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HIGH STEREOSELECTIVITY IN COBALT(III)-7,7'-Me-sal_2en COMPLEX CONTAINING L-PROLINE

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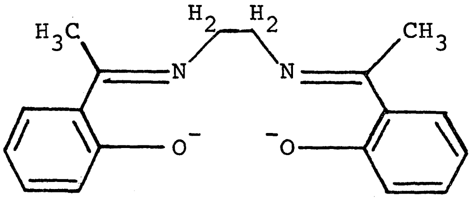
A new mixed cobalt(III) complex containing 7,7'-Me-sal_2en and L-proline, cis-β-[Co(7,7'-Me-sal_2en)(L-pro)], has been prepared from [Co(7,7'-Me-sal_2en)] and L-proline in methanol (80%) by air oxidation. The reaction has proceeded stereoselectively to form $(-)_{435}$-isomer, followed by slow isomerization to form finally $(+)_{435}$-isomer (100%).

Many studies have been undertaken for stereoselectivity in inert cobalt(III) complexes.$^{1-4)}$ However, it is often difficult to distinguish between kinetic and thermodynamic stereoselectivities in the inert cobalt(III) complexes. By the way, it is well known that cobalt(III)-Schiff-base complexes are generally substitution labile.$^{5-7)}$ Since the origin of the stereoselectivity in labile complexes is thought to be thermodynamic, a study of the stereoselectivity of the cobalt(III)-Schiff-base complexes is very interesting. In this letter, we report the stereoselectivity in mixed cobalt(III) complex containing 7,7'-Me-sal_2en (N,N'-ethylenebis(7,7'-dimethyl-salicylideneimine) dianion) as Schiff-base ligand and L-proline.



7,7'-Me-sal_2en

The complexes were prepared from [Co(7,7'-Me-sal_2en)]$^{8)}$ and L-proline in methanol (80%) by air oxidation: L-Proline (2.2 g) in 50 ml of water was added to the suspension of [Co(7,7'-Me-sal_2en)] (5.0 g) in 200 ml of methanol and the mixture was stirred vigorously for about fifteen minutes at room temperature. By this procedure, green solution was obtained. The methods for isolation and recrystallization of the complexes are listed in Table 1. The yields were 70 - 90%. Anal., Calcd for [Co(7,7'-Me-sal_2en)(L-pro)] = $CoC_{23}H_{26}N_3O_4$: C, 59.10; H, 5.61; N, 8.99%. Found for complexes recrystallized from chloroform, sample (1): C, 59.02; H, 5.72; N, 9.07%, sample (3): C, 58.89; H, 5.74; N, 8.85%, sample (5): C, 58.92; H, 5.66; N, 9.03%. Calcd for [Co(7,7'-Me-sal_2en)(L-pro)]·$2H_2O$ = $CoC_{23}H_{30}N_3O_6$: C, 54.87; H, 6.01; N, 8.35%. Found for complexes recrystallized from methanol, sample (2): C, 54.72; H, 5.83; N, 8.49%, sample (4): C, 54.92; H, 5.97; N, 8.40%, sample (6): C, 54.88; H, 6.02; N, 8.31%, sample (7): C, 54.85; H, 5.89; N, 8.37%.

From Table 1, following facts are seen; 1) rapid reaction of [Co(7,7'-Me-sal_2en)]

Table 1. The preparative method of cis-β-[Co(7,7'-Me-sal$_2$en)(L-pro)] complex

Reaction time and temp.	Optical rotation of reaction solution at 435nm	Method of isolation	Optical rotation of crude product at 435nm	Solvent for recrystallization	$[M]_{435}$ (°m^{-1}mol^{-1}l) in CHCl$_3$	Sample number
30 min. room temp.	$(-)_{435}$	extraction in CHCl$_3$ and concentration	$(-)_{435}$	CHCl$_3$	-10300	(1)
				CH$_3$OH	+32300	(2)
ca. 4 hrs. room temp	$(\pm)_{435}$	concentration	$(\pm)_{435}$	CHCl$_3$	+800	(3)
				CH$_3$OH	+32400	(4)
1 day room temp	$(+)_{435}$	concentration	$(+)_{435}$	CHCl$_3$	+32300	(5)
				CH$_3$OH	+32400	(6)
ca. 4 hrs. 60°C	$(+)_{435}$	concentration	$(+)_{435}$	CH$_3$OH	+32400	(7)

with L-proline under air oxidation results in the formation of $(-)_{435}$-complex (sample (1)), and 2) the $(-)_{435}$-complex slowly and completely isomerizes to $(+)_{435}$-complex in methanol. The isomerization is also found in chloroform but the rate is much more slow than in methanol.

Fig. 1 shows NMR spectra of the complexes. The NMR spectra of $(-)_{435}$-complex (sample (1)) in CD$_3$OD at T = ca. 70 min. and T = ca. 24 hrs. were found to correspond to those of $(\pm)_{435}$-complex (sample (3)) and $(+)_{435}$-complex (sample (2), (4), (6), and (7)) in CDCl$_3$, respectively. These NMR spectral behaviors clearly indicate; 1) narrow doublet of methyl signal of coordinated 7,7'-Me-sal$_2$en corresponds to $(-)_{435}$-isomer and wide doublet to $(+)_{435}$-isomer, 2) the isolated $(-)_{435}$-complex (sample (1)) is the mixture of $(-)_{435}$-isomer and $(+)_{435}$-isomer ($(-)_{435}$-complex/$(+)_{435}$-complex = 2 - 2.2), and 3) the $(-)_{435}$-complex gradually and completely isomerizes to $(+)_{435}$-complex in methanol.

Fig. 2 shows AB and CD spectra of the complexes in methanol. The AB and CD spectra of $(-)_{435}$-complex at 24 hrs. after dissolution were found to correspond to those of $(+)_{435}$-complex. Since the AB and CD spectra of $(-)_{435}$-complex at T = 0 and $(+)_{435}$-complex quite resemble with each other except the reversed CD sign, it is assumed that the isomerization occurs between the complexes having the same geometrical configuration with respect to the coordinated atoms.

Generally six isomers are thought for [Co(7,7'-Me-sal$_2$en)(L-pro)]: Δ_L- and Λ_L-cis-α, Δ_L- and Λ_L-cis-β_1(fac), and Δ_L- and Λ_L-cis-β_2(mer). However, since the cis-α structure is very unstable due to its strained structure and it is not known for its existence, cis-β structure is most probable. Molecular model test[9] suggests that Λ_L-cis-β_2 structure is impossible to exist due to its intramolecular steric hindrance. As it is assumed that the $(-)_{435}$- and $(+)_{435}$-isomers have the same geometrical configuration respecting the coordinated atoms, cis-β_1 structure is assumed to the isolated

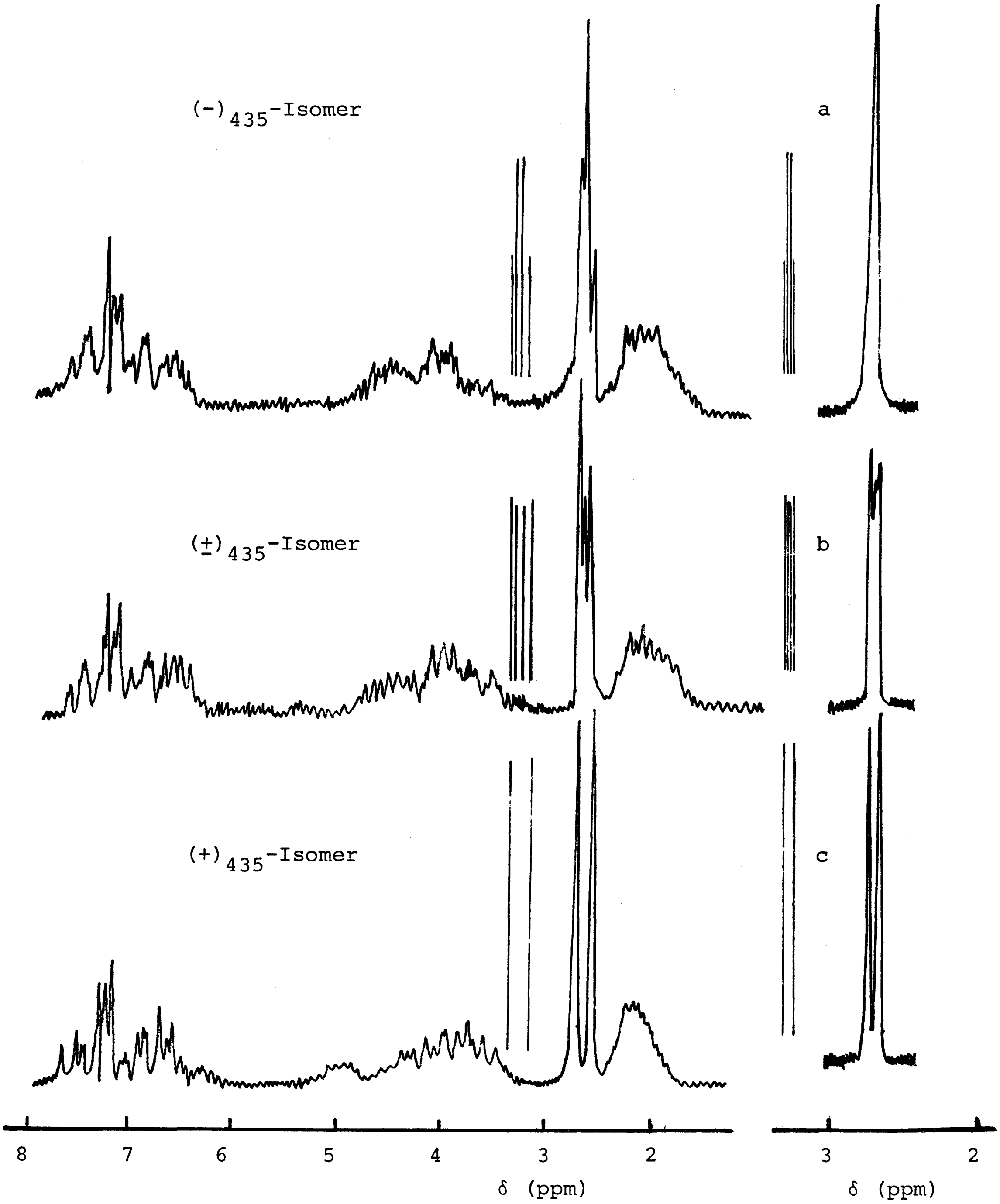


Fig. 1. NMR spectra of cis-β-[Co(7,7'-Me-sal$_2$en)(L-pro)] complexes in $CDCl_3$. a, b, and c are time dependence of NMR spectra of $(-)_{435}$-complex in CD_3OD: a, T = 0; b, T = 80 min.; c, T = 24 hrs.

complexes. The cis-β structure is supported by the characteristic multiplet of CH_2-CH_2 signal (ca. 4 ppm) of the coordinated 7,7'-Me-sal$_2$en.$^{7,10)}$

The isomerization rate constant, k_{obs}, was determined by using the time dependence of the optical rotation at 435 nm of $(\pm)_{435}$-complex: $k_{obs} = 7.95 \pm 0.05 \times 10^{-5}$ sec^{-1} at 24°C in methanol.

From these results, it is assumed that the origin of the stereoselective formation of $(+)_{435}$-complex (stable form) is thermodynamic but that of $(-)_{435}$-complex

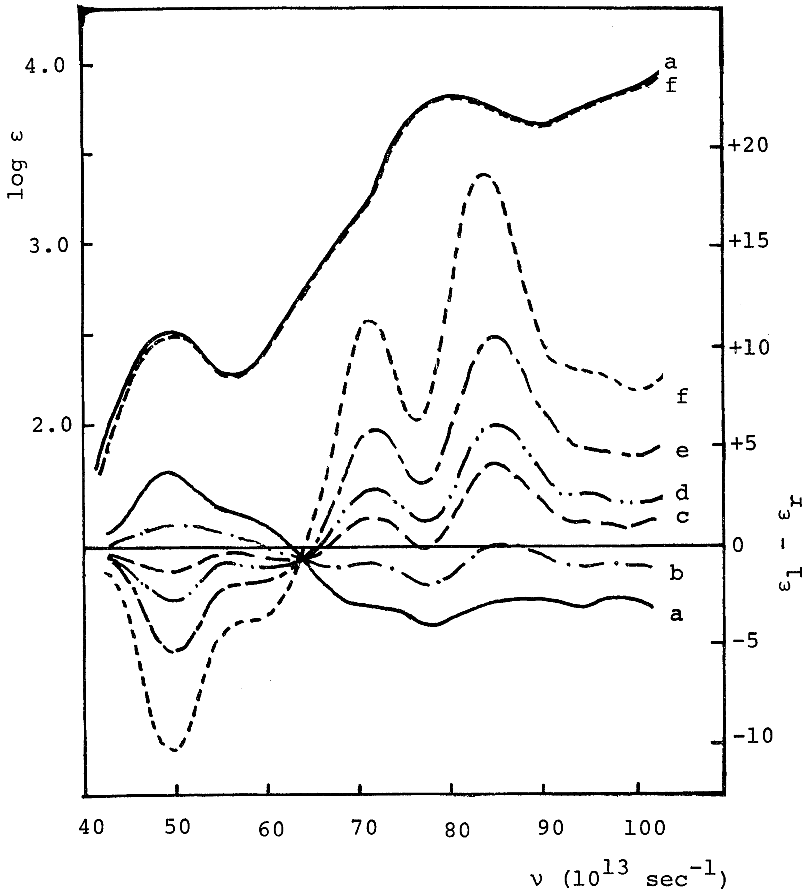


Fig. 2. The time dependence of AB and CD spectra of $(-)_{435}$-[Co(7,7'-Me-sal$_2$en)-(L-pro)] in methanol at room temperature.

a, T = 0;
b, T = 40 min.;
c, T = 80 min.;
d, T = 130 min.;
e, T = 240 min.;
f, T = 24 hrs.

The AB and CD spectra of $(-)_{435}$-complex at T = 24 hrs. (f) coincide with those of $(+)_{435}$-complex in methanol.

(unstable form), kinetic. The detailed investigation is now undergoing together with the study for other amino acidato complexes.

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References

1) M. Shibata and A. Nakahara,"Preparation of Metal Complexes and Reactivity of Ligand", Kagaku no Ryoiki, Special number 90, Nankodo, Tokyo, 1970,p.141 and references therein.
2) M. Shibata, Kagaku no Ryoiki, 29, No. 5, p. 26 (1975).
3) M. Goto, H. Matsushita, M. Saburi, and S. Yoshikawa, Inorg. Chem.,12, 1498 (1973) and references therein.
4) M. Saburi and S. Yoshikawa, Bull. Chem. Soc. Jap., 47, 1184 (1974).
5) G. Costa, Coord. Chem. Rev., 8, 63 (1972).
6) Y. Fujii, Bull. Chem. Soc. Jap., 47, 2856 (1974).
7) D. Cummins, B. M. Higson, and E. D. McKenzie, J. Chem. Soc., Dalton, 1359 (1973).
8) A. Bigotto, et al., Inorg. Chim. Acta Reviews, 4, 41 (1970).
9) M. Calligaris, G. Manzini, G. Nardin, and L. Randaccio, J. Chem. Soc., Dalton, 543 (1972).
10) Y. Fujii, et al., Bull. Chem. Soc. Jap., 45, 2459 (1972).

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