pure Λ-β_2-isomer
L-thr	DMF	36.0	−4700	−41000	$(4.9\pm0.5)\times10^{-5}$	1 : 1
L-leu	DMF	36.0	+1400	−18000	$(9.2\pm0.2)\times10^{-6}$	1 : 1
L-ile	DMF	36.0	+3000	+12000	$(2.4\pm0.5)\times10^{-5}$	1 : 1
L-phe	DMF	36.0	−59800	−18300	$(3.2\pm0.1)\times10^{-5}$ [b]	3 : 1

a) About 1 min after dissolution. b) Isomerization constant (observed value) from the Λ-β_2-isomer to the Δ-β_2-isomer.

TABLE 4. AB AND CD SPECTRAL DATA OF β_2-[Co(5,6-BENZO-sal$_2$en)(L-aa)] [a]

L-aa	Solvent	1st band		CT and π-π^* bands	
		$\tilde{\nu}/10^3$ cm^{-1} (log ε)	$\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)	$\tilde{\nu}/10^3$ cm^{-1} (log ε)	$\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
L-ala	MeOH	16.81(2.66)	16.95(+2.77) 20.00(+0.36)	23.92(3.86) 24.88(3.91)	22.73(−1.18) 24.39(−3.02) 26.32(−4.73)
	DMF	17.54(2.68)	17.33(+1.85) 20.41(+0.53)	23.64(3.85) 24.75(3.90)	22.22(−0.62) 23.81(−1.77) 25.97(−3.51)
L-met	MeOH	16.81(2.71)	17.04(+4.42) 20.41(+0.75)	24.10(3.93) 25.00(3.98)	22.73(−1.68) 24.69(−5.77) 26.67(−6.33)
	DMF	17.39(2.68)	17.37(+2.37) 20.20(+0.85)	23.61(3.90) 24.75(3.95)	22.22(−0.79) 24.10(−2.16) 26.32(−4.77)
L-val	MeOH	16.86(2.66)	17.15(+3.22)	24.10(3.86) 25.00(3.90)	22.73(−1.20) 24.39(−3.69) 26.46(−5.33)
	DMF	17.54(2.67)	16.95(−1.85) 21.05(−2.75)	23.64(3.89) 24.81(3.93)	24.10(+4.16) 26.67(+3.05)
L-leu	MeOH	16.84(2.67)	16.81(+3.38) 20.41(+0.72)	24.10(3.92) 25.00(3.96)	22.73(−1.43) 24.10(−3.51) 26.32(−6.02)
	DMF	17.39(2.66)	17.39(+2.88) 20.41(+0.89)	23.64(3.88) 24.69(3.93)	22.22(−0.93) 23.81(−2.24) 26.32(−6.02)
L-ile	MeOH	16.89(2.67)	17.24(+3.39) 20.00(+0.41)	24.10(3.93) 25.00(3.96)	22.73(−1.42) 24.10(−3.54) 26.32(−6.01)
	DMF	17.54(2.64)	16.81(−1.28) 21.05(−2.24)	23.81(3.86) 25.00(3.91)	23.98(+3.07) 27.03(+1.84)
L-thr	MeOH	16.84(2.62)	16.81(+9.46) 20.62(+2.19)	23.92(3.85) 24.94(3.90)	22.47(−3.70) 24.39(−13.30) 26.32(−16.18)
	DMF	17.64(2.65)	17.33(+6.51) 20.62(+2.55)	23.81(3.88) 24.88(3.92)	22.47(−1.42) 24.10(−8.52) 26.11(−13.38)
L-phe	MeOH	16.81(2.67)	16.86(+7.58) 20.57(+2.10)	24.10(3.91) 25.00(3.95)	22.83(−3.99) 24.69(−10.43) 26.53(−12.46)
	DMF	17.45(2.67)	17.39(+2.59) 20.00(+0.88)	23.92(3.90) 25.00(3.94)	22.22(−0.82) 24.39(−2.72) 26.32(−5.34)

a) Data are those under the equilibrium conditions.

The mutarotation of representative complexes in DMF is shown in Fig. 6. The numerical data are given in Table 3. Although the mutarotation in DMF is slow, the curves are very similar to those in methanol, and the plots of $\ln(a_\infty - a_t)$ *vs.* the time give a straight line. The AB spectra show no clear time dependence during the mutarotation. These facts indicate that the complexes have properties in DMF similar to those in methanol. However, L-val- and L-ile-complexes exhibit a plus rotation under the equilibrium conditions in DMF, suggesting that they favor the Δ-β_2-configuration in DMF more than the Λ-β_2-configuration.

The AB and CD spectra of representative complexes in DMF under the equilibrium conditions are shown in Figs. 3—5. Although some shift of the AB and CD spectra is observed as compared with those in methanol, the AB and CD spectra in DMF of L-ala-, L-met-, L-leu-, L-thr-, and L-phe-complexes closely resemble those in methanol, indicating that the complexes take the *cis*-β_2-structure and prefer the Λ-β_2-isomer rather than the Δ-β_2-isomer in DMF. In the case of the L-val- and L-ile-complexes, the AB spectra in DMF are similar to those in methanol, while the CD spectra in DMF show signs different from those in methanol. When the vicinal effect of the coordinated L-amino acidates is subtracted from the CD curves of the L-val- and L-ile-complexes in DMF, it becomes clear that the resulting CD curves ((f) in Figs. 4 and 5) are almost in a mirror-image relation with the rectified CD curves ((g) in Figs. 4 and 5) in methanol. From these facts, it can be concluded that the L-val- and L-ile-complexes prefer the Δ-β_2-isomer in DMF rather than the Λ-β_2-isomer. It is interesting that the stereoselectivity changes depending upon the kind of solvent.

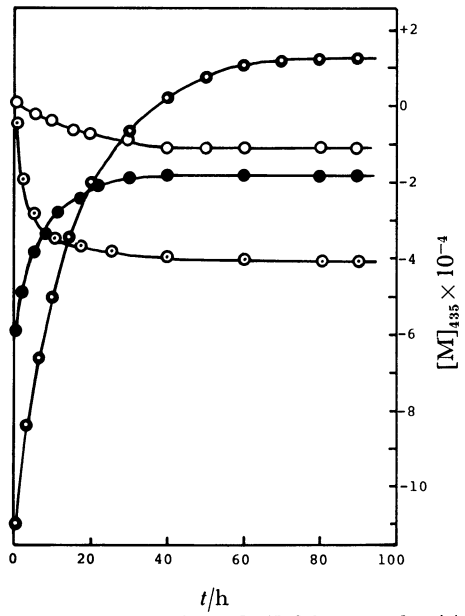


Fig. 6. Mutarotation of β_2-[Co(5,6-benzo-sal$_2$en)(L-aa)] in DMF at 36 °C.
—○—: L-ala-complex, —⊙—: L-thr-complex, —O—: L-val-complex, —●—: L-phe-complex.

From the molar rotation of the 5,6-benzo-sal$_2$en complexes soon after dissolution in DMF (Table 3), it can be assummed that: 1) the L-ala-, L-met-, L-leu-, L-ile-, and L-thr-complexes were isolated as a 1 : 1 mixture of Λ- and Δ-β_2-isomers, 2) the L-val-complex was isolated as the pure Λ-β_2-isomer, and 3) the L-phe-complex was isolated as a 3 : 1 mixture of Λ- and Δ-β_2-isomers. The isomeric ratios of the L-ala-, L-met-, L-thr-, and L-val-complexes will be confirmed below from the ^{1}H NMR spectra of the complexes in DMF.

Stereoselectivity of 5,6-Benzo-sal$_2$en Complexes. Figure 7 shows the representative ^{1}H NMR spectra of the complexes in DMF-d_7 and in a mixed solvent of CD_3OD and DMF-d_7. The numerical data are listed in Table 5. Since the 5,6-benzo-sal$_2$en complexes are not so fully soluble in CD_3OD, the mixed solvent of CD_3OD and DMF-d_7 (20%) was used here in place of CD_3OD. The CD spectra of the complexes in the mixed solvent of methanol and DMF (20%) are almost the same as those in methanol. Thus, we regarded the ^{1}H NMR spectra in the mixed solvent as close to those in CD_3OD.

Table 5. ^{1}H NMR spectral data of β_2-[Co(5,6-benzo-sal$_2$en)(L-aa)] under the equilibrium conditions δ [a]

L-aa	HC=N	$-CH_2-CH_2-$[b]	R (Amino acid)		Others
L-ala	8.45[1] 9.30[1]	4.1	1.36 1.48[1.4]	1.56 1.68[1.6]	c)
L-met	8.40[1] 9.30[1]	4.1	2.13[1.2]	2.01[1.8]	2.15—2.75 (broad multiplet of $-C\underline{H}_2-C\underline{H}_2-S-CH_3$), c)
L-val	8.48[1] 9.30[1]	4.1	0.84[0.8] 0.95[1.7]	1.06[2.2] 1.15[1.3]	c)
	8.58[1][d] 9.38[1][d]	4.4[d]	0.86[1.5][d] 0.89[3.0][d]	1.11[1.5][d]	c)
L-thr	8.47[1] 9.30[1]	4.1	1.19 1.30[1.1]	1.25 1.36[1.9]	c)
L-leu	8.44[1] 9.25[1]	4.1	0.95[b]		1.75 (broad multiplet of $-C\underline{H}_2-C\underline{H}(CH_3)_2$), c)
L-ile	8.53[1] 9.35[1]	4.1	0.85[0.2] 0.97[2.2]	1.07[2.9] 1.18[0.7]	c)
L-phe	8.19[1] 9.31[1]	4.1	3.3 (multiplet of $-C\underline{H}_2-\phi$)		6.7—8.5 (multiplets of naphtyl and phenyl signals)

a) Data in CD_3OD+DMF-d_7 (20%), [ ] represents the relative peak area. b) Broad multiplet. c) 6.8—8.4 (multiplet of naphtyl signal). d) Soon after dissolution in DMF-d_7.

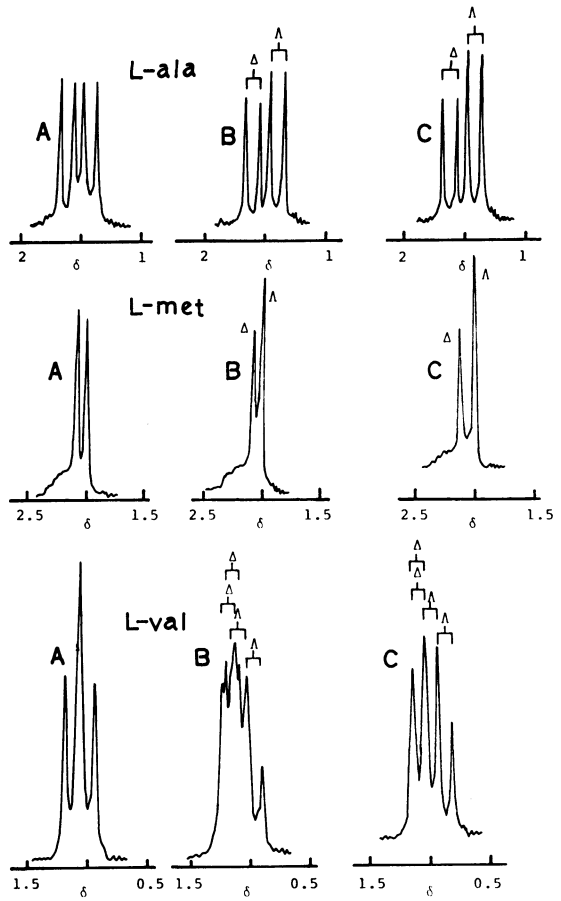


Fig. 7. The representative ^{1}H NMR spectra of β_2-[Co(5,6-benzo-sal$_2$en)(L-aa)].
A: Soon after dissolution in DMF-d_7, B: under the equilibrium conditions in DMF-d_7, C: under the equilibrium conditions in CD_3OD+DMF-d_7 (20%).

Table 6. Stereoselectivity of β_2-[Co(5,6-benzo-sal$_2$en)(L-aa)]

L-aa	[Λ]/[Δ] (in MeOH)	SS(%)[a]	[Λ]/[Δ] (in DMF)	SS(%)[a]
L-ala	1.25 (1.2—1.3)[b]	11.5	1.15 (1.1—1.2)[c]	6.9
L-met	1.45 (1.4—1.5)[b]	18.4	1.17 (1.1—1.2)[c]	8.0
L-val	1.27 (1.2—1.3)[b]	11.8	1.32[d]	−13.7
L-thr	2.61 (2.6—2.8)[b]	44.6	1.85 (1.7—1.9)[c]	29.8
L-leu	1.37	15.6	1.30	13.1
L-ile	1.39	16.2	1.18[d]	−8.2
L-phe	2.20	36.9	1.27	11.6

a) Value of $([\Lambda]-[\Delta])/([\Lambda]+[\Delta])\times 100(\%)$ from the CD spectra. b) Isomeric ratio from the ^{1}H NMR spectra in CD_3OD+DMF-d_7(20%). c) Isomeric ratio from the ^{1}H NMR spectra in DMF-d_7. d) Value of [Δ]/[Λ].

The signal of the coordinated 5,6-benzo-sal$_2$en ligand showed no observable time dependence, and the signals of all the complexes are very similar to each other. On the other hand, as is shown in Fig. 7, the alkyl signal of the coordinated L-amino acidates exhibits a time dependence. From the time dependence, it is confirmed that only two species of isomer are involved in the mutarotation of the L-ala-, L-met-, L-val-, and L-thr-complexes. Further, by a comparison with the mutarotation at 435 nm, the assignment of the alkyl peaks for Λ- and Δ-β_2-isomers becomes possible. From the relative peak area of the alkyl peaks soon after dissolution in DMF-d_7, it can be confirmed that the L-ala-, L-met-, and L-thr-complexes were isolated as a 1 : 1 mixture of the two isomers, but the L-val-complex was isolated as the pure Λ-β_2-isomer. On the other hand, from the relative peak areas of the alkyl peaks under the equilibrium conditions, the isomeric ratio between the two isomers under the equilibrium conditions can be estimated in the cases of L-ala-, L-met-, and L-thr-complexes; the values are listed in Table 6.

In the case of the L-val-complex, the alkyl signal under the equilibrium conditions is somewhat complicated due to the overlap of the peaks of the two isomers, although it is confirmed from a careful inspection that the Λ-β_2-isomer somewhat predominates over the Δ-β_2-isomer in the mixed solvent of CD_3OD and DMF-d_7, while the selectivity is reversed in DMF-d_7.

In the cases of the L-leu-, L-ile-, and L-phe-complexes, the alkyl signal is complicated due to the overlap of the peaks. Therefore, the isomeric ratio of these complexes was estimated from the $\Delta\varepsilon$ value of the main CD band in the 1st-absorption-band region of the complexes by the use of the following equation:

$$([\Lambda]-[\Delta])/([\Lambda]+[\Delta]) = (\Delta\varepsilon^A-\Delta\varepsilon^B)/(\Delta\varepsilon^C-\Delta\varepsilon^B), \quad (1)$$

where [Λ] and [Δ] represent the concentrations of the Λ- and Δ-β_2-isomers under the equilibrium conditions respectively; $\Delta\varepsilon^A$ denotes the CD intensity of the complexes at the main CD band near 580 nm under the equilibrium conditions; $\Delta\varepsilon^B$ stands for the vicinal effect of the coordinated L-amino acidates at the same wave length as that of $\Delta\varepsilon^A$, and $\Delta\varepsilon^C$ represents the CD intensity of the pure Λ-β_2-isomer at the main CD band near 580 nm. In this study, as the $\Delta\varepsilon^C$ value of various L-amino acidato complexes with 5,6-benzo-sal$_2$en, we used the $\Delta\varepsilon$ value of the pure Λ-β_2-isomer of the [Co(5,6-benzo-sal$_2$en)(L-val)] complex soon after dissolution in DMF. This is because: 1) it is only in the L-val-complex that the pure Λ-β_2-isomer can be isolated, however, 2) the $\Delta\varepsilon^C$ value can be regarded as almost a constant for the following reasons: 1) as is shown in Fig. 8, the vicinal effect of the coordinated L-amino acidates is almost a constant in the 1st-absorption region for various L-amino acidato complexes, and it is small in value as compared with the configurational effect of the complexes, and 2) as is shown in Table 7, the $\Delta\varepsilon^C$ value is almost a constant in sal$_2$en and in α-Me-sal$_2$en complexes. Indeed, as is shown in Table 6, the isomeric ratios of the L-ala-, L-met-, and L-thr-complexes, which were estimated from the CD intensity of the complexes and the $\Delta\varepsilon^C$ value of the L-val-complex, well fitted with the isomeric ratios estimated from the ^{1}H NMR spectra of the complexes.

Figure 8 shows the CD spectra of the 1 : 1 mixture of Λ- and Δ-β_2-isomers soon after dissolution in DMF; these spectra correspond to the vicinal effect of the coordinated

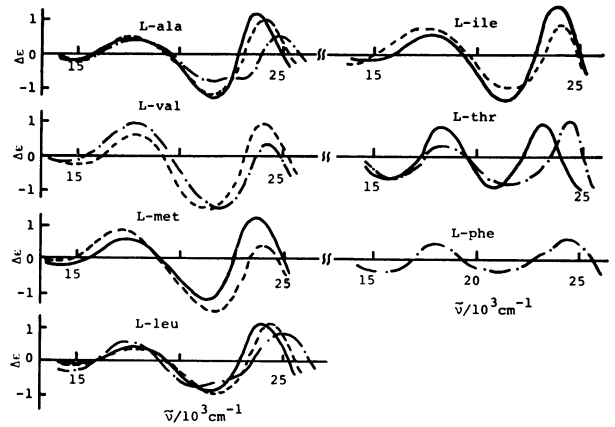


Fig. 8. Vicinal CD of β_2-[Co(Schiff base)(L-aa)] in DMF.
------: sal$_2$en complex, -·-·-: α-Me-sal$_2$en complex, ——: 5,6-benzo-sal$_2$en complex.

Table 7. The CD intensity of pure Λ-β_2-isomers in DMF

Complex	$\tilde{\nu}/10^3$ cm^{-1}($\Delta\varepsilon$)
Λ-β_2-[Co(sal$_2$en)(L-thr)]·H$_2$O	17.24(+14.99)
Λ-β_2-[Co(sal$_2$en)(L-phe)]·4.5H$_2$O	17.15(+15.21)
Λ-β_2-[Co(α-Me-sal$_2$en)(L-ile)]·1.5H$_2$O	16.95(+14.08)
Λ-β_2-[Co(α-Me-sal$_2$en)(L-met)]·2H$_2$O	16.95(+14.14)
Λ-β_2-[Co(5,6-benzo-sal$_2$en)(L-val)]·H$_2$O	17.45(+20.71)

L-amino acidates. The vicinal CD's in the 1st-absorption-band region are very similar to each other; therefore, in the calculation of Eq. 1, we used the vicinal CD's of β_2-[Co(sal$_2$en)(L-val)] and β_2-[Co(α-Me-sal$_2$en)-(L-phe)] for the $\Delta\varepsilon^B$ values of the 5,6-benzo-sal$_2$en complexes with L-val and L-phe respectively. From the similarity in the vicinal CD spectra, it is assumed that all the L-amino acidates take conformations quite similar to each other.

From Table 6, the following conclusions can be drawn: 1) the 5,6-benzo-sal$_2$en complexes have an inclination to prefer the Λ-β_2-isomer rather than the Δ-β_2-isomer in methanol and in a mixed solvent of methanol and DMF, 2) the stereoselectivity of 5,6-benzo-sal$_2$en complexes in methanol increases in the following order of L-amino acidates: L-ala=L-val<L-ile=L-leu<L-met<L-phe<L-thr, 3) this order is not parallel with the increasing order of steric bulkness of the alkyl group of amino acidates, as has been observed for sal$_2$en and α-Me-sal$_2$en complexes,[9] 4) the degree of the stereoselectivity of 5,6-benzo-sal$_2$en complexes in methanol is somewhat lower than that of sal$_2$en and α-Me-sal$_2$en complexes,[9] 5) the stereoselectivity of 5,6-benzo-sal$_2$en complexes in DMF is lower than that in methanol, and 6) in the case of L-val- and L-ile-complexes, which have the secondary β-carbon atom at the alkyl group of amino acid, they exhibit an inclination to prefer the Λ-β_2-isomer rather than the Λ-β_2-isomer in DMF.

Solvent Effect on the Stereoselectivity of Complexes. In order to get information about the stereoselectivity of Co(Schiff base)-complexes with L-amino acidates in various solvents, we measured the AB and CD spectra of Co(sal$_2$en)-, Co(α-Me-sal$_2$en)-, and Co(5,6-benzo-sal$_2$en)-complexes with L-ala, L-met, L-val, and L-phe in H$_2$O, MeOH, EtOH, PrOH, BuOH, DMF, and acetone. The numerical data are given in Tables 8—10, while representative AB and CD spectra in various solvents are shown in Figs. 9 and 10. Although some extent of shift (within 20 nm) with the variation of solvents is observed for the absorption and the associated CD bands in all the complexes, the AB spectral pattern and the intensity of each complex are very similar to those in methanol; this indicates that each complex takes the *cis*-β_2-structure in these solvents. The CD

Table 8. AB and CD spectral data (1st band) and stereoselectivity of β_2-[Co(5,6-benzo-sal$_2$en) (L-aa)] in various solvents

Solvent (pK_a)[20]		L-ala λ/nm (ε or $\Delta\varepsilon$)	SS(%)	L-met λ/nm (ε or $\Delta\varepsilon$)	SS(%)	L-val λ/nm (ε or $\Delta\varepsilon$)	SS(%)	L-phe λ/nm (ε or $\Delta\varepsilon$)	SS(%)
H$_2$O[a] (14.0)	AB	592(496)	7.3	592(495)	10.4	592(490)	2.9	592(477)	34.4
	CD	587(1.94)		589(2.84)		579(1.48)		593(7.07)	
MeOH (15.1)	AB	594(457)	11.5	594(508)	18.4	594(455)	11.8	594(469)	37.0
	CD	589(2.77)		587(4.42)		583(3.22)		593(7.58)	
EtOH (15.9)	AB	588(478)	9.3	593(510)	13.2	592(520)	15.6	594(484)	41.2
	CD	586(2.34)		585(3.40)		581(3.97)		590(8.42)	
n-PrOH (16.1)	AB	588(492)	7.8	591(509)[b]	12.5	590(505)	15.1	593(501)	41.8
	CD	583(2.04)		583(3.26)[b]		579(3.87)		588(8.53)	
n-BuOH (16.1)	AB	588(468)	7.6	592(489)[b]	11.4	590(505)	14.0	590(531)	42.3
	CD	583(2.00)		582(3.05)[b]		579(3.65)		588(8.73)	
i-PrOH (17.1)	AB	587(497)	5.4	587(536)[b]	9.1	588(521)	15.9	590(504)	44.0
	CD	583(1.56)		581(2.60)[b]		577(4.03)		585(8.96)	
s-BuOH (17.6)	AB	583(485)	4.0	585(529)[b]	9.7	588(473)	17.0	587(479)	44.0
	CD	578(1.29)		578(2.71)[b]		577(4.24)		586(8.97)	
t-BuOH (19.2)	AB	580(491)	2.5	582(516)[b]	9.0	587(531)	22.2	589(509)	46.6
	CD	576(0.99)		575(2.58)[b]		575(5.28)		586(9.48)	
DMF	AB	570(479)	6.9	575(475)	8.0	573(476)	−13.7	573(467)	11.6
	CD	577(1.85)		575(2.37)		590(−1.80)		575(2.59)	
Acetone	AB	575(496)	6.9	578(533)[b]	8.1	576(514)	−16.4	577(467)	9.4
	CD	575(1.86)		575(2.40)[b]		595(−2.35)		570(2.14)	

a) 40% DMF is present. b) 20% DMF is present.

Table 9. AB and CD spectral data (1st band) and stereoselectivity of β_2-[Co(sal$_2$en)(L-aa)] in various solvents

Solvent (pK_a)[20]		L-ala λ/nm (ε or Δε)	SS(%)	L-met λ/nm (ε or Δε)	SS(%)	L-val λ/nm (ε or Δε)	SS(%)	L-phe λ/nm (ε or Δε)	SS(%)
H_2O (14.0)	AB	586(308)	0.7	580(405)[a]	13.2	590(289)	3.7	585(299)	42.1
	CD	586(0.66)		594(2.35)[a]		580(0.94)		603(6.53)	
MeOH (15.1)	AB	585(401)	17.2	584(447)[b]	20.6	585(399)	18.5	585(398)	53.2
	CD	588(2.95)		593(3.44)[b]		585(3.14)		592(8.18)	
EtOH (15.9)	AB	585(408)	14.2	582(440)[b]	17.6	585(400)	20.9	585(388)	52.7
	CD	588(2.50)		593(3.00)[b]		585(3.49)		592(8.05)	
n-PrOH (16.1)	AB	585(435)	13.8	582(454)[b]	16.6	585(408)	24.1	585(435)	60.4
	CD	587(2.44)		590(2.85)[b]		584(3.97)		590(9.24)	
n-BuOH (16.1)	AB	584(410)	11.7	580(445)[b]	16.8	583(398)	21.5	584(430)	56.8
	CD	587(2.13)		590(2.89)[b]		584(3.58)		590(8.70)	
i-PrOH (17.1)	AB	585(435)	8.4	582(448)[b]	16.6	585(436)	30.4	584(433)	59.9
	CD	586(1.64)		590(2.85)[b]		584(4.90)		588(9.16)	
s-BuOH (17.6)	AB	584(427)	6.9	580(446)[b]	16.5	583(429)	34.4	583(415)	64.8
	CD	583(1.42)		588(2.84)[b]		584(5.49)		588(9.89)	
t-BuOH (19.2)	AB	583(480)	1.0	580(464)[b]	16.4	582(435)	37.2	583(460)	66.9
	CD	575(0.95)		586(2.82)[b]		584(5.90)		586(10.20)	
DMF	AB	579(435)	6.4	577(532)	17.0	579(431)	0.0	578(435)	22.6
	CD	580(1.35)		587(2.91)		560(0.34)		583(3.64)	
						635(−0.31)			
Acetone	AB	577(415)	5.5	575(430)	16.0	577(429)	−3.0	575(431)	27.3
	CD	575(1.21)		586(2.76)		555(0.06)		582(4.95)	
						618(−0.66)			

a) DMF (30%) is added. b) DMF (10%) is added.

Table 10. AB and CD spectral data (1st band) and stereoselectivity of β_2-[Co(α-Me-sal$_2$en)(L-aa)] in various solvents

Solvent (pK_a)[20]		L-ala λ/nm (ε or Δε)	SS(%)	L-met λ/nm (ε or Δε)	SS(%)	L-val λ/nm (ε or Δε)	SS(%)	L-phe λ/nm (ε or Δε)	SS(%)
H_2O (14.0)	AB	580(370)	4.3	584(370)	3.8	585(346)	40.0	585(350)	69.9
	CD	600(0.88)		604(3.84)		611(6.02)		612(9.65)	
MeOH (15.1)	AB	580(397)	25.4	582(358)	24.9	581(383)	41.5	583(356)	65.4
	CD	601(3.77)		602(3.90)		607(6.37)		616(9.03)	
EtOH (15.9)	AB	580(395)	19.2	581(360)	26.7	580(390)	41.4	582(367)	68.2
	CD	601(2.92)		598(4.15)		606(6.36)		616(9.41)	
n-PrOH (16.1)	AB	579(405)	17.9	580(372)	25.8	580(394)	41.2	580(377)	67.2
	CD	600(2.73)		598(4.02)		603(6.32)		614(9.28)	
n-BuOH (16.1)	AB	577(397)	17.9	580(362)	25.2	580(392)	39.5	580(368)	67.6
	CD	599(2.72)		598(3.94)		603(6.00)		613(9.33)	
i-PrOH (17.1)	AB	577(405)	11.9	580(356)	21.5	580(362)	41.8	580(374)	64.9
	CD	600(1.93)		596(3.43)		603(6.41)		612(8.96)	
s-BuOH (17.6)	AB	573(407)	9.3	579(367)	20.5	577(390)	39.2	577(362)	66.4
	CD	598(1.57)		594(3.00)		600(5.95)		600(9.17)	
t-BuOH (19.2)	AB	572(400)	5.0	578(382)	21.2	577(392)	41.5	577(380)	67.3
	CD	596(0.98)		590(3.40)		600(6.37)		600(9.29)	
DMF	AB	575(389)	7.5	578(391)	16.2	575(401)	6.3	577(378)	25.6
	CD	585(1.32)		585(2.71)		576(1.56)		586(3.59)	
Acetone	AB	574(395)	8.1	575(389)	16.8	573(404)	7.5	575(373)	27.5
	CD	580(1.41)		585(2.80)		573(1.72)		585(3.85)	

pattern of each complex in various solvents is also very similar to that in methanol; however, the CD intensity varies depending upon the kind of solvent in some complexes. Especially in the case of [Co(5,6-benzo-sal$_2$en)(L-val)], the CD spectra in DMF and acetone are almost in a mirror-image relation with that in methanol when the vicinal effect is rectified, as has been mentioned previously.

In order to certify that the variation in the CD intensity in various solvents comes mainly from the variation in the isomeric ratio between the *Λ*- and *Δ*-β_2-isomers, the ^{1}H NMR spectra of several complexes were measured in various solvents. Some representative ^{1}H NMR spectra are shown in Fig. 11. Indeed, the relative isomeric ratio changes depending upon the solvent, and the isomeric ratios estimated from the ^{1}H NMR spectra fit well with the isomeric ratios estimated from the CD intensity by the use of Eq. 1. On the other hand, the CD intensity of *Λ*$_{SS}$-β_2-[Co(α-Me-sal$_2$en)(*N*-Bz-L-ala)][12] and *Λ*-β_2-Co(sal$_2$-(*S*,*S*)-chxn)-complexes with L-ala and D-ala,[13] the stereoselectivity of which reaches almost 100% for stereochemical reasons, was nearly constant (the variation in the CD intensity in the 1st-absorption-band region in various

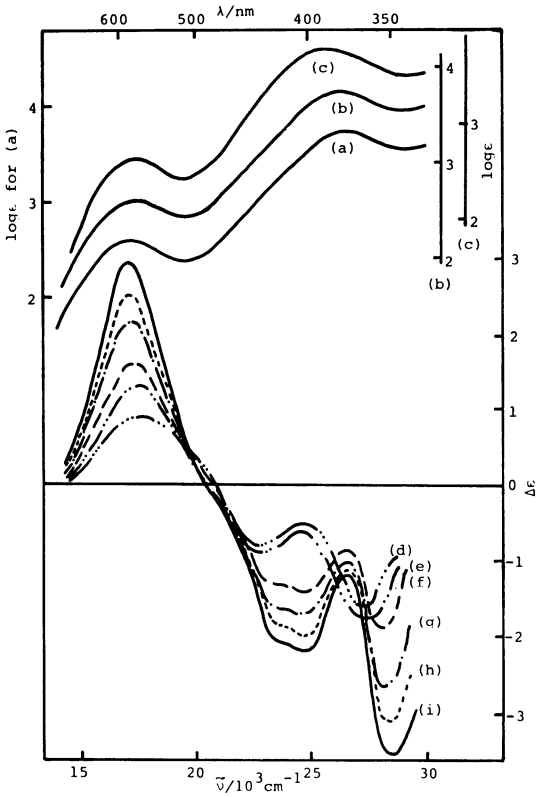


Fig. 9. AB and CD spectra of β_2-[Co(sal$_2$en)(L-ala)] in various solvents under the equilibrium conditions.
(a): MeOH, (b): *i*-PrOH, (c): DMF, (d): *t*-BuOH, (e): DMF, (f): *i*-PrOH, (g): *n*-BuOH, (h): EtOH, (i): MeOH.

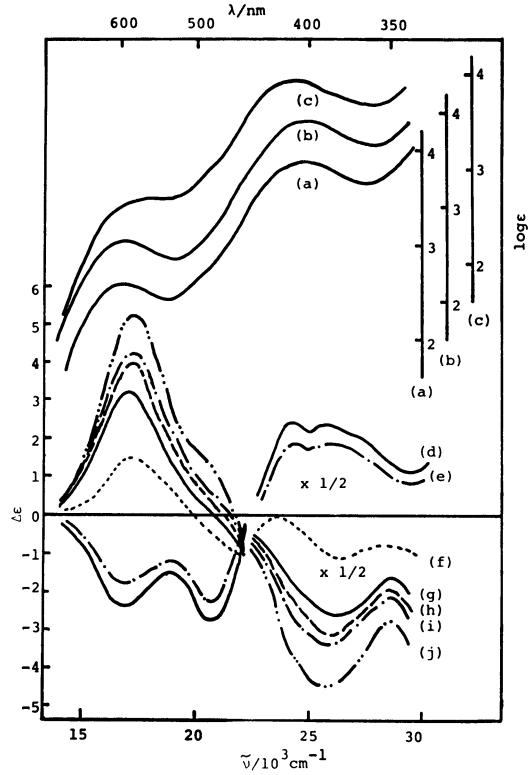


Fig. 10. AB and CD spectra of β_2-[Co(5,6-benzo-sal$_2$en)-(L-val)] in various solvents under the equilibrium conditions.
(a): MeOH, (b): *n*-BuOH, (c) DMF, (d): acetone, (e): DMF, (f): H_2O (40% DMF), (g): MeOH, (h): EtOH, (i): *s*-BuOH, (j): *t*-BuOH.

solvents was within a few %) even when the solvent was changed. These facts indicate that: 1) the effect of the solvent on the CD intensity of a pure isomer (so-called solvent effect) is very small in [Co(Schiff base)-(L-aa)] complexes, and thus 2) the CD variation in the equilibrium mixtures of Λ- and Δ-β_2-isomers with the variation in the solvents can be safely ascribed to the change in the isomeric ratio of the complexes. The stereoselectivities of the complexes in various solvents, which were estimated from the CD intensity, are given in Tables 8—10.

It becomes clear from Tables 8—10 that 1) the stereoselectivity in DMF and acetone is generally lower than that in alcoholic solvents, 2) the stereoselectivity of all the L-ala-complexes and of the 5,6-benzo-sal$_2$en complex with L-met increases with a decrease in the pK_a value of alcoholic solvents, whereas 3) the stereoselectivity of the L-val- and L-phe-complexes with sal$_2$en and 5,6-benzo-sal$_2$en increases with the increase in the pK_a value, and 4) the stereoselectivity of the L-met-complex with sal$_2$en and of the L-met-, L-val-, and L-phe-complexes with α-Me-sal$_2$en is almost constant in all the alcoholic solvents.

As may be seen in Figs. 9 and 10 and Tables 8—10, the 1st absorption band and the associated CD band at about 580 nm of all the complexes shift to the lower-energy side in the order of DMF = acetone < *t*-BuOH < *s*-BuOH < *i*-PrOH ≦ *n*-BuOH ≦ *n*-PrOH ≦ EtOH < MeOH ≦ H_2O. On the other hand, the CT and π-π*

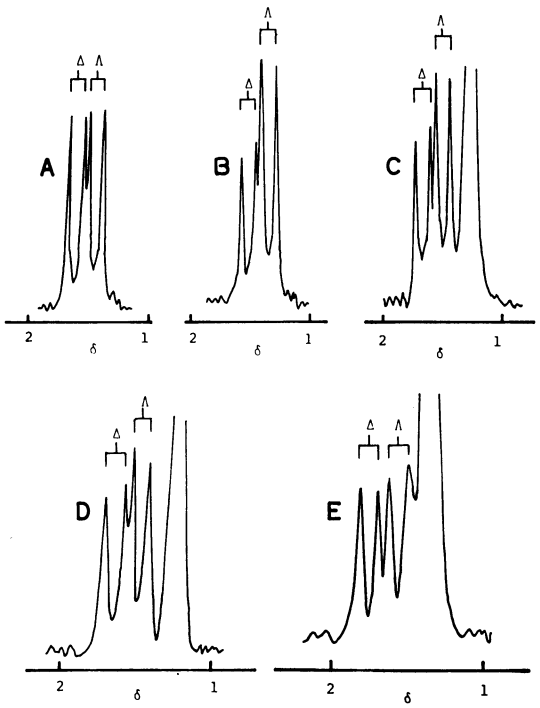


Fig. 11. ^{1}H NMR spectra of β_2-[Co(sal$_2$en)(L-ala)] in various solvents under the equilibrium conditions.
A: D_2O (20% DMF), B: CD_3OD, C: C_2D_5OD, D: *i*-C_3D_7OD, E: *t*-C_4D_9OD.

bands from 440 to 360 nm and the associated CD bands shift to the higher-energy side in the same order of solvents. These spectral shifts are characteristic of the alcoholic solvents, and are proportional to the decrease in the pK_a values of alcoholic solvents. Therefore, it can be assummed that the alcoholic solvents interact with the complexes by making a hydrogen bond with their OH group. It is known that the coordinated phenolic oxygen atoms of metal-Schiff base complexes act as proton acceptors[14] and as Lewis bases.[15-17] Accordingly it may be mainly at the phenolic oxygen atoms that the hydrogen bonding with alcoholic solvents occurs. When the hydrogen bonding is the stronger, the more the ligand-field strength of the phenolic oxygen atoms can be expected to decrease. It may be as the result of this effect that the 1st absorption band and the associated CD band shift to the lower-energy side, in parallel with the decrease in the pK_a value of the alcoholic solvents, that is, in parallel with the increase in the hydrogen-bonding ability of alcoholic solvents. The higher energy shift of the CT and π-π^* bands and the associated CD bands with the increase in the hydrogen-bonding ability may be due to the stabilization of the π-conjugate system of the Schiff-base ligand by the hydrogen bonding and the alternative instabilization of the π^*-orbital.[18]

The molecular models suggest that: 1) when complexes take the Δ-β_2-structure, the alkyl group of the coordinated L-amino acidates faces one of the phenolic oxygen atoms (O_1 in Fig. 12) of the Schiff-base ligand, whereas 2) when they take the Λ-β_2-structure, the alkyl group somewhat faces one of the Schiff-base chelate rings (B in Fig. 12), which inclines about 30° from the O–Co–N plane.[10,19] However, in either case, the alkyl group does not approach them so closely that any quite strong intramolecular steric interaction seems to exist in either isomer. This corresponds to the finding that the stereoselectivity in DMF and acetone, in which the solvation by the hydrogen bonding is not expected, is generally very small, as has been observed above. In the case of 5,6-benzo-sal$_2$en complexes with L-val and L-ile, as is shown in Fig. 13, the alkyl group has a bulky secondary β-carbon atom, so that the alkyl group approaches the 5,6-benzo-group of the chelate ring B when the complexes take the Λ-β_2-structure. Therefore, the L-val and L-ile-complexes with 5,6-benzo-sal$_2$en favor the Δ-β_2-isomer more than the Λ-β_2-isomer in DMF and acetone.

On the other hand, in alcoholic solvents, solvation at the phenolic oxygen atoms by the hydrogen bonding should be considered. As has been mentioned above, one of the phenolic oxygen atoms (O_1 in Fig. 12) of the Δ-β_2-isomer faces the alkyl group of the coordinated L-amino acidates, but the phenolic oxygen atom of the Λ-β_2-isomer does not. This corresponds to the fact that the alkyl group of L-amino acidates in the Δ-β_2-isomers sterically hinders the alcoholic solvents from approaching to one of the phenolic oxygen atoms, but there is no such steric hindrance in the Λ-β_2-isomer. Therefore, in alcoholic solvents, the Λ-β_2-isomer is more stabilized by the hydrogen bonding than the Δ-β_2-isomer is. A plausible presentation of the difference in hydrogen-bond formation is shown in Fig. 14. Since the steric bulkiness of alkyl groups of L-aa increases generally in the order of L-ala<L-met<L-val<L-phe, it is assummed that the steric hindrance of the alkyl groups for the solvation of alcoholic solvents increases in the order of L-ala<L-met<L-val<L-phe. In fact, the stereoselectivity in alcoholic solvents does indeed increase in this order.

From the above results and discussion, the free energy difference for the isomerization equilibrium between Δ- and Λ-β_2-isomers can be written as follows:

$$\Delta G = -RT\ln([\Lambda]/[\Delta]) = \Delta G^{I} + \Delta G^{S}, \quad (2)$$

where $[\Lambda]$ and $[\Delta]$ represent the concentrations of Λ- and Δ-β_2-isomers respectively under the equilibrium conditions, ΔG^{I} denotes the free energy difference between the two isomers for the intramolecular steric interaction, and ΔG^{S} means the free energy difference for the hydrogen bonding with alcoholic solvents. In DMF and acetone, the ΔG value comes mainly from

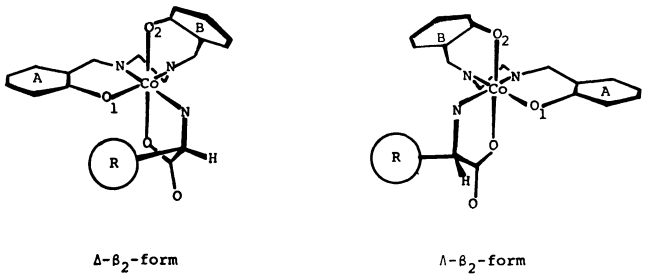


Fig. 12. Steric structure of β_2-[Co(Schiff base)(L-aa)].

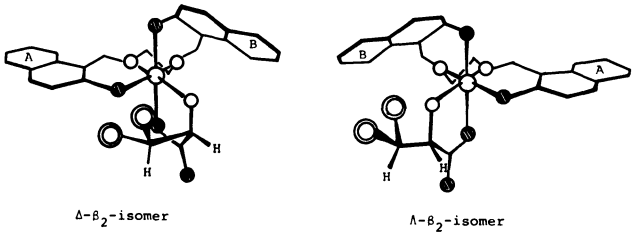


Fig. 13. Steric structure of β_2-[Co(5,6-benzo-sal$_2$en)(L-val)].
●: Represents oxygen atom, ○: represents nitrogen atom, ◎: represents methyl group.

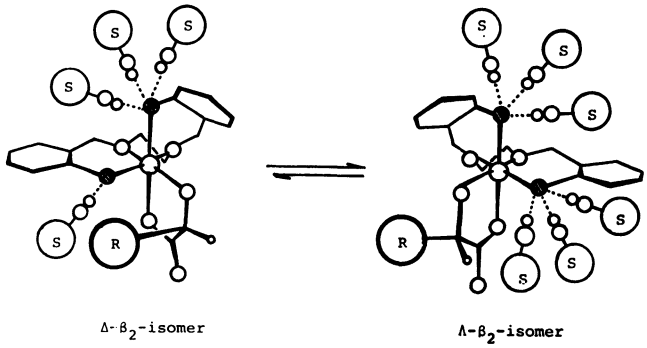


Fig. 14. Plausible feature for hydrogen bond formation with alcoholic solvent.
●: Represents phenolic oxygen atom, and S represents solvent molecule.

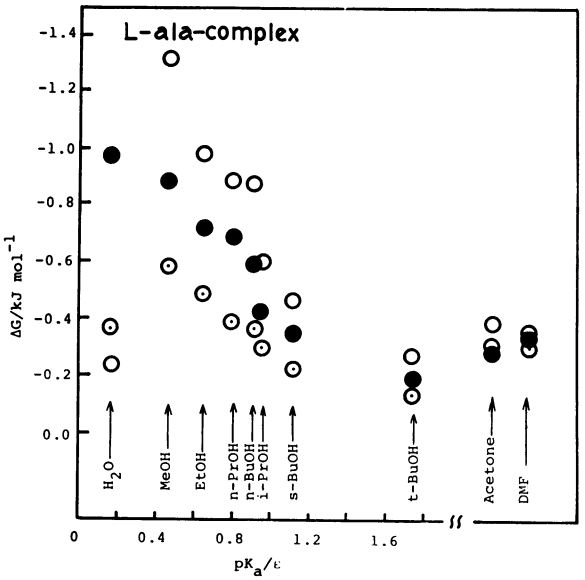


Fig. 15. Plot of ΔG value *vs.* pK_a/ε of alcoholic solvents (L-ala-complex).
⊙: 5,6-Benzo-sal$_2$en, ●: sal$_2$en, ○: α-Me-sal$_2$en.

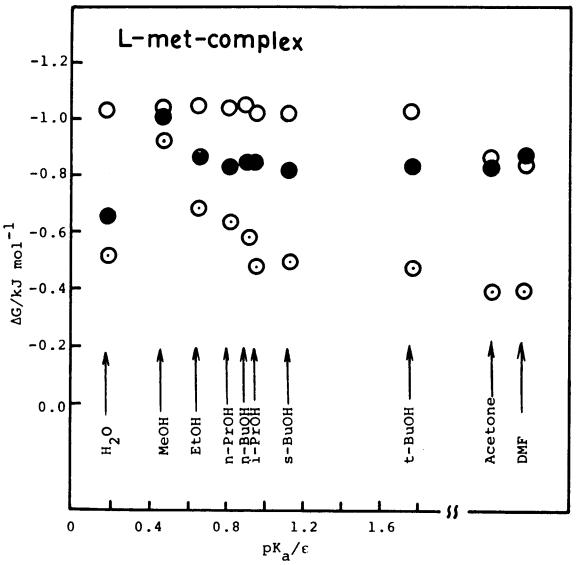


Fig. 16. Plot of ΔG value *vs.* pK_a/ε of alcoholic solvents (L-met-complex).
⊙: 5,6-Benzo-sal$_2$en, ●: sal$_2$en, ○: α-Me-sal$_2$en.

ΔG^I. On the other hand, in alcoholic solvents, the ΔG value comes from both ΔG^I and ΔG^S. However, the degree of stereoselectivity of all the complexes in DMF and acetone is generally much lower than that in alcoholic solvents. Therefore, in alcoholic solvents, the contribution of ΔG^I is assummed to be much smaller than that of ΔG^S.

When the entropy term is neglected and the hydrogen bonding is assummed to be electrostatic,[21] ΔG^S can be written as follows:

$$\Delta G^S = (q_1 q_2 N_\Lambda)/\varepsilon r_\Lambda - ((q_1 q_2 N_\Delta)/\varepsilon r_\Delta, \quad (3)$$

where q_1 and q_2 represent the charge of the phenolic oxygen atom (q_1) and that of the OH-proton of alcoholic solvents (q_2) respectively, ε denotes the dielectric

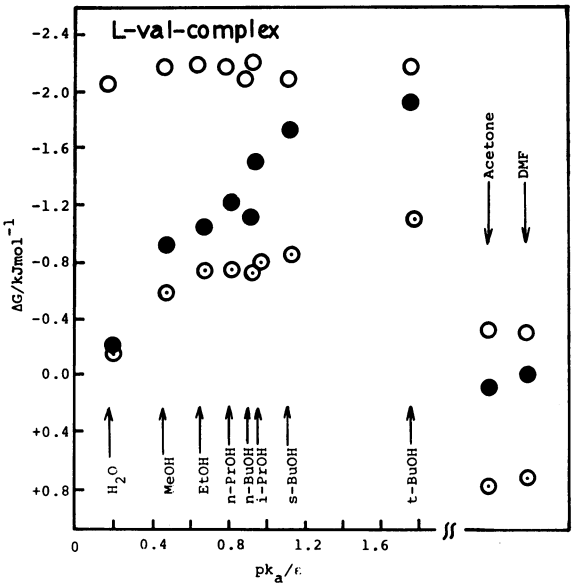


Fig. 17. Plot of ΔG value *vs.* pK_a/ε of alcoholic solvents (L-val-complex).
⊙: 5,6-Benzo-sal$_2$en, ●: sal$_2$en, ○: α-Me-sal$_2$en.

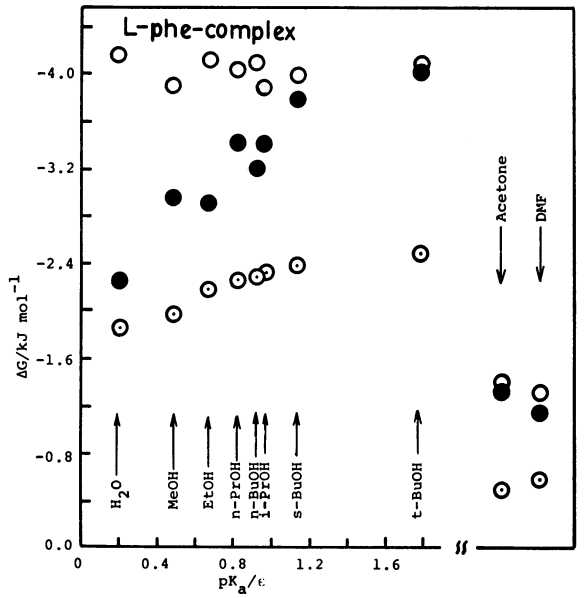


Fig. 18. Plot of ΔG value *vs.* pK_a/ε of alcoholic solvents (L-phe-complex).
⊙: 5,6-Benzo-sal$_2$en, ●: sal$_2$en, ○: α-Me-sal$_2$en.

constant of alcoholic solvents, and N_Λ and N_Δ represent the number of hydrogen-bonded solvent molecules at the phenolic oxygen atoms of Λ- and Δ-β_2-isomers at the mean distances of r_Λ and r_Δ respectively. Here, in order to simplify the explanation, we will use the following assumptions: 1) the hydrogen-bonding distance, r, is the same in both Λ- and Δ-β_2-isomers, and only the number of the hydrogen-bonding solvent molecules differs between the Λ- and Δ-β_2-isomers; 2) the distance, r, is the same for all the L-amino acidato complexes, and 3) the distance is the same for all the alcoholic solvents, and only the number of the hydrogen-bonding

solvent molecules differs among the alcoholic solvents. On the basis of the above assumptions, Eq. 3 is written as follows:

$$\Delta G^{S} = q_1 q_2 (N_\Lambda - N_\Delta)/\varepsilon r. \quad (4)$$

In this paper, as the measure of q_2, we used the pK_a values of the alcoholic solvents. Figures 15—18 show the plots of the ΔG value, calculated from the isomeric ratios in Tables 8—10, *vs.* the pK_a/ε value.

The pK_a/ε value increases in the order of $H_2O <$ MeOH $<$ *n*-PrOH $<$ *n*-BuOH $<$ *i*-PrOH $<$ *s*-BuOH $<$ *t*-BuOH; this order corresponds to the decreasing order of the hydrogen-bonding ability of the solvents. Hence, if the term of q_2 in Eq. 4 is related predominantly to the stereoselectivity of complexes, the ΔG value in alcoholic solvents decreases in parallel with the increasing order of the pK_a/ε value. It may be that, in this case, the ΔG values of all the L-ala-complexes and the L-met-complex with 5,6-benzo-sal_2en decrease in parallel with the increasing order of the pK_a/ε value of alcoholic solvents. Since a water molecule is very small and has quite a strong hydrogen-bonding ability, when the alkyl group of L-aa is not so bulky as those of L-ala and L-met, the value of $(N_\Lambda - N_\Delta)$ in Eq. 4 is expected to be small in water; indeed, the estimated ΔG values of the L-ala- and L-met-complexes are small in water. As may be seen in Fig. 15, the degree of variation in the ΔG value *vs.* the pK_a/ε value of alcoholic solvents becomes greater in the order of 5,6-benzo-sal_2en $<$ sal_2en $<$ α-Me-sal_2en; this suggests that the q_1 value of Schiff-base ligands increases in this same order. This order corresponds to the electron-donating ability of the substituent on the Schiff-base skeleton.

On the other hand, it can also be expected from Eq. 4 that, when the steric bulkiness of solvent molecule is higher, it becomes difficult to make the effective hydrogen bonding at the phenolic oxygen atoms of the Schiff-base ligand. This corresponds to the fact that the higher is the steric bulkiness of the solvent molecule, the larger is the value of $(N_\Lambda - N_\Delta)$. It may be that, in this case, the ΔG values of the sal_2en and 5,6-benzo-sal_2en complexes with L-val and L-phe increase with the increase in pK_a/ε, as may be seen in Figs. 17 and 18. This is because the increasing order of the steric bulkiness of alcoholic solvents is $H_2O <$ MeOH $<$ EtOH $<$ *n*-PrOH $<$ *n*-BuOH $<$ *i*-PrOH $<$ *s*-BuOH $<$ *t*-BuOH, and this order is parallel with the increasing order of their pK_a/ε values.

As has been observed above, the hydrogen-bonding ability and the steric bulkiness of alcoholic solvents affect the stereoselectivity of the complexes as if they were the reverse of each other. Therefore, if both effects are cancelled out, the ΔG value can be expected to be almost constant. It may be that, in this case, the α-Me-sal_2en complexes with L-met, L-val, and L-phe, sal_2en complex with L-met, and 5,6-benzo-sal_2en complex with L-phe, show a nearly constant ΔG value in various alcoholic solvents.

From these results and discussion, the following conclusion can be drawn: 1) the difference in steric hindrance between Λ- and Λ-β_2-isomers for the hydrogen-bond formation with alcoholic solvents plays an important role in the stereoselectivity of [Co(Schiff base)(L-aa)] complexes. 2) The higher the steric bulkiness of the alkyl group of coordinated L-aa, the higher the steric hindrance for the hydrogen-bond formation. 3) When the hydrogen-bonding ability of alcoholic solvents is higher, the stereoselectivity of the complexes becomes higher. 4) When the the steric bulkiness of the alcoholic solvents is higher, the stereoselectivity of the complexes becomes higher. 5) However, the effects of 3) and 4) are reversed in the case of usual alcoholic solvents.

The authors wish to express their deep thanks to Professor J. Hidaka and Dr. K. Okamoto of Tsukuba University and to Professor K. Sone and Dr. Y. Fukuda of Ochanomizu University for their kind assistance with the CD spectral measurements. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 547038) from the Ministry of Education, Science and Culture.

References

1) B. F. Anderson, D. A. Buckingham, G. J. Gainsford, G. B. Robertson, and A. M. Sargeson, *Inorg. Chem.*, **14**, 1658 (1975).

2) M. Yamaguchi, S. Yamamatsu, T. Furusawa, S. Yano, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **19**, 2010 (1980).

3) M. Yamaguchi, S. Yano, M. Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **53**, 691 (1980).

4) M. Saburi and S. Yoshikawa, "Chemistry of Octahedral Complexes," Kagaku Sosetsu, **13**, Gakkai Shuppan Center, Tokyo (1976), p. 109.

5) B. Bosnich, *J. Am. Chem. Soc.*, **89**, 6143 (1967).

6) C. J. Hawkins, G. A. Lawrance, R. M. Peachey, *Aust. J. Chem.*, **30**, 2115 (1977); C. J. Hawkins and M. L. McEniery, *ibid.*, **32**, 1433 (1979).

7) B. Bosnich and J. M. Harrowfield, *J. Am. Chem. Soc.*, **94**, 989 (1972).

8) K. Kashiwabara, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **52**, 772 (1979).

9) Y. Fujii, T. Isago, M. Sano, N. Yanagibashi, S. Hirasawa, and S. Takahashi, *Bull. Chem. Soc. Jpn.*, **49**, 3509 (1976).

10) Y. Kushi, R. Tamura, M. Kuramoto, T. Yoshizawa, H. Yoneda, and Y. Fujii, *J. Chem. Soc., Chem. Commun.*, **1978**, 266.

11) The following abbreviations are used: L-ala=L-alaninate, L-met=L-methioninate, L-val=L-valinate, L-leu=L-leucinate, L-ile=L-isoleucinate, L-phe=L-phenylalaninate, L-thr=L-threoninate, L-tyr=L-tyrosinate, L-trp=L-tryptophanate, L-aa=L-amino acidate, Those of Schiff-base ligands are shown in Table 2.

12) Y. Fujii, M. Matsufuru, A. Saito, and S. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **54**, 2029 (1981).

13) Y. Fujii, M. Sano, and Y. Nakano, *Bull. Chem. Soc. Jpn.*, **50**, 2609 (1977).

14) J. R. Thornback and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1978**, 110.

15) M. D. Hobday and T. D. Smith, *J. Chem. Soc., A*, **1971**, 1453.

16) M. D. Hobday and T. D. Smith, *J. Chem. Soc., A*, **1971**, 3424.

17) L. F. Lindoy and W. E. Moody, *J. Am. Chem. Soc.*, **97**, 2275 (1975); L. F. Lindoy, H. C. Lip, and H. W. Louie,

J. Am. Chem. Soc., **101**, 841 (1979).
18) B. Bosnich, *J. Am. Chem. Soc.*, **90**, 627 (1968).
19) M. Calligaris, G. Manzini, G. Nardin, and L. Ransaccio, *J. Chem. Soc., Dalton Trans.*, **1972**, 543; N. A. Bailey, B. M. Higson, and E. D. McKenzie, *ibid.*, **1972**, 503.
20) E. P. Serjieant and B. Dempsey, "Inoization Constants of Organic Acids in Aqueous Solution," IUPAC Chemical Data Series-No. 23, Pergamon Press, Oxford (1979).
21) J. E. Huheey, "Inorganic Chemistry," Harper and Row, New York (1972), p. 193.