

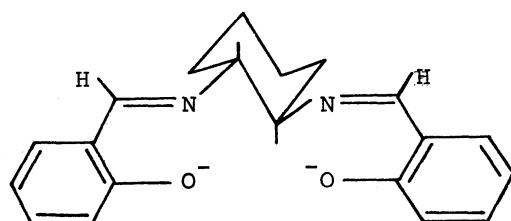
HIGH STEREOSELECTIVITY IN N,N'-(S,S)-1,2-CYCLOHEXYLENEBIS(SALICYLIDENE-
IMINATO) (sal_2 -(S,S)-chxn) COBALT(III) COMPLEXES CONTAINING AMINO ACIDS
AND OPTICAL RESOLUTION OF AMINO ACIDS WITH COBALT(II)- sal_2 -(S,S)-chxn

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A series of new mixed ligand cobalt(III) complexes with the general formula of $[\text{Co}(\text{sal}_2\text{-(S,S)-chxn})(\text{aa})]$ (aa = anion of gly, ala, val, leu, or thr) has been prepared. They take stereoselectively Λ -cis- β_1 (fac)-structure. The optical resolution of eleven amino acids with cobalt(II)- sal_2 -(S,S)-chxn complex has been examined. The optical purities of the amino acids resolved in 1 : 2 reaction molar ratio have been 8 - 50%.

In a previous communication,¹⁾ we reported the stereoselectivity in cobalt(III)-Schiff-base complex containing L-proline, $[\text{Co}(7,7'\text{-Me-sal}_2\text{en})(\text{L-pro})]$, in which the stereoselectivity comes from the chiral amino acid ligand. In this connection, we wish to report another type of stereoselectivity coming from a chiral Schiff-base ligand in cobalt(III)- sal_2 -(S,S)-chxn complexes with amino acids, and an optical resolution of eleven amino acids with cobalt(II)- sal_2 -(S,S)-chxn.



sal_2 -(S,S)-chxn

The complexes were prepared from $[\text{Co}(\text{sal}_2\text{-(S,S)-chxn})]^{2)}$ and amino acids in methanol (60%) by air oxidation. The crude complexes were obtained by extracting the reaction products with chloroform and then by evaporating off the solvent to dryness. They were recrystallized from methanol or chloroform. The anal. data are listed in Table 1.

STEREOSELECTIVITY Fig. 1 shows the representative absorption (AB) and CD spectra of the complexes in methanol. As the AB and CD spectra of all the complexes are very similar to one another and as the spectra quite resemble those of Λ -cis- β_1 (fac)-isomer

Table 1. Elemental Analyses Data

Complex	C(%)	H(%)	N(%)
	Found (Calcd)	Found (Calcd)	Found (Calcd)
[Co(sal ₂ -(S,S)-chxn)(gly)]·H ₂ O	56.29(56.06)	5.66(5.56)	8.73(8.91)
[Co(sal ₂ -(S,S)-chxn)(L-ala)]·4.5H ₂ O	50.31(50.37)	6.42(6.43)	7.68(7.66)
[Co(sal ₂ -(S,S)-chxn)(D-ala)]·CHCl ₃	48.65(48.38)	4.48(4.57)	7.11(7.05)
[Co(sal ₂ -(S,S)-chxn)(L-val)]·0.5CHCl ₃ ·H ₂ O	53.39(53.44)	5.67(5.72)	7.23(7.33)
[Co(sal ₂ -(S,S)-chxn)(D-val)]·0.5CHCl ₃ ·H ₂ O	53.68(53.44)	5.64(5.72)	7.22(7.33)
[Co(sal ₂ -(S,S)-chxn)(L-leu)]·0.5CHCl ₃	55.68(55.92)	5.96(5.76)	7.24(7.33)
[Co(sal ₂ -(S,S)-chxn)(D-leu)]·0.5CHCl ₃	55.75(55.92)	5.81(5.76)	7.32(7.33)
[Co(sal ₂ -(S,S)-chxn)(L-thr)]·H ₂ O	57.61(57.72)	5.52(5.65)	8.30(8.41)
[Co(sal ₂ -(S,S)-chxn)(D-thr)]·H ₂ O	57.92(57.72)	5.54(5.65)	8.39(8.41)

of [Co(7,7'-Me-sal₂en)(L-pro)]¹⁾ except for the reversed CD sign, all the complexes are assumed to take preferentially Λ -cis- β_1 (fac)-structure. As shown in Fig. 2, PMR signals of alkyl groups of the coordinated amino acids consist each of the peaks which correspond to only one isomer. Therefore, it is clear from these data that the stereoselectivity in all the complexes is complete, independently of the configuration of the coordinated amino acids.

Although the isomerization reaction such as seen in [Co(7,7'-Me-sal₂en)(L-pro)] is not observed for the cobalt(III)-sal₂-(S,S)-chxn complexes, the substitution reaction of the coordinated amino acids with a large excess of free amino acid (XH) is observed to proceed rapidly in methanol (60%) to give Λ -cis- β_1 (fac)-[Co(sal₂-(S,S)-chxn)(X)]. This fact means that the stereoselectivity is so high that any conversion of the configuration of the coordinated sal₂-(S,S)-chxn ligand is not observed through the substitution reaction of the coordinated amino acid ligand. The molecular model indicates that Λ -configuration is much more strain free than Δ in the cobalt(III)-sal₂-(S,S)-chxn complex, when the complex takes cis- β -structure. This is due to the steric requirement of (S,S)-chxn moiety.³⁾

STEREOSPECIFICITY In order to study a stereospecificity of cobalt(III)-sal₂-(S,S)-chxn complex to L- or D-amino acid, we examined the reactions of [Co(sal₂-(S,S)-chxn)] with various racemic amino acids in 1 : 2 molar ratio by air oxidation. The stereospecificity of the complex was estimated from the optical purities of the unreacted amino acids. The unreacted amino acids were separated from [Co(sal₂-(S,S)-chxn)(aa)] by extracting the complex with chloroform and isolated by concentrating the aqueous

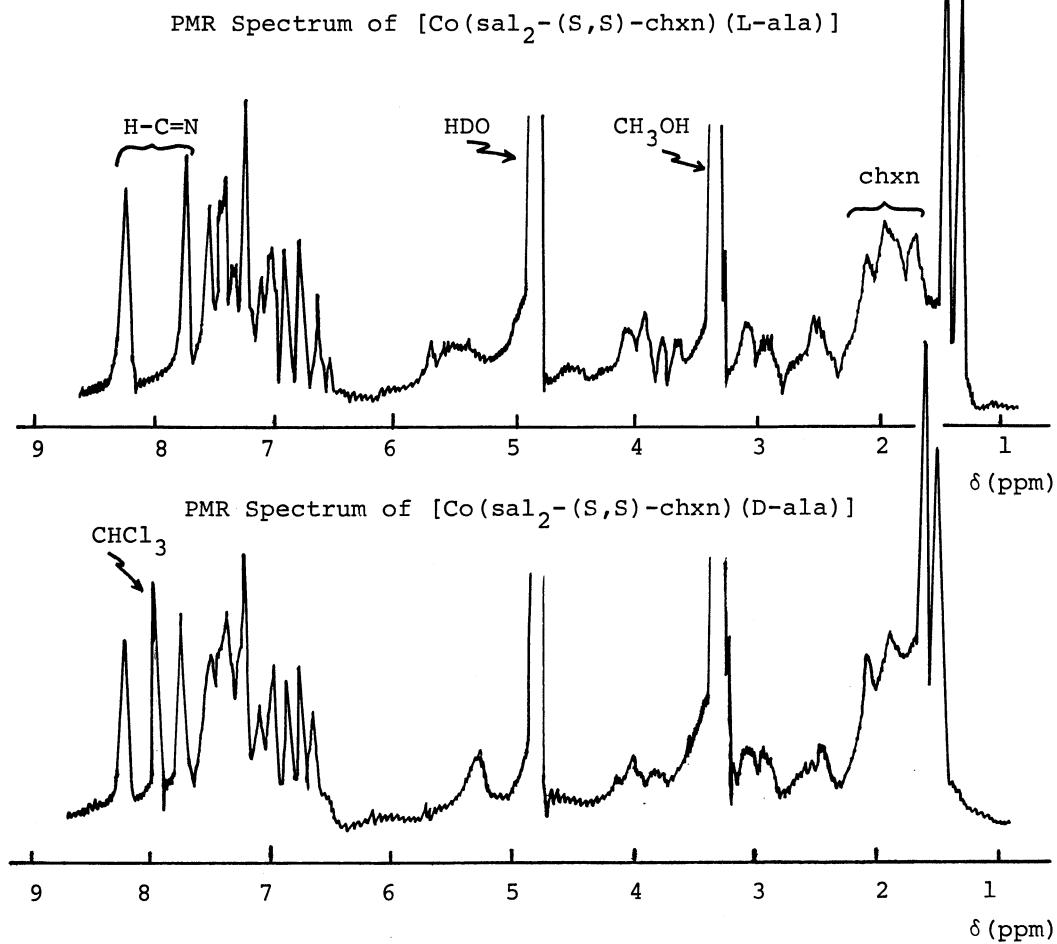
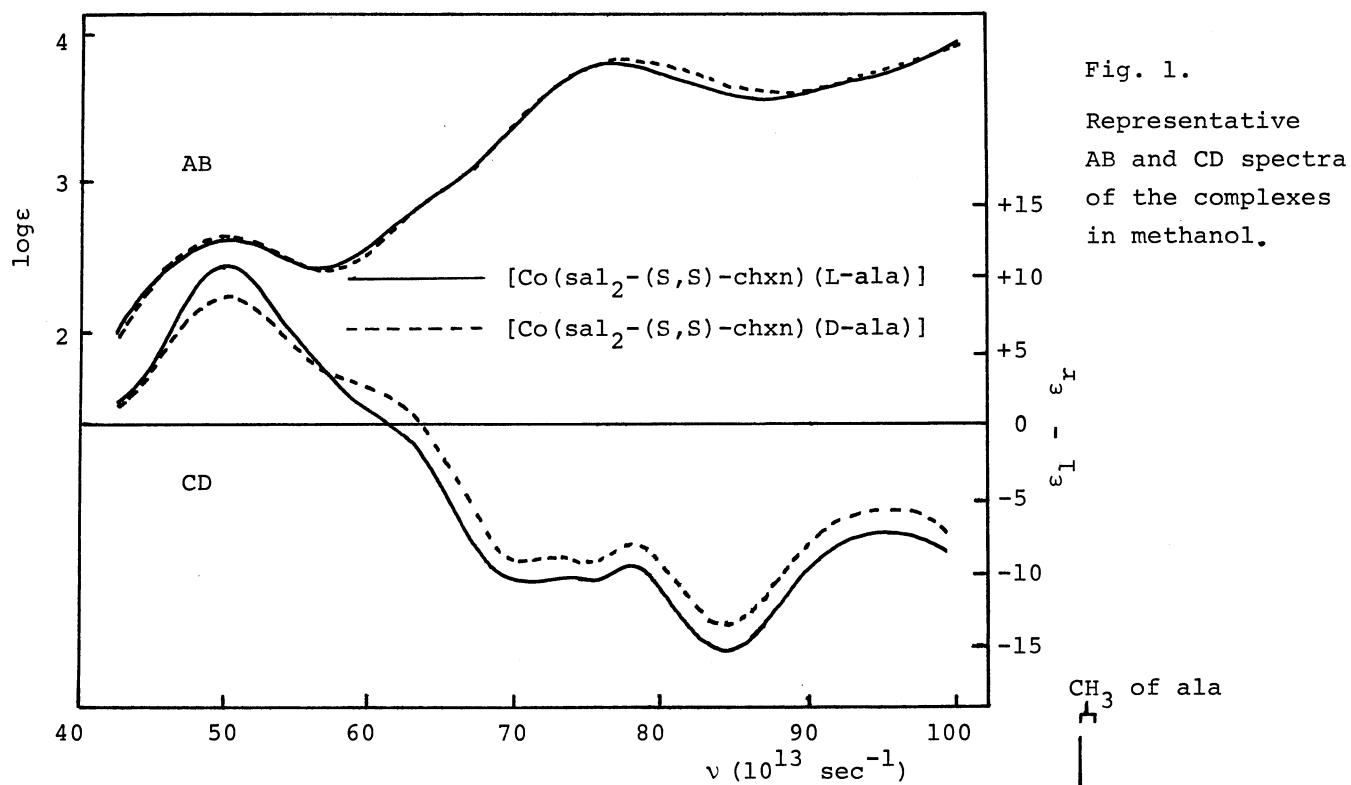
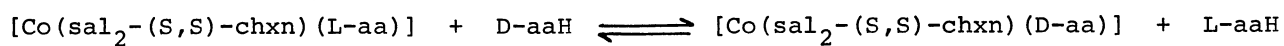
Fig. 2. Representative PMR spectra of the complexes in CD_3OD .

Table 2. Optical Purity of Unreacted Amino Acids in the Reactions of $[\text{Co}(\text{sal}_2-(\text{S},\text{S})-\text{chxn})]$ with Racemic Amino Acids in 1 : 2 Molar Ratio

Amino Acid	Configuration of Unreacted Amino Acid	Optical Purity (%)	Amino Acid	Configuration of Unreacted Amino Acid	Optical Purity (%)
ALA	D(R)	6 - 10	ASP	D(R)	16 - 18
VAL	D(R)	6 - 8	GLU	D(R)	6 - 8
LEU	D(R)	6 - 8	PHE	D(R)	29 - 31
MET	D(R)	6 - 8	TRP	D(R)	41 - 43
SER	D(R)	10 - 12	PRO	L(S)	48 - 50
THR	D(R)	27 - 30			

solution to dryness. The chemical yields were 90 - 100% (half of the added amino acid corresponds to the yield of 100%). The optical purities of the unreacted amino acids are summarized in Table 2. From these experiments, following facts become clear that the cobalt(III)- $\text{sal}_2-(\text{S},\text{S})-\text{chxn}$ complex favors L-amino acids more than D-amino acids except for proline and the increasing order of the stereospecificity is $\text{ALA} \sim \text{MET} \sim \text{VAL} \sim \text{LEU} \sim \text{GLU} < \text{SER} < \text{ASP} < \text{THR} < \text{PHE} < \text{TRP} < \text{PRO}$. Since the coordinated amino acids in the complexes are labile for substitution, as mentioned above, following equilibrium is thought to be established in the reaction solution:



Therefore, the stereospecificity is presumably thermodynamic in origin.^{4),5)}

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