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SYNTHESIS OF OPTICALLY ACTIVE COBALT(SALEN) TYPE COMPLEXES AND THEIR ASYMMETRIC REACTIVITY TOWARD PROPYLENE OXIDE

HARUHIKO AOI, MICHIHIRO ISHIMORI, SADAO YOSHIKAWA and TEIJI TSURUTA*
Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo (Japan)
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Summary

An optically active Co(I)(salen) type complex, lithium *N,N'*-bis(salicylaldehyde)-1(*R*), 2(*R*)-1,2-*trans*-cyclohexanediiminatocobalt(I), was prepared by reducing the Co^{II} complex, *N,N'*-bis(salicylaldehyde)-1(*R*),2(*R*)-1,2-*trans*-cyclohexanediiminatocobalt(II), with $LiAlH_4$. The structure of the Co^I complex was determined on the basis of the structure of the corresponding Co^{II} complex and was confirmed by usual physicochemical methods. Furthermore, characteristics of the absorption and circular dichroism(CD) spectra of the Co^I complex were compared with those of the reported structure of $Na^+[Co(I)(salen)]^-$. Highly asymmetric selectivity was found in a resolution reaction of *DL*-propylene oxide by use of the above optically active lithium cobalt(I) complex as a catalyst.

Introduction

The square-planar tetradentate Schiff base complexes of cobalt such as cobaloxime, Co(salen), etc. have been widely studied as model compounds for coenzyme B_{12}. The formation and cleavage of the Co—C bonding have been suggested to play significant roles in various types of reactions involving Co(salen) type complexes [1,2]. The highly nucleophilic character of Co^I species was reported by Schrauzer and other workers [1,2]. There have been few attempts, however, to apply such complexes having optically active co-planar ligands as catalysts for asymmetric reactions.

The purpose of this study is to examine the possibility of resolution reactions using an optically active Co^I complex prepared by reducing an optically active Co^{II}(salen) type complex having a well-defined structure. This paper presents the results of studies on (i) the synthesis and structure determination of an optically active Co^{II}(salen) type complex, *N,N'*-bis(salicylaldehyde)-1(*R*), 2(*R*)-1,2-*trans*-cyclohexanediiminatocobalt(II), $Co^{II}(sal)_2$(R—CHXDA), (ii) reduction of $Co^{II}(sal)_2$(R—CHXDA) to the Co^I complex, $Li^+[Co^I(sal)_2(R—CHXDA)]^-$, with $LiAlH_4$, and (iii) the resolution reaction of *DL*-propylene oxide by use of $Li^+[Co^I(sal)_2(R—CHXDA)]^-$.

Experimental

(1) Measurements

Magnetic susceptibility measurements were carried out on Nippon—Komitsu Type 100 Electromagnet and Mettler H16GD equipment using Hg[Co(NCS)$_4$] as a calibrant. Absorption spectra were measured using a Shimadzu automatic recording spectrophotometer Model MPS-50L. The CD spectra were taken on a JASCO Model J-20 spectrometer. Optical rotations were observed using a JASCO Model ORD/UV-5 spectropolarimeter. Infrared spectra were measured with a Hitachi Model EDI-G3 spectrometer. GLC analyses were carried out with a Hitachi Model K-53 Gas Chromatograph equipped with a column containing PEG, Silicone GESE-30 or PEG/Silicone DC-550 (3/1 mixture).

(2) Preparation of cobalt complexes

Reagents used were purified by usual methods, as described elsewhere [3].

1(R),2(R)-1,2-trans-cyclohexanediamine, (R—CHXDA). Racemic 1,2-*trans*-cyclohexanediamine was resolved with *d*-tartaric acid according to Asperger's method [4]. $[\alpha]^{24}_{589} = -44.1°$ (free diamine; 3% methanolic solution), $[\alpha]^{24}_{589} = -15.8°$ (dihydrochloride salt; 20% aqueous solution), lit. [4] $[\alpha]^{25}_{589} = -15.8°$ (dihydrochloride salt; 20% aqueous solution).

N,N'-Bis(salicylaldehyde)-1(R),2(R)-1,2-trans-cyclohexadiimine, (salH)$_2$-(R—CHXDA). R—CHXDA and twice the number of moles of salicylaldehyde

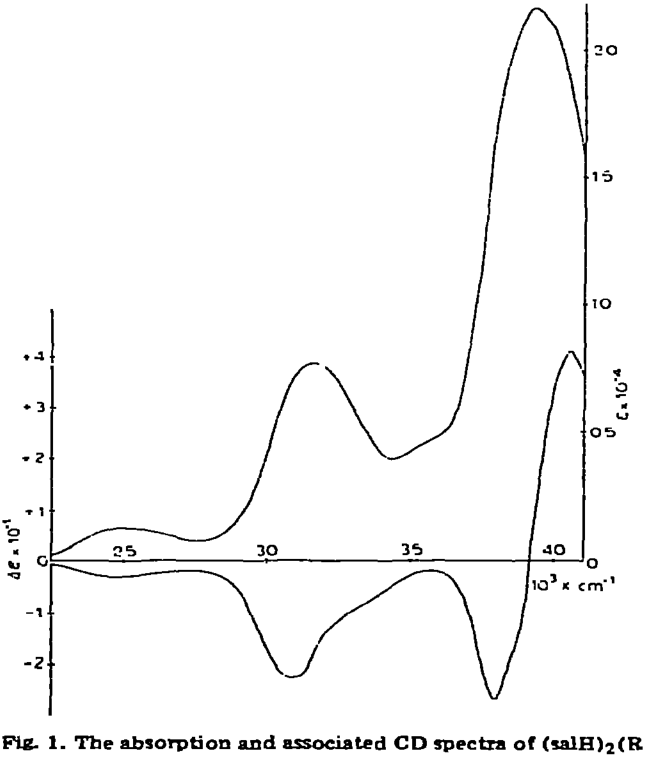

Fig. 1. The absorption and associated CD spectra of (salH)$_2$(R—CHXDA).

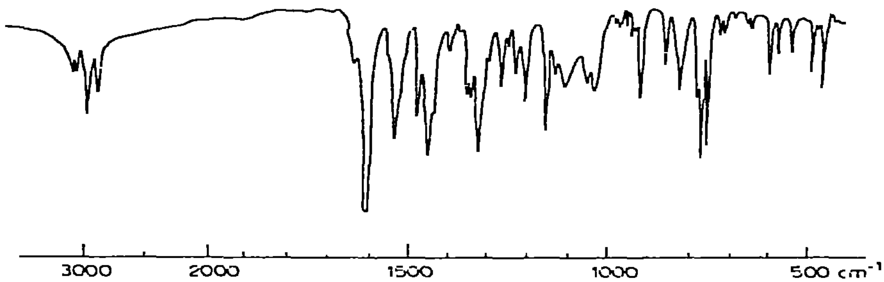

Fig. 2. The infrared spectrum of Co^{II}(sal)$_2$(R—CHXDA).

were dissolved in ethanol and stirred for 20 min at 60°, followed by evaporation of the solvent. Yellow needle-like crystals were obtained from a mixture of n-hexane and cyclohexane. $[\alpha]^{25}_{589} = -644.4°$ (1% methanolic solution). The absorption and associated CD spectra of (salH)$_2$(R—CHXDA) are shown in Fig. 1.

Co^{II}(sal)$_2$(R—CHXDA). When the ligand (salH)$_2$(R—CHXDA) (0.0162 mol) and anhydrous cobalt acetate (0.0162 mol) were reacted in 1-propanol (50 ml) at 60° for 1 h with stirring, orange-red powder precipitated. After cooling, it was filtered off and washed with cyclohexane. The precipitate was purified by suspension in refluxing 1-propanol, followed by filtration and washing with cyclohexane. All procedures were carried out under a dry nitrogen atmosphere. The infrared spectrum of the Co^{II} complex is shown in Fig. 2. (Found: C, 63.42; H, 5.08; N, 7.52. $C_{20}H_{20}N_2O_2Co$ calcd.: C, 63.33; H, 5.31; N, 7.38%.)

Co^{I} complexes, Li$^+$[Co(I)(sal)$_2$(R-CHXDA)]$^-$ and Na$^+$[Co(I)(sal)$_2$(R—CHXDA)]$^-$. Co^{II}(sal)$_2$(R—CHXDA) (0.05 mmol) was suspended in solvent such as THF (50 ml), and an equimolar amount of $LiAlH_4$ or sodium sand added and stirred for 3 h at room temperature under a dry nitrogen atmosphere. A blue-green solution of the Co^{I} complex was obtained.

(3) Reaction of Li$^+$[Co(I)(sal)$_2$(R—CHXDA)]$^-$ with DL-propylene oxide

DL-propylene oxide (70 mmol) was added to a benzene (10ml)/dioxane (5ml) solution of the Co^{I} complex prepared by reaction between the Co^{II} complex (0.36 mmol) and $LiAlH_4$ in ratios of 1/1, 1/0.5 and 1/0.33. The mixture was sealed in an ampule under dry nitrogen and allowed to stand at an appropriate temperature. When *DL*-propylene oxide was mixed with the Co^{I} solution, the color of the solution changed immediately from blue-green to dark-green. No further change in color was observed during the reaction. After an appropriate reaction time, non-reacted epoxide and acetone formed were analyzed by gas chromatography. The optical rotation of the recovered propylene oxide was measured.

Results and discussion

(1) The structure of Co(II)(sal)$_2$(R—CHXDA)

The magnetic moment, μ_{eff}, of the Co^{II} complex measured by the method of Gouy was 2.41 B.M., indicating a low-spin square-planar structure [5] for this complex. The proposal of a square-planar structure is also supported by the absorption spectra of the Co^{II} complex, shown in Fig. 3, which are similar to those

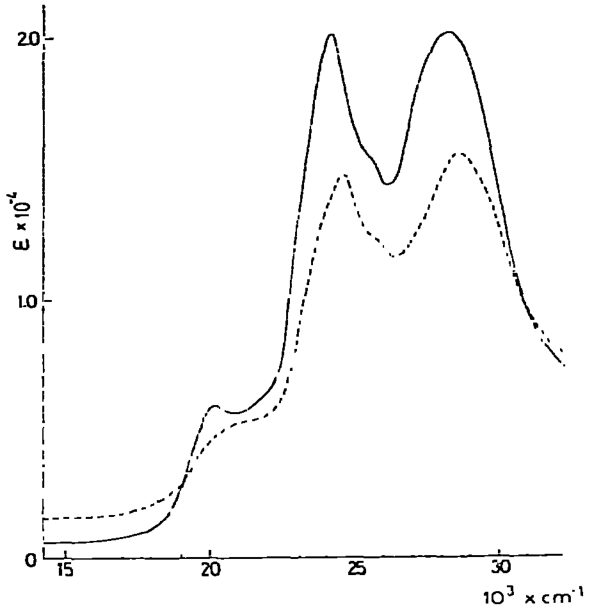

Fig. 3. The absorption spectra of $Co^{II}(sal)_2(R—CHXDA)$.
—— in benzene solution
- - - - in THF solution

of Co^{II}(salen) [6,7], *N,N′*-bis(salicylaldehyde)ethylenediiminatocobalt(II), and $Co^{II}(sal)_2$(—) (pn) [8], *N,N′*-bis(salicylaldehyde)(—)propylenediiminatocobalt(II). This shows that the electronic structure around the central cobalt atom is similar to those of Co^{II}(salen) and $Co^{II}(sal)_2$ (—) (pn).

In the R—CHXDA—Schiff base chelate, the central chelate ring is believed to be locked in the λ conformation [9] because of the steric requirement of the R—CHXDA moiety. The CD spectra of $Co^{II}(sal)_2$(R—CHXDA) shown in Fig. 4 are consistent with the λ conformation of the central chelate ring, because the CD spectra exhibit closely similar shapes but opposite sign to that of $Co^{II}(sal)_2$(—) (pn). The latter Co^{II} complex was reported to possess the δ conformation of the central chelate ring [8].

From the results given above, it was concluded that $Co^{II}(sal)_2$(R—CHXDA) is a low-spin square-planar cobalt^{II} complex having the λ conformation of the central chelate ring, as shown in Fig. 5.

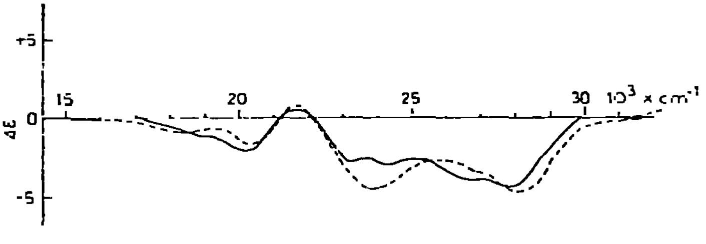

Fig. 4. The CD spectra of $Co^{II}(sal)_2(R—CHXDA)$.
—— in benzene solution
- - - - in THF solution

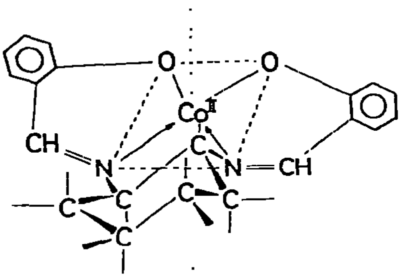

Fig. 5. The structure of $Co^{II}(sal)_2(R—CHXDA)$.

(2) *The structure of $Li^+[Co^I(sal)_2(R—CHXDA)]^-$*

The absorption and CD spectra of $Li^+[Co(I)(sal)_2(R—CHXDA)]^-$ prepared by reducing $Co^{II}(sal)_2(R—CHXDA)$ with an equimolar amount of $LiAlH_4$ are shown in Figs. 6 and 7. The absorption spectrum in Fig. 6 is very similar to that of $Na^+[Co^I(salen)]^-$, observed by Calderazzo and Floriani [6]. To confirm this, $Na^+[Co^I(sal)_2(R—CHXDA)]^-$ was synthesized. As shown in Fig. 6, the absorption spectrum of $Na^+[Co^I(sal)_2(R—CHXDA)]^-$ is also similar to those of $Na^+[Co^I(salen)]^-$ and $Li^+[Co^I(sal)_2(R—CHXDA)]^-$. Furthermore, by comparing the CD spectrum of $Li^+[Co^I(sal)_2(R—CHXDA)]^-$ with that of $Na^+[Co^I(sal)_2(R—CHXDA)]^-$, it can be concluded that these two complexes have almost the same structure.

(3) *Reaction of $Li^+[Co^I(sal)_2(R—CHXDA)]^-$ with DL-propylene oxide*

Owing to the nucleophilic character of the Co^I complex [1,2], it is anticipated that kinetic resolution of a racemic substrate might be possible when an optically active cobalt(I) complex is used in a nucleophilic reaction. Resolutions of *DL*-propylene oxide were examined using the optically active Co^I complex, $Li^+[Co^I(sal)_2(R—CHXDA)]^-$ prepared by the reaction of $Co^{II}(sal)_2(R—CHXDA)$ with $LiAlH_4$, as described in Experimental section. The results are summarized in Table 1.

Highly asymmetric selectivity was found in a series of reactions with propyl-

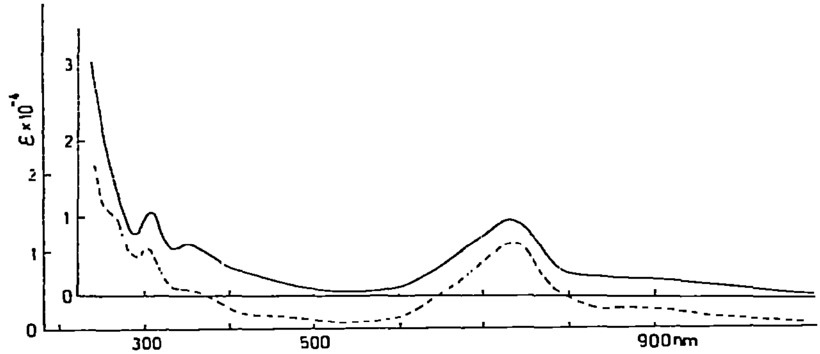

Fig. 6. The absorption spectra of Co^I complexes.
- - - - $Li^+[Co^I(sal)_2(R—CHXDA)]^-$ in THF
—— $Na^+[Co^I(sal)_2(R—CHXDA)]^-$ in THF

TABLE 1

ASYMMETRIC REACTION OF $Li^+[Co^I(sal)_2(R\text{—}CHXDA)]^-$ WITH PROPYLENE OXIDE (PO) AND WITH 1,2-BUTENE OXIDE (BO)

Substrate	Co^{II}/[a] $LiAlH_4$ (mol/mol)	Substrate/ Co^{II} (mol/mol)	Solvent [b]	Temp. (°C)	Time (days)	Conversion [c] (%)	$[\alpha]^{20}_{589}$ [d] (°)	$\langle L/L+D \rangle$ [e] (%)	N [f]	Ketone [g] formed (%)
PO	3.0	200	Bz/Diox	25	16	3.0	+0.42	95	18	100
PO	2.0	200	Bz/Diox	25	16	8.3	+0.93	84	34	100
PO	2.0	200	Bz/Diox	25	14	7.1	+0.78	84	28	92
PO	1.5	200	Bz/Diox	25	14	4.1	+0.30	80		53
PO	1.0	200	Bz/Diox	25	17	5.4	+0.31	68		40
PO	$LiAlH_4$ [h]	100	Bz	22	15	4.6	0	0		0
PO	Co^{II} [h]	100	Bz	22	15	0				0
BO	2.0	200	Bz/Diox	25	16	8.5	+0.78	84	34	96
BO	1.0	100	Bz/Diox	24	15	14.2	+1.01	75		58

[a] $Co^{II} = Co^{II}(sal)_2(R\text{—}CHXDA)$. [b] Bz = benzene. Diox = dioxane. [c] PO (or BO) consumed (mol)/PO (or BO) initial (mol) × 100. [d] Specific rotation of PO recovered. [e] L-PO (or BO) percent in the total conversion of D- and L-PO (or BO). $\langle L/L + D \rangle = \frac{1}{2}\{1 + (L-D/L+D)\} \times 100$ where $(L-D/L+D)$ is the optical purity of the reacted monomer. The optical purity of the reacted monomer is evaluated by the eqn. $(L-D/L+D) = [\alpha]/[\alpha_0] \times \{100-(\text{conversion})/(\text{conversion})\}$, where $[\alpha]/[\alpha_0]$ is the optical purity of the unreacted monomer. $[\alpha_0]^{21}_{589} = +15°$ for pure D-PO [12] (cf. Ref. 13). $[\alpha_0]^{16}_{589} = +12.4°$ for pure D-1,2—BO [14]. [f] Recycling number for $Li^+[Co^I(sal)_2(R\text{—}CHXDA)]^-$. N = PO consumed/$Li^+[Co^I(sal)_2(R\text{—}CHXDA)]^-$. Calcd. on the assumption $[Li^+[Co^I(sal)_2(R\text{—}CHXDA)]^-] = [LiAlH_4]$ used. [g] Acetone or methyl ethyl ketone formed (mol)/PO or BO consumed (mol) × 100. [h] $LiAlH_4$ or Co^{II} complex was used as a catalyst.

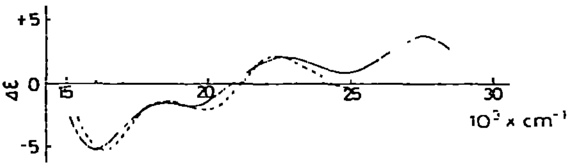

Fig. 7. The CD spectra of Co^I complexes.
- - - - $Li^+[Co^I(sal)_2(R—CHXDA)]^-$ in THF
—— $Na^+[Co^I(sal)_2(R—CHXDA)]^-$ in THF

ene oxide, as shown by $\langle\!\langle L/L + D \rangle\!\rangle$ (see Table 1) calculated from the optical activities of unreacted propylene oxides recovered; in particular, the selectivity, $\langle\!\langle L/L + D \rangle\!\rangle$, for the system at the ratio $Co^{II}/LiAlH_4$ = 3.0 was 95%. The values of $\langle\!\langle L/L + D \rangle\!\rangle$, however, decreased with decreasing ratio of $Co^{II}/LiAlH_4$; that is, the systems at the ratios of 2.0, 1.5 and 1.0 gave in 84, 80 and 68% selectivity, respectively.

As shown in the last column of Table 1, the main reaction product was found to be acetone; at molar ratios $Co^{II}/LiAlH_4$ = 3.0 and 2.0, the reacted propylene oxide was isomerized to acetone quantitatively. The formation of acetone indicates that the ring opening reaction of propylene oxide takes place by a process of CH_2—O bond cleavage, as might be expected from the nucleophilic character* of the Co^I complex. The apparent lower percentages of acetone formed in the systems at the ratios $Co^{II}/LiAlH_4$ = 1.0 and 1.5 are considered to be due to side reactions involving $LiAlH_4$ which may be present in the reaction systems because of incomplete reaction between $LiAlH_4$ and the Co^{II} complex; $LiAlH_4$ reacts with the acetone formed and with propylene oxide to give metal alkoxides, which may react further with propylene oxide [10]. The apparent lower selectivity observed in the systems at low ratios of Co^{II} complex to $LiAlH_4$ described above might also be explained by such side reactions. The reaction of propylene oxide with $LiAlH_4$ in the absence of the Co^{II} complex was also examined; only 2-propanol was obtained. The Co^{II} complex itself did not show any reaction with propylene oxide.

The above experimental results indicate that the nucleophilicity of the Co^I species is the driving force behind this asymmetric ring-opening reaction, the Co^I species being recycled as demonstrated by the recycling number of the catalyst, N (propylene oxide consumed/Co^I species), given in Table 1.

The reaction of 1,2-butene oxide with the Co^I complex was next examined for comparison with that of propylene oxide. Highly asymmetric selectivity was found, the main reaction product being methyl ethyl ketone, the product formed by CH_2—O bond scission. The ethyl substituent did not seem to differ significantly from a methyl substituent in terms of the asymmetric selectivity and reaction mechanism.

On the basis of the above experimental results, a probable mechanism for the resolution of DL-epoxide and the isomerization of epoxide to ketone may be as shown in Scheme 1. Co^I species attacks the β-carbon of propylene oxide by

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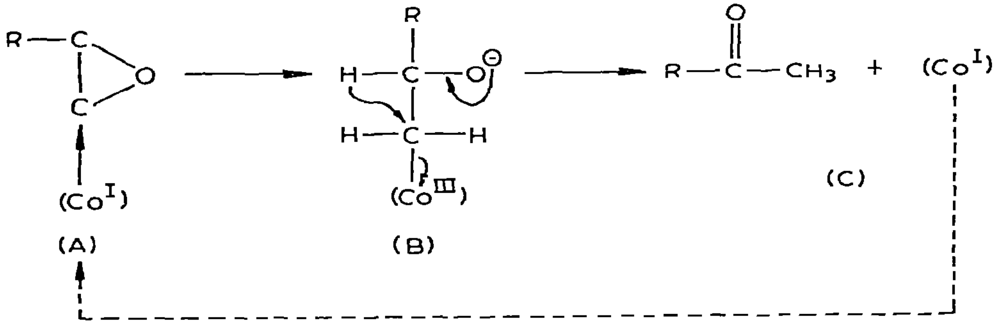
* It is generally accepted that propylene oxide reacts with nucleophilic reagents mainly by CH_2—O bond scission [11].

SCHEME 1



an S_N2 mechanism [16] (Scheme 1 A → B); the propylene oxide moiety in B is isomerized to acetone by hydride shift involving electron transfer from the oxygen to the cobalt atom (Scheme 1 B → C), as proposed by Schrauzer [15] in the case of β-hydroxyalkylcobaloxime. The Co^I species regenerated by this process is recycled and is available as a nucleophilic reagent to attack another molecule of propylene oxide. It is considered that kinetic resolution takes place at the first stage of the above scheme; that is, the optically active Co^I species reacts preferentially with *L*-propylene oxide, leaving unreacted propylene oxide containing a higher ratio of *D*-propylene oxide.

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