Stereochemistry and Reactivity of Metal–Schiff-base Complexes. I. Preparation and Thermodynamic Stereoselectivity of Mixed Ligand Cobalt(III) Complexes Containing *N,N'*-Ethylenebis(salicylideneamine) Dianion (sal_2en) or *N,N'*-Ethylenebis(7-methylsalicylideneamine) Dianion (7,7'-Me-sal_2en) and L-Amino Acid Anion

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Two series of new mixed ligand cobalt (III) complexes with the general formulas of [Co(sal_2en)(L-aa)] and [Co(7,7'-Me-sal_2en)(L-aa)] (where L-aa=anion of L-ala, L-val, L-leu, L-isoleu, L-met, L-thr, L-phe, L-tyr, or L-trp) have been prepared and characterized. All are labile for both isomerization and substitution reactions and each exists in an equilibrium mixture of Λ_L- and Δ_L-*cis*-β_1(fac)-isomers ($\Lambda_L > \Delta_L$) in methanol. The isomer's ratios, Λ_L/Δ_L, were estimated from their PMR spectra, and the following facts were found: The increasing order of the ratios is L-ala∼L-met∼L-leu<L-val<L-isoleu<L-thr<L-phe∼L-tyr<L-trp, and the ratios are larger in 7,7'-Me-sal_2en-complexes than in sal_2en-complexes for each amino acid.

Many studies have been undertaken about the steroselectivity in inert cobalt(III) complexes. However, it is often difficult to distinguish between kinetic and thermodynamic stereoselectivities in the inert cobalt(III) complexes.[1–9] On the other hand, it is well known that mixed ligand cobalt(III) complexes containing Schiff-bases are generally substitution labile.[10–15] Since the origin of the stereoselectivity in labile complexes is thought to be thermodynamic, a study of the stereoselectivity of the mixed ligand cobalt(III)–Schiff-base complexes is very interesting. Another interest is from the stereochemical viewpoint. That is, as shown in Fig. 1, the steric stucture of *cis*-β-[Co(sal_2en)(acac)] is extremely distorted as compared with those of the usual cobalt(III) complexes.[16–19] Especially, chelates A and C are so close that an intramolecular steric interaction is expected between them. Therefore, if an optically active bidentate ligand coordinates at the site of the chelate C, such a complex may show high stereoselectivity. In this paper, we report the preparation, the properties and the thremodynamic stereoselectivity of the mixed ligand cobalt(III) complexes containing sal_2en or 7,7'-Me-sal_2en as a Schiff-base ligand and L-amino acid anion.

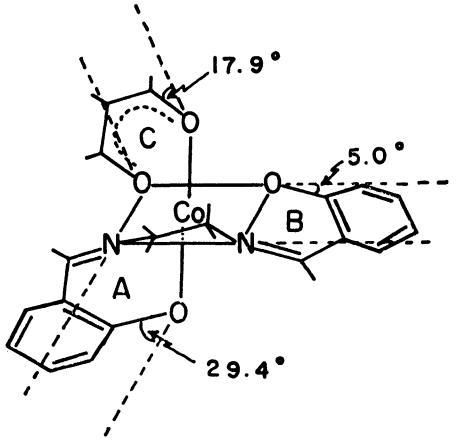


Fig. 1. The distorted chelate skeleton in [Co(sal_2en)(acac)].[17] ---- shows the normal bond direction.

Experimental

Preparation of the Complexes. All the complexes were synthesized from [Co(sal_2en)][20] or [Co(7,7'-Me-sal_2en)][21] and amino acids by air oxidation.

1) Co(III)-sal_2en Series Complexes: Amino acid (0.015 mol) partially dissolved in 25 ml of water was added to a suspension of [Co(sal_2en)] (5.0 g, 0.015 mol) in 130 ml of methanol. In the cases of L-ala, L-val, and L-asp, the amino acid solution was partially neutralized with KOH (0.2 g for L-ala and L-val, 0.5 g for L-asp). The mixture was stirred vigorously in open air at room temperature for the time periods listed in Table 1. The unreacted materials were then removed by filtration, and a brownish green solution was obtained. The methods for isolation and purification of the crude product are as follows.

i) [Co(sal_2en)(gly)], [Co(sal_2en)(L-isoleu)], [Co(sal_2en)(L-met)], [Co(sal_2en)(L-ser)], and [Co(sal_2en)(L-asp)]: The brownish green solution was concentrated to about a half volume at room temperature and to this solution was added water (100 ml). Chloroform (80 ml, twice) was then added and the complex was extracted. Concentrating the solution to a small volume (about 40 ml for gly, L-met, and L-asp) or to dryness (for L-ser and L-isoleu) at room temperature, a green product was obtained. It was recrystallized from methanol–acetone–water (10 : 2 : 1) for gly and L-isoleu or from chloroform for L-met, L-ser, and L-asp. Green crystals were obtained except for L-isoleu (powder).

ii) [Co(sal_2en) (L-ala)], [Co(sal_2en)(L-val)], and [Co(sal_2en)(L-leu)]: Upon concentrating the brownish green solution to about 30 ml under reduced pressure at room temperature, green crystals were deposited. They were recrystallized from methanol–acetone–water (10 : 2 : 1) for L-ala and L-val or from methanol containing 0.1% (gravimetric) KOH for L-leu.

iii) [Co(sal_2en) (L-thr)], [Co(sal_2en)(L-phe)], and [Co(sal_2en)(L-trp)]: Concentrating the brownish green solution to a half or one third volume at room temperature, a green product was obtained. It was recrystallized from methanol for L-thr and L-trp or from methanol–acetone–water (10 : 2 : 1) for L-phe.

iv) [Co(sal_2en) (L-tyr)]: After concentrating the brownish green solution to about a half volume, water (300 ml) and

chloroform (100 ml) were added. The water layer was concentrated to about 100 ml at 50 °C under reduced pressure. The green powder thus obtained was purified by dissolving it in chloroform, followed by filtration and concentration to dryness.

The yields are summarized in Table 1 and the analytical data are listed in Table 2.

2) Co(III)-7,7'-Me-sal$_2$en Series Complexes: Amino acid (0.017 mol) partially dissolved in 50 ml of water was added to a suspension of [Co(7,7'-Me-sal$_2$en)] (5.0 g, 0.014 mol) in 200 ml methanol. The mixture was stirred vigorously in open air for about 3 h at room temperature. In the case of L-tyr, the reaction was continued for a day. After filtration of the solution, the green solution thus obtained was concentrated to a small volume (50—100 ml). Green crystals were obtained and recrystallized from methanol. In the cases of L-leu and L-ser, their complexes were recrystallized from acetone and *N,N*-dimethylformamide, respectively. Yields, 60—90%. The anal. data are listed in Table 2.

In both series of complexes, L-ser- and L-asp-complexes are hardly soluble in methanol. Therefore, we did not measure their AB, CD, and PMR spectra. The IR spectra of all the complexes showed asym. ν(COO) at about 1625—1635 cm^{-1}.

Measurements. The electronic absorption spectra were

Table 1. Abbreviations of amino acids and preparative conditions for [Co(sal$_2$en)(L-aa)] complexes

Amino acid	Abbreviation	Reaction time[b] (h)	Solvent for recrystallization	Yield (%)
Glycine	gly	1	Methanol-acetone-water (10 : 2 : 1)	10
L-Alanine	L-ala	2.5	Methanol-acetone-water (10 : 2 : 1)	25
L-Valine	L-val	1	Methanol-acetone-water (10 : 2 : 1)	10
L-Leucine	L-leu	1	Methanol containing 0.1% KOH	10
L-Isoleucine	L-isoleu	2.5	Methanol-acetone-water (10 : 2 : 1)	10[a]
L-Methionine	L-met	0.5	Chloroform	25
L-Serine	L-ser	1	Chloroform	13
L-Threonine	L-thr	0.5	Methanol	10[a]
L-Phenylalanine	L-phe	2.5	Methanol-acetone-water (10 : 2 : 1)	20
L-Tyrosine	L-tyr	24	Chloroform	10
L-Triptophan	L-trp	0.5	Methanol	30
L-Aspartic acid	L-asp	1	Chloroform	10

a) Obtained as a powder. b) Longer reaction time produces brown complex.

Table 2. Elemental analyses data

Number	Complex	C (%)		H (%)		N (%)	
		Found	(Calcd)	Found	(Calcd)	Found	(Calcd)
1	[Co(sal$_2$en)(gly)]·2H$_2$O	50.04	(49.66)	5.17	(5.09)	9.74	(9.65)
2	[Co(sal$_2$en)(L-ala)]·3H$_2$O	48.87	(48.83)	5.50	(5.61)	9.15	(9.00)
3	[Co(sal$_2$en)(L-val)]·2H$_2$O	52.92	(52.80)	6.01	(5.91)	8.92	(8.80)
4	[Co(sal$_2$en)(L-leu)]·2.5H$_2$O	52.61	(52.80)	6.26	(6.24)	8.58	(8.40)
5	[Co(sal$_2$en)(L-isoleu)]·H$_2$O	56.03	(55.82)	6.04	(5.96)	8.78	(8.88)
6	[Co(sal$_2$en)(L-met)]·2CHCl$_3$	39.00	(38.78)	3.80	(3.68)	5.67	(5.90)
7	[Co(sal$_2$en)(L-ser)]·2CHCl$_3$	38.07	(37.78)	3.44	(3.32)	6.32	(6.29)
8	[Co(sal$_2$en)(L-thr)]·H$_2$O	52.08	(52.07)	5.42	(5.24)	9.17	(9.11)
9	[Co(sal$_2$en)(L-aspH)]	52.31	(52.53)	4.45	(4.41)	9.08	(9.19)
10	[Co(sal$_2$en)(L-phe)]·4.5H$_2$O	52.45	(52.63)	5.52	(5.83)	7.44	(7.34)
11	[Co(sal$_2$en)(L-tyr)]·CHCl$_3$	49.39	(49.19)	3.92	(4.03)	6.88	(6.73)
12	[Co(sal$_2$en)(L-trp)]·3.5H$_2$O	53.31	(53.38)	5.47	(5.31)	9.20	(9.22)
13	[Co(7,7'-Me-sal$_2$en)(gly)]·3H$_2$O	49.77	(49.90)	5.89	(5.86)	8.69	(8.73)
14	[Co(7,7'-Me-sal$_2$en)(L-ala)]	56.94	(57.15)	5.62	(5.48)	9.61	(9.52)
15	[Co(7,7'-Me-sal$_2$en)(L-val)]·2H$_2$O	54.71	(54.65)	6.27	(6.38)	8.40	(8.31)
16	[Co(7,7'-Me-sal$_2$en)(L-leu)]·2H$_2$O	55.52	(55.49)	6.53	(6.60)	8.25	(8.09)
17	[Co(7,7'-Me-sal$_2$en)(L-isoleu)]·1.5H$_2$O	56.30	(56.45)	6.77	(6.52)	8.24	(8.23)
18	[Co(7,7'-Me-sal$_2$en)(L-met)]·2H$_2$O	51.73	(51.39)	6.31	(6.00)	7.45	(7.82)
19	[Co(7,7'-Me-salen)(L-ser)]	54.98	(55.15)	5.43	(5.29)	9.11	(9.19)
20	[Co(7,7'-Me-sal$_2$en)(L-thr)]·3.5H$_2$O	49.60	(49.44)	5.89	(6.22)	7.63	(7.86)
21	[Co(7,7'-Me-sal$_2$en)(L-aspH)]·0.5H$_2$O	53.72	(53.45)	5.21	(5.10)	8.36	(8.50)
22	[Co(7'7'-Me-sal$_2$en)(L-phe)]·2.5H$_2$O	57.65	(57.65)	6.02	(5.91)	7.60	(7.47)
23	[Co(7'7'-Me-sal$_2$en)(L-tyr)]·2.5H$_2$O	56.17	(56.06)	5.78	(5.75)	7.00	(7.26)
24	[Co(7,7'-Me-sal$_2$en)(L-trp)]·2H$_2$O	57.40	(57.24)	5.34	(5.46)	9.05	(9.21)

measured with a Hitachi EPS-3 Spectrophotometer. The CD spectra were recorded with a JASCO J-20 Automatic Recording Spectropolarimeter. Optical rotations at 435 nm were recorded with a JASCO DIP-180 Automatic Polarimeter. The IR spectra were recorded with a Hitachi EPI-S2 Spectrometer in KBr pellets. The PMR spectra were measured with a Hitachi R-20 Spectrometer (60 MHz) at 35 °C in CD_3OD by using TMS as the internal reference.

Results and Discussion

Properties of the Complexes. All the complexes except for the gly-complexes **1** and **13** exhibit mutarotations in methanol; the data are summarized in Table 3. Some representative mutarotations are shown in Fig. 2. It is seen that there are two patterns of mutarotation; one is for the complexes **2**—**6**, **14**—**16**, **20**, **22**, and **23**, which show quite small rotations soon after dissolution but show large $(-)_{435}$-rotations at equilibrium conditions, The other is for the complexes **8**, **10**, **12**, **17**, **18**, and **24**, which show quite large $(-)_{435}$-rotations soon after dissolution but decrease their magnitudes at equilibrium conditions. As mentioned later, each of the complexes exists as only *cis*-β_1(fac)-geometrical isomer in methanol. Therefore, the mutarotations correspond to the isomerization reaction between $(-)_{435}$- and $(+)_{435}$-isomers. The plots of $\log(\alpha_\infty-\alpha_t)$ *vs.* time give linear relations. Accordingly, the observed isomerization rates, k_{obsd}, can be estimated as listed in Table 3. Since the following equilibrium reaction is thought to occur in solution,

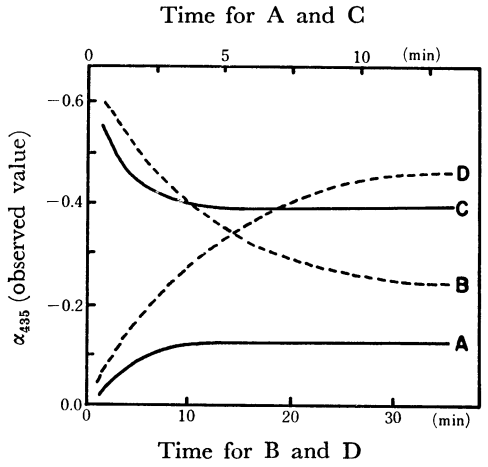


Fig. 2. The representative mutarotations of the complexes in methanol at 25 °C. A: [Co(sal$_2$en)(L-met)], B: [Co(7,7′-Me-sal$_2$en)(L-met)], C: [Co(sal$_2$en)(L-phe)], D: [Co(7,7′-Me-sal$_2$en)(L-phe)].

$(+)_{435}$-isomer $\underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}}$ $(-)_{435}$-isomer, the isomerization rate constants from $(+)_{435}$-isomer to $(-)_{435}$-isomer, k_{+1}, and from $(-)_{435}$-isomer to $(+)_{435}$-isomer, k_{-1}, are written by $k_{+1}=2.303[S/(S+1)]k_{obsd}$ and $k_{-1}=2.303[1/(S+1)]k_{obsd}$ respectively, where S is the stereoselectivity in each complex at the equilibrium condition, $S=(-)_{435}$-isomer/$(+)_{435}$-isomer.[22] The estimated rate constants, k_{+1} and k_{-1}, are also listed in Table 3. It is seen that the isomerization rates are fairly rapid,

Table 3. Mutarotation at 435 nm of the complexes in methanol (T=25 °C)

Amino acid and number of complex	Concentration of the soln. (mol l^{-1}) ×10^3	α_{435} with 1 cm cell (° cm^{-1}) (soon after dissolution)[a]	α_{435} with 1 cm cell (° cm^{-1}) (at equilibrium condition)	$[M]^{25}_{435}$ at equilibrium condition (° m^{-1} mol l^{-1})	Isomerization rate, k_{obsd} (s^{-1})	Isomerization rate constants (s^{-1}) k_{+1} ($\Delta\rightarrow\Lambda$),	k_{-1} ($\Lambda\rightarrow\Delta$)
[Cosal$_2$en)(L-Amino acid anion)] Complex							
L-ala (2)	1.70	+0.038	−0.109	−6400	1.7×10^{-2}	2.4×10^{-2}	1.6×10^{-2}
L-val (3)	1.63	+0.028	−0.110	−6700	1.3×10^{-2}	1.8×10^{-2}	1.2×10^{-2}
L-leu (4)	1.61	+0.033	−0.117	−7300	1.4×10^{-2}	1.9×10^{-2}	1.3×10^{-2}
L-isoleu (5)	1.74	−0.007	−0.140	−8000	1.1×10^{-2}	1.5×10^{-2}	1.0×10^{-2}
L-met (6)	1.24	+0.016	−0.119	−9600	1.3×10^{-2}	1.8×10^{-2}	1.2×10^{-2}
L-thr (8)	1.50	−0.736	−0.440	−29300	8.5×10^{-3}	1.6×10^{-2}	3.9×10^{-3}
L-phe (10)	1.34	−0.657	−0.375	−28000	1.4×10^{-2}	2.6×10^{-2}	6.3×10^{-3}
L-tyr (11)	1.27	−0.311[b]	−0.382	−30100	1.4×10^{-2}	2.7×10^{-2}	5.6×10^{-3}
L-trp (12)	1.28	−0.549	−0.482	−37700	8.4×10^{-3}	1.7×10^{-2}	2.1×10^{-3}
[Co(7,7′-Me-sal$_2$en)(L-Amino acid anion)] Complex							
L-ala (14)	1.68	+0.019	−0.215	−12800	1.0×10^{-3}	1.5×10^{-3}	7.5×10^{-4}
L-val (15)	1.59	+0.011	−0.335	−21100	1.7×10^{-3}	2.6×10^{-3}	1.0×10^{-3}
L-leu (16)	1.61	−0.036	−0.227	−14100	1.0×10^{-3}	1.5×10^{-3}	7.5×10^{-4}
L-isoleu (17)	1.56	−0.677	−0.313	−20100	1.6×10^{-3}	2.7×10^{-4}	9.7×10^{-4}
L-met (18)	1.56	−0.649	−0.223	−14300	1.4×10^{-3}	2.2×10^{-3}	1.1×10^{-3}
L-thr (20)	1.50	+0.033	−0.453	−30200	8.0×10^{-4}	1.5×10^{-3}	2.8×10^{-4}
L-phe (22)	1.39	+0.021	−0.445	−32000	1.6×10^{-3}	3.3×10^{-3}	3.5×10^{-4}
L-tyr (23)	1.36	+0.008	−0.515	−37900	1.5×10^{-3}	3.1×10^{-3}	3.3×10^{-4}
L-trp (24)	1.29	−0.606	−0.540	−41900	1.2×10^{-3}	2.6×10^{-3}	1.6×10^{-4}

a) Estimated value from k_{obs} by extrapolating to time=0; this value contains some error because it takes a few minutes to dissolve the complex in methanol, the + or − rotation is perhaps due to the error and/or the vicinal effect of the coordinated amino acid. b) This complex shows medium $(-)_{435}$-rotation soon after dissolution by exception.

as compared with those of the usual cobalt(III) complexes.[23] As the complexes easily isomerize to establish equilibrium conditions in methanol with $(-)_{435}$-rotations, the stereoselectivity in these complexes at equilibrium conditions is thermodynamic in origin, and $(-)_{435}$-isomers are more stable than $(+)_{435}$-isomers.

It should be noted that the complexes are labile not only for the isomerization reaction mentioned above but also for the substitution reaction of the coordinated amino acid anion. For example, the substitution rate, k_{obsd}, in the following reaction in methanol is observed to be 2.2×10^{-2} s^{-1} mol l^{-1} at 25 °C:

[Co(7,7′-Me-sal$_2$en)(L-phe)] + D-phe$^-$
⟶ [Co(7,7′-Me-sal$_2$en)(D-phe)] + L-phe$^-$

From the above mutarotations and the time dependnt PMR spectra mentioned later, the following facts become clear that the complexes **2**—**6**,**14**—**16**, **20**, **22**, and **23** are isolated each as an 1 : 1 mixture of $(-)_{435}$-and $(+)_{435}$-isomers, but the complexes **8**, **10**, **12**, **17**, **18**, and **24** are isolated each as a pure $(-)_{435}$-isomer. The discrepancy of the composition of the two isomers between the solid state and solution is perhaps due to the solubility of the complexes. That is, when the isomerization is rapid, only the least soluble isomer may be preferentially isolated.

Structure of the Complexes. Figure 3 shows representative AB and CD spectra of the complexes at equilibrium conditions. All the AB and CD spectral data are summarized in Tables 4 and 5.

All the complexes reveal nearly the same AB spectra and very similar CD spectra at equilibrium conditions.

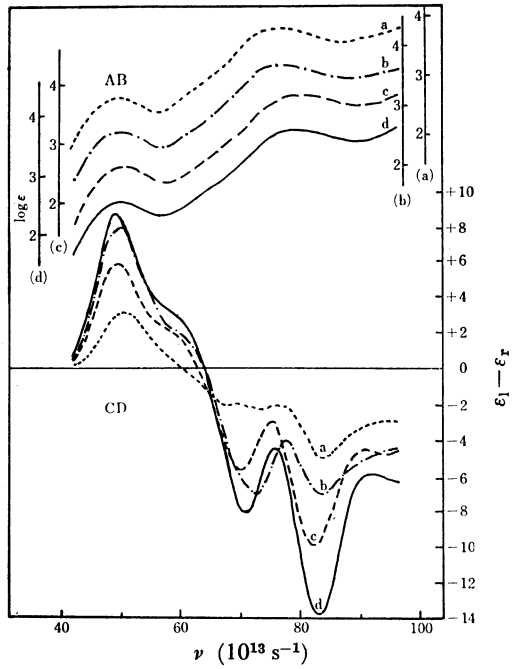
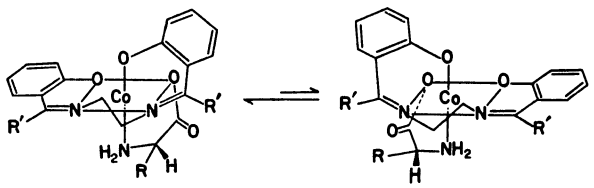


Fig. 3. The representative AB and CD spectra of the complexes in methanol at equilibrium conditions. a: [Co(sal$_2$en) (L-val)], b: [Co(sal$_2$en) (L-phe)], c: [Co(7,7′-Me-sal$_2$en) (L-val)], d: [Co(7,7′-Me-sal$_2$en) (L-phe)]. (a), (b), (c), and (d) are log ε value for the corresponding complexes.

The AB spectra soon after dissolution are also nearly the same as those at the equilibrium conditions in all the complexes. Therefore, these results suggest that 1) $(-)_{435}$- and $(+)_{435}$-isomers in each complex have the same geometrical configuration and 2) the geometrical configuration is the same for all the complexes. It is known that *cis*-α-structure is unstable in cobalt(III)–Schiff-base complexes and the existence of such a complex has not yet been found.[16,19] On the other hand, the *cis*-β-structure is well known.[16-21] Therefore, all the complexes may take either *cis*-β_1(*fac*)- or *cis*-β_2(*mer*)-structure. Another experiment[24] shows that [Co(sal$_2$-(*S*,*S*)-chxn(aa)] complex (where sal$_2$-(*S*,*S*)-chxn indicates the dianion of (1*S*,2*S*)-*N*,*N*′-1,2-cyclohexylenebis(salicylideneamine) and aa, amino acid anion) takes stereoselectively the *Λ*-*cis*-β-structure with a large $(-)_{435}$-rotation and its AB and CD spectra are quite similar to those of $(-)_{435}$-isomers obtained here. Thus, the *Λ*-configuration is assigned to the $(-)_{435}$-isomers and *Δ* to the $(+)_{435}$-isomers. As mentioned later, the results of the stereoselectivity in the complexes show that there exists intramolecular steric repulsion between the alkyl group of the coordinated amino acid anion and H–C=N or CH_3–C=N groups of the Schiff-base ligand, and that the repulsion is stronger in $(+)_{435}$-isomer than in $(-)_{435}$-isomer. The molecular model indicates that such a steric interaction is stronger in Δ_L-configuration than Λ_L, if the complex takes the *cis*-β_1(*fac*)-structure, but is stronger in Λ_L-configuration than in Δ_L, if the complex takes the *cis*-β_2(*mer*)-structure. Therefore, all the complexes are suggested to take the *cis*-β_1(*fac*)-structure. The proposed structures are shown in Fig. 4.

Stereoselectivity. All the PMR specrtal data are summarized in Tables 6 and 7, and the representative PMR spectra are shown in Fig. 5.

In complexes **2**—**6**, **8**, and **14**—**18**, the signal of H-C=N or CH_3–C=N protons of the Schiff-base ligand shows no time dependence; the signal appears only as two peaks with equal intensity, not onoy soon after dissolution but also at the equilibrium condition. However, the signal of the coordinated amino acid anion shows a clear time dependence. For example, as shown in Figs. 5 A and A′, the L-ala-complex **2** shows two kinds of signals with equal intensity for the methyl group of the coordinated L-alanine anion soon after dissolution, but these two signals change in their intensities at the equilibrium condition. Similar behaviors are observed for the complexes **3**—**6**,



Λ_L-*cis*-β_1(fac) ($(-)_{435}$-isomer) Δ_L-*cis*-β_1(fac) ($(+)_{435}$-isomer)

Fig. 4. The proposed structure of the complexes and the equilibrium in methanol. R=H or CH_3.

TABLE 4. AB AND CD SPECTRAL DATA FOR [Co(sal$_2$en)(Amino acid anion)] IN METHANOL AT THE EQUILIBRIUM CONDITION (Wave numbers are in 10^3 cm^{-1})

Amino acid and No. of complex	AB(log ε_{max})	CD($\Delta\varepsilon_{max}$)	Amino acid and No. of complex	AB(log ε_{max})	CD($\Delta\varepsilon_{ext}$)
gly (1)	16.95(2.53)		L-met (6)	17.00(2.62)	17.00 (+2.62)
	21.23(2.74)*			21.23(2.73)*	19.61 (+0.90)
	24.39(3.57)*			24.39(3.63)*	23.81 (−2.11)
	25.98(3.78)			25.98(3.82)	25.00 (−2.55)
L-ala (2)	16.95(2.65)	17.09(+3.07)			28.57 (−3.78)
	21.23(2.73)	19.61(+0.66)	L-thr (8)	16.95(2.55)	17.00 (+8.64)
	24.39(3.56)*	23.53(−2.20)		21.23(2.74)*	20.83 (+1.32)
	25.98(3.77)	25.00(−2.36)		24.39(3.58)*	24.88 (−7.80)
		28.74(−3.53)		25.98(3.79)	28.41(−10.92)
L-val (3)	16.95(2.62)	17.18(+3.12)	L-phe (10)	16.95(2.59)	16.89 (+7.97)
	21.23(2.75)*	19.61(+0.75)		21.23(2.65)*	20.83 (+2.47)
	24.39(3.62)*	23.26(−2.18)		22.73(3.03)*	24.61 (−6.80)
	25.98(3.79)	25.00(−2.20)		24.39(3.55)*	28.17 (−7.02)
		28.49(−4.97)		25.98(3.74)	
L-leu (4)	16.95(2.62)	16.98(+2.79)	L-tyr (11)	17.04(2.64)	16.67 (+8.13)
	21.23(2.74)*	19.61(+0.60)		21.93(2.75)*	20.41 (+1.63)
	24.39(3.55)*	23.53(−2.00)		23.87(3.64)*	23.81 (−6.97)
	25.98(3.75)	25.00(−2.10)		25.97(3.84)	24.69 (−7.73)
		28.57(−3.40)			28.09(−10.46)
L-isoleu (5)	16.95(2.58)	16.95(+2.22)	L-trp (12)	16.95(2.61)	16.95(+11.03)
	21.23(2.78)*	18.52(+1.09)		21.74(2.68)*	20.83 (+2.47)
	24.39(3.58)*	23.15(−1.70)		24.69(3.66)*	24.61 (−8.94)
	25.98(3.79)	25.00(−2.05)		25.98(3.80)	28.57(−11.77)
		27.93(−3.11)			

* shoulder

TABLE 5. AB AND CD SPECTRAL DATA FOR [Co(7,7′-Me-sal$_2$en)(Amino acid anion)] IN METHANOL AT THE EQUILIBRIUM CONDITION (Wave numbers are in 10^3 cm^{-1})

Amino acid and No. of complex	AB(log ε_{max})	CD($\Delta\varepsilon_{ext}$)	Amino acid and No. of complex	AB(log ε_{max})	CD($\Delta\varepsilon_{ext}$)
gly (13)	17.09(2.46)		L-met (18)	17.24(2.57)	16.72 (+5.10)
	21.74(2.72)*			21.74(2.75)*	19.61 (+1.40)
	24.69(3.45)*			24.69(3.53)*	23.70 (−5.11)
	26.67(3.72)			26.67(3.82)	27.86 (−7.45)
L-ala (14)	17.09(2.48)	16.67 (+3.86)	L-thr (20)	17.09(2.57)	16.61 (+8.26)
	21.74(2.74)*	19.80 (+0.80)		21.74(2.73)*	19.61 (+2.69)
	24.69(3.45)*	23.64 (−3.74)		24.69(3.46)*	23.81 (−8.24)
	26.67(3.76)	27.78 (−5.85)		26.67(3.76)	28.01(−13.77)
L-val (15)	17.09(2.56)	16.67 (+5.86)	L-phe (22)	17.09(2.56)	16.61 (+8.71)
	21.74(2.73)*	19.80 (+1.98)		21.74(2.74)*	19.80 (+3.18)
	24.69(3.50)*	23.53 (−5.67)		24.69(3.48)*	23.81 (−8.05)
	26.67(3.77)	27.55 (−9.86)		26.67(3.76)	27.78(−13.77)
L-leu (16)	17.09(2.56)	16.61 (+4.38)	L-tyr (23)	17.09(2.57)	16.64(+11.14)
	21.74(2.74)*	19.61 (+1.36)		22.22(2.93)*	19.61 (+4.13)
	24.69(3.40)*	23.64 (−4.04)		25.00(3.61)*	23.92(−10.35)
	26.67(3.78)	27.78 (−6.70)		27.40(3.77)	27.93(−16.34)
L-isoleu (17)	17.09(2.55)	16.67 (+6.26)	L-trp (24)	17.09(2.56)	16.64(+12.35)
	21.74(2.73)*	19.61 (+2.28)		22.22(2.73)*	19.61 (+4.53)
	24.69(3.51)*	23.53 (−6.25)		25.00(3.57)*	23.87(−11.22)
	26.67(3.80)	27.55(−10.40)		27.40(3.84)	27.93(−16.90)

* shoulder

Table 6. PMR spectral data for [Co(sal$_2$en)(Amino acid anion)] in methanol (δ, ppm)

Amino acid and No. of complex	Soon after dissolution		At equilibrium condition	
	H-C=N of sal$_2$en[a]	R of amino acid	H-C=N of sal$_2$en[a]	R of Amino acid
gly (1)	8.00(1) 8.30(1)	(c)	8.00(1) 8.30(1)	(c)
L-ala (2)	7.92(1) 8.26(1)	CH_3(a) 1.44 1.56(1.5) CH_3(b) 1.26 1.38(1.5)	7.92(1) 8.26(1)	CH_3(a) 1.44 1.56(1.2) CH_3(b) 1.26 1.38(1.8)
L-val (3)	8.00(1) 8.28(1)	CH_3(a) 0.97 1.09(1.5); 0.92 1.04(1.5) CH_3(b) 0.80 1.02(1.5); 0.70 0.82(1.5)	8.00(1) 8.28(1)	CH_3(a) 0.97 1.09(1.2); 0.92 1.04(1.2) CH_3(b) 0.80 1.02(1.8); 0.70 0.82(1.8)
L-leu (4)	8.00(1) 8.30(1)	CH_3, 0.95[b]	8.00(1) 8.30(1)	CH_3, 0.90[b]
L-isoleu (5)	8.02(1) 8.30(1)	CH_3, 0.95[b]	8.02(1) 8.30(1)	CH_3, 0.95[b]
L-met[c] (6)	8.03(1) 8.32(1)	CH_3(a) 2.10(1.5) CH_3(b) 2.02(1.5)	8.03(1) 8.32(1)	CH_3(a) 2.10(1.2) CH_3(b) 2.02(1.8)
L-thr (8)	7.90(1) 8.24(1)	CH_3(b) 1.10 1.21(3)	7.90(1) 8.24(1)	CH_3(a) 1.19 1.30(0.6) CH_3(b) 1.10 1.21(2.4)
L-phe (10)	(b) 8.25(2)	(c)	(a) 7.97 8.27(0.4) (b) 8.25(1.6)	(c)
L-tyr[c] (11)	(a) 7.97(*ca.* 0.2) (b) 8.26(*ca.* 1.8)	(c)	(a) 7.97(0.17) (b) 8.26(1.83)	(c)
L-trp (12)	(b) 8.11(2)	(c)	(a) 7.82(0.11) (b) 8.11(1.89)	(c)

( ) corresponds to the number of proton(s). (a), peak(s) corresponding to $(+)_{435}$-isomer. (b), peak(s) due to $(-)_{435}$-isomer. (c), not clear due to overlap with other peaks.
a) CH_2-CH_2 protons appear at 3.4—4.6 ppm as broad multiplet, phenyl protons appear between 6.5 and 7.5 ppm as multiplet. b) Center of broad multiplet. c) This complex shows $CHCl_3$ signal at 7.77 ppm.

14—16, and **20** (in the case of L-thr-complex **20**, as shown in Fig. 5 C′, the CH_3–C=N singal splits into three peaks soon after dissolution). These PMR spectral behaviors clearly indicate that the complexes **2—6**, **14—16**, and **20** exist each as an 1 : 1 mixture of the two isomers soon after dissolution, but they exist each as a mixture of the two isomers in which one isomer is over the other at equilibrium conditions. On the other hand, as shown in Figs. 5 B and B′, the L-met-complex **18** shows only one signal for the methyl group of the coordinated L-methionine anion soon after dissolution ,but the signal decreases its intensity and another methyl signal appears at a somewhat lower field at the equilibrium condition. Similar behaviors are seen for the complexes **8** and **17**. Therefore, it is concluded that these three complexes are isolated each as a pure isomer, but they exist each in a mixture of two isomers in solution. By comparison of the time dependences between the optical rotations at 435 nm of the complexes and their PMR spectra, the signals of the alkyl groups of amino acid anions at higher field are assigned to those for $(-)_{435}$-isomers and the lower field signals to $(+)_{435}$-isomers. Thus, the isomer's ratio, $(-)_{435}$-isomer/$(+)_{435}$-isomer, can easily be estimated from the PMR intensity ratio. The ratios for the complexes **2**, **3**, **6**, **8**, **14**, **15**, **18**, and **20** are listed in Table 8.

On the contrary, as shown in Figs. 5 D, D′ and E and E′, the complexes **10—12** and **22—24** in which the amino acid anions have phenyl group show the time dependences not only for the signals of the amino acid anions but for the signals of H–C=N or CH_3–C=N. This is due to the anisotropic effect of the phenyl group. Since the PMR spectral behaviors of these H–C=N and CH_3–C=N signals are similar to those of the alkyl signals of amino acid anions mentioned above, the compositions of $(-)_{435}$- and $(+)_{435}$-isomers both soon after dissolution and at equilibrium conditions are easily estimated; the isomer's ratios in the complexes **10—12** and **22—24** at the equilibrium conditions are listed in Table 8.

In the cases of the L-leu- and L-isoleu-complexes

TABLE 7. PMR DATA FOR [Co(7,7′-Me-sal$_2$en)(Amino acid anion)] IN METHANOL (δ, ppm)

Amino acid and No. of complex	Soon after dissolution		At equilibrium condition	
	CH_3-C=N of 7,7′-Me-sal$_2$en[a]	R of amino acid	CH_3-C=N of 7,7′-Me-sal$_2$en[a]	R of amino acid
gly (13)	2.72(3) 2.84(3)	(c)	2.72(3) 2.84(3)	(c)
L-ala (14)	2.72(3) 2.84(3)	CH_3(a) {1.46 (1.5) 1.58 CH_3(b) {1.26 (1.5) 1.48	2.72(3) 2.84(3)	CH_3(a) {1.46 (1.0) 1.58 CH_3(b) {1.26 (2.0) 1.48
L-val (15)	2.72(3) 2.84(3)	CH_3(a) {0.93 (3.0) 1.05 CH_3(b) {{0.65 (1.5) 0.77 {0.85 (1.5) 0.97	2.72(3) 2.84(3)	CH_3(a) {0.93 (1.7) 1.05 CH_3(b) {{0.65 (2.2) 0.77 {0.85 (2.1) 0.97
L-leu (16)	2.73(3) 2.85(3)	CH_3 9.08[b]	2.73(3) 2.85(3)	CH_3 9.06[b]
L-isoleu (17)	2.72(3) 2.83(3)	CH_3(b) (0.83, 0.89, 0.92, 0.95)	2.72(3) 2.83(3)	CH_3 (0.83, 0.89, 0.92, 0.95, 1.00, 1.03)[c]
L-met (18)	2.69(3) 2.81(3)	CH_3(b) 2.00(3.0)	2.69(3) 2.81(3)	CH_3(a) 2.05(1.0) CH_3(b) 2.00(2.0)
L-thr (20)	(b) 2.67(1.5) (a) 2.69(1.5) 2.82(3.0)	CH_3(a) {1.18 (1.5) 1.29 CH_3(b) {1.07 (1.5) 1.18	2.67(3) 2.82(3)	CH_3(a) {1.18 (0.48) 1.29 CH_3(b) {1.07 (2.52) 1.18
L-phe (22)	(b) 2.40(1.5) (a) 2.72(1.5) (b) 2.81(1.5) (a) 2.84(1.5)	(c)	(b) 2.40(2.72) (a) 2.72(0.28) (b) 2.81(2.73) (a) 2.84(0.27)	(c)
L-tyr (23)	(b) 2.40(1.5) (a) 2.70(1.5) (b) 2.80(1.5) (a) 2.85(1.5)	(c)	(b) 2.40(2.74) (a) 2.70(0.26) (b) 2.80(2.74) (a) 2.85(0.26)	(c)
L-trp (24)	(b) 2.73(3) (b) 2.01(3)	(c)	(a) 2.80(0.17) (a) 2.61(0.17) (b) 2.73(2.83) (b) 2.01(2.83)	(c)

( ) represents the number of proton(s). (a), peak(s) corresponding to $(+)_{435}$-isomer. (b), peaks corresponding to $(-)_{435}$-isomer. (c), not clear due to overlap with other peaks.
a) CH_2-CH_2 signal appears at 3.4—3.6 ppm as broad multiplet and that of phenyl protons at 6.5—7.7 ppm as multiplet. b) Center of broad multiplet. c) Complicated multiplet.

4, **5**, **16**, and **17**, due to the complicated overlaps of the alkyl signals, their PMR spectra give no fine information about the isomer's ratios at equilibrium conditions. Therefore, the ratios were estimated from their rotational values at 435 nm or from their CD strengths at 589 nm. That is, the ratio in the complex **17** was estimated by using the $[M]_{435}$-value for its pure $(-)_{435}$-isomer, which was estimated from the kinetic data by extrapolating to time=0, and the $[M]_{435}$-value at the equilibrium condition. The ratio in the complex **16** was obtained by using the $[M]_{435}$-value of pure $(-)_{435}$-isomer of the complex **17** as the $[M]_{435}$-value for a pure $(-)_{435}$-isomer of the complex **16**. In these estimations, we used the following assumptions: that the $[M]_{435}$-values for $(-)_{435}$- and $(+)_{435}$-isomers are the same in each complex, except for the reversed sign, and that the values are quite similar in both L-isoleu- and L-leu-complexes, because the vicinal effect of the coordinated amino acid anion is generally very small as compared with the configurational effect of the chelated ligands.[25–27] However, recently it has been shown for the $[Co(aa)_2(en)]^+$ complex that the vicinal effect is fairly large in some kinds of amino acids.[28] Nearly the same result was also obtained for the [Co(tfac$_2$en)(L-aa)] complex (tfac$_2$en=dianion of *N*,*N*′-ethylenebis(trifluoroacetylacetoneamine)).[29] Thus, the stereoselectivity determined by using CD or ORD strengths may not be so exact as compared with that by PMR intensity. The isomer's ratios in the complexes **4** and **5** were estimated by nearly the same method as those in the complexes **16** and **17**, but by using the $\Delta\varepsilon_{589}$-values at the first absorption region for the complexes **4** and **5** and by using the $\Delta\varepsilon_{589}$-value for pure $(-)_{435}$-isomer of the complex **3**, which was calculated from the $\Delta\varepsilon_{589}$-value of the complex **3** at the equilibrium condition and its isomer's ratio at the same condition.

From the data for the isomer's ratios (Table 8), the

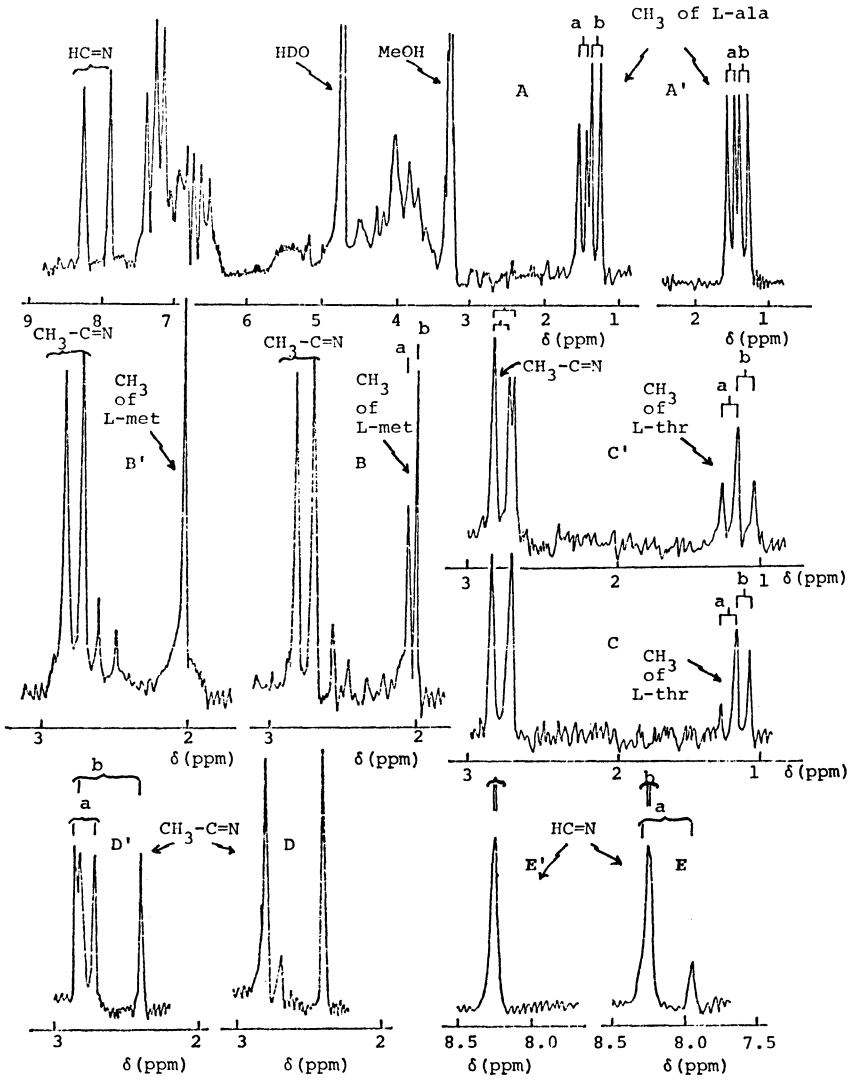


Fig. 5. The representative PMR spectra of the complexes in CD_3OD. A and A′ are PMR spectra of [Co(sal$_2$en)(L-ala)] (1) at the equilibrium condition (A) and soon after dissolution (A′). B and B′ are those of [Co(7,7′-Me-sal$_2$en)(L-met)] (18) at the equilibrium condition (B) and soon after dissolution (B′). C and C, D and D′, and E and E′ are those of [Co(7,7′-Me-sal$_2$en)(L-thr)] (20), [Co(7,7′-Me-sal$_2$en)(L-phe)] (22), and [Co(sal$_2$en)(L-phe)] (10) at the equilibrium conditions (C, D, and E) and soon after dissolution (C′, D′, and E′). The signal of a corresponds to $(+)_{435}$-isomer and that of b to $(-)_{435}$-isomer for all the PMR spectra.

Table 8. Stereoselectivity in the complexes at equilibrium conditions

Amino acid	R-Group	Isomer's ratio, sal$_2$en-complex	$(-)_{435}$-Isomer/$(+)_{435}$-isomer 7,7′-Me-sal$_2$en-complex
L-ala	$-CH_3$	1.4—1.6	1.9—2.1
L-met	$-(CH_2)_2-S-CH_3$	1.4—1.6	1.9—2.1
L-leu	$-CH_2-CH(CH_3)_2$	1.3—1.5[b]	1.9—2.1[a]
L-val	$-CH(CH_3)_2$	1.4—1.6	2.4—2.6
L-isoleu	$-CH(CH_3)(C_2H_5)$	1.2—1.4[b]	2.7—2.9[a]
L-thr	$-CH(CH_3)(OH)$	3.9—4.1	5.2—5.4
L-phe	$-CH_2-C_6H_5$	3.9—4.1	9— 10
L-tyr	$-CH_2-C_6H_4OH$	4.7—4.9	9— 10
L-trp	$-CH_2-C_8H_6N$	7.9—8.3	15— 18

a) Estimated value from α_{435}. b) Estimated value from $\Delta\varepsilon_{589}$.

following facts become clear: that 1) the ratios increase in the order of the amino acid, L-ala∼L-met∼L-leu∼L-val∼L-isoleu<L-thr∼L-phe∼L-tyr<L-trp for sal$_2$en-complexes and L-ala∼L-met∼L-leu<L-val<L-isoleu<L-thr<L-phe∼L-tyr<L-trp for 7,7′-Me-sal$_2$en-complexes; 2) the increasing order coincides with the increasing order of the steric crowding of the alkyl group of the amino acid, especially the steric crowding at the β-carbon atom; and 3) the ratio is larger in 7,7′-Me-sal$_2$en-complexes than in sal$_2$en-complexes for each amino acid. These results show that the stereoselectivity in these complexes at least depends on the intramolecular steric repulsion between the alkyl group of the amino acid anion and the hydrogen atom or methyl group at the C=N bonds of the Schiff-base ligand, and thus the steric interaction is stronger in 7,7′-Me-sal$_2$en-than in the sal$_2$en-complexes. Since the stereoselectivity in these Schiff-base complexes is thermodynamic in origin, as mentioned above, it is also shown that the steric interaction is stronger in $(+)_{435}$-isomer (unstable) than $(-)_{435}$-isomer (stable).

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