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Stereoselectivity in Diastereomeric Tetrahedral Metal(II) Complexes of Chiral Salicylideneamines: Crystal Structure and Molecular Mechanics Calculation of Bis[*N*-(*l*-menthyl)salicylideneaminato]cobalt(II)

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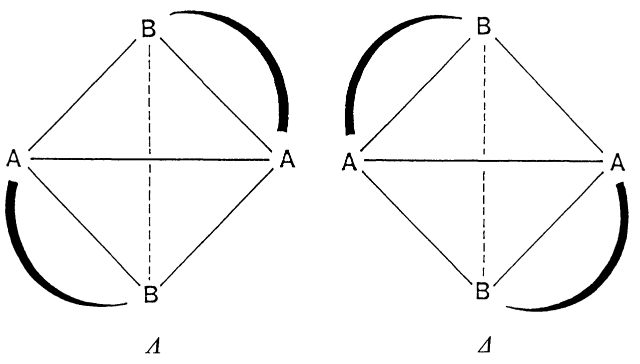
Stereoselectivity of bis[*N*-(*l*-menthyl)salicylideneaminato]cobalt(II) [Co(sal-ment)$_2$] has been studied by single crystal X-ray analysis and molecular mechanics calculations. The X-ray analysis has revealed a nearly tetrahedral surrounding (dihedral angle of 82.5°) and Δ configuration about the metal ion. Molecular mechanics calculations were made based on MM2 program, assuming a tetrahedral surrounding about the metal ion and fixing the four donor atoms and six atoms adjacent to the donor atoms at the positions as determined by the single crystal X-ray analysis. The most stable structure obtained from the MM2 calculation coincides well with that from the crystal structure analysis. Together with the X-ray structural results for [Cu(sal-ment)$_2$] and bis[*N*-[(*R*)-1-phenylethyl]salicylideneaminato]cobalt(II) [Co(sal-Rmb)$_2$] studied in this study and for related [Zn(sal-Rmb)$_2$] and [Cu(sal-Rmb)$_2$] studied previously, the factors responsible for the stereoselectivities of those bis(salicylideneaminato)metal(II) complexes have been discussed.

Studies of enantiomeric and diastereomeric metal complexes have been stimulated by the interests to elucidate the correlation between circular dichroism induced in the visible region and the absolute configuration about the metal ion and to explore the factors responsible for the stereoselective behavior found for those complexes.$^{1)}$ Tetrahedral or pseudo-tetrahedral bis-chelate complexes of the general type [M(A–B)$_2$] are enantiomeric and can in principle exist in two absolute configurations, Δ and $\Lambda$$^{2)}$ (see Fig. 1). The resolution of the enantiomers has been hardly attained with a very few exceptions$^{3)}$ because of the lability of tetrahedral complexes. The stereoselectivities of diastereomeric tetrahedral or pseudo-tetrahedral complexes of bidentate salicylideneamines or related Schiff bases have been investigated by ^{1}H NMR$^{2,4-8)}$ and circular dichroism$^{8,9)}$ spectroscopies and single crystal X-ray structural analysis.$^{9,10)}$ It is generally accepted that interligand non-covalent interactions plays an important role in the predominant formation of one of the diastereomers.$^{11)}$ A direct evidence for the operation of such interligand noncovalent interactions was obtained for tetrahedral bis[*N*-[(*R*)-1-phenylethyl]salicylideneaminato]zinc(II) [Zn(sal-Rmb)$_2$]$^{9)}$ where the chiral *N*-substituent of one ligand is in a close contact with the adjacent chelate ring of the other ligand, affording Λ configuration about the zinc(II) ion. In bis[*N*-[(*R*)-1-phenylethyl]salicylideneaminato]copper(II) [Cu(sal-Rmb)$_2$]$^{10)}$ the preferred configuration about the copper is pseudo-tetrahedral and of Δ. In this complex an interligand interaction occurs between the hydrogen attached to the asymmetric carbon in the *N*-substituent and the phenolic oxygen of the adjacent chelate ring. As seen in the above examples, the factors contributing to the stereoselectivity of diastereomeric tetrahedral complexes of salicylideneamines are not straightforward.



Λ Δ

Fig. 1. Two absolute configurations (Δ and Λ) for tetrahedral complexes.

In this study the stereoselectivity of bis[*N*-(*l*-menthyl)salicylideneaminato]cobalt(II) [Co(sal-ment)$_2$] has been studied by single-crystal X-ray method and molecular mechanics calculations by MM2 program. Further, we have examined the crystal structures of bis[*N*-(*l*-menthyl)salicylideneaminato]copper(II) [Cu(sal-ment)$_2$] and bis[*N*-[(*R*)-1-phenylethyl]salicylideneaminato]cobalt(II) [Co(sal-Ramb)$_2$] and found that the former is isomorphous to [Co(sal-ment)$_2$] and the latter to [Zn(sal-Rmb)$_2$].$^{9)}$ From the inspection of both the X-ray analytical results for those complexes and the molecular mechanics calculations for [Co(sal-ment)$_2$] it is aimed to elucidate the main factors responsible for stereoselectivities of the tetrahedral or pseudo-tetrahedral complexes of salicylideneamines.

Experimental

Preparations. [Co(sal-ment)$_2$] and [Cu(sal-ment)$_2$] were prepared by the literature methods.$^{8)}$

[Co(sal-Rmb)$_2$]. An ethanolic solution of (*R*)-1-phenylethylamine purchased from Tokyokasei Chemical Co. (0.48 g, 4 mmol) and salicylaldehyde (0.48 g, 4 mmol) was refluxed for 2 h. To this were added powdered NaHCO$_3$

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Table 1. Crystal Data for [Co(sal-ment)$_2$]

Formula	$CoO_2N_2C_{34}H_{48}$
F.W.	575.70
Crystal system	Trigonal
Space group	$P3_1$
a/Å	8.971(3)
c/Å	34.01(1)
Volume/Å	2370(2)
Z	3
D_x/g cm^{-3}	1.21
R/%	7.65
R_w/%	8.27
Observed reflection $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2167

Table 2. Atomic Parameters of [Co(sal-ment)$_2$]

Atom	x	y	z	B_{eq}/Å^2
Co	0.4101(2)	0.4099(2)	−0.0172(1)	2.74(6)
O1	0.397(1)	0.225(1)	0.0138(3)	3.1(3)
O2	0.228(1)	0.398(1)	−0.0482(3)	3.9(4)
N1	0.608(2)	0.442(2)	−0.0495(3)	3.0(4)
N2	0.437(1)	0.608(1)	0.0163(3)	2.6(4)
C1	0.532(2)	0.209(2)	0.0222(4)	2.9(5)
C2	0.534(2)	0.131(2)	0.0573(4)	3.7(5)
C3	0.675(3)	0.116(2)	0.0666(5)	5.6(8)
C4	0.816(2)	0.170(2)	0.0411(5)	5.6(7)
C5	0.818(2)	0.255(2)	0.0079(4)	3.7(5)
C6	0.679(2)	0.275(2)	−0.0017(4)	3.4(5)
C7	0.702(2)	0.374(2)	−0.0384(4)	3.1(5)
C8	0.663(2)	0.545(2)	−0.0868(4)	3.3(5)
C9	0.712(2)	0.725(2)	−0.0750(5)	4.0(5)
C10	0.773(2)	0.849(2)	−0.1109(4)	4.5(6)
C11	0.814(3)	1.031(2)	−0.0991(6)	6.0(8)
C12	0.628(2)	0.772(2)	−0.1418(4)	4.3(6)
C13	0.582(2)	0.593(2)	−0.1531(4)	4.3(6)
C14	0.515(2)	0.472(2)	−0.1176(4)	3.9(6)
C15	0.445(3)	0.282(2)	−0.1263(4)	5.1(8)
C16	0.571(3)	0.245(3)	−0.1469(6)	6.8(10)
C17	0.274(2)	0.206(3)	−0.1476(5)	5.9(8)
C18	0.216(2)	0.532(2)	−0.0570(4)	3.2(5)
C19	0.131(2)	0.534(2)	−0.0928(4)	3.9(6)
C20	0.115(2)	0.675(2)	−0.1018(4)	4.3(6)
C21	0.170(2)	0.810(2)	−0.0790(5)	4.8(7)
C22	0.255(2)	0.819(2)	−0.0425(6)	5.2(6)
C23	0.279(2)	0.680(2)	−0.0307(4)	3.2(5)
C24	0.375(2)	0.702(2)	0.0051(4)	3.4(5)
C25	0.543(2)	0.663(2)	0.0524(5)	4.4(7)
C26	0.727(2)	0.717(2)	0.0425(4)	3.4(5)
C27	0.848(2)	0.770(2)	0.0763(5)	5.0(6)
C28	1.027(2)	0.813(3)	0.0634(5)	6.1(7)
C29	0.776(3)	0.631(2)	0.1078(6)	6.1(8)
C30	0.593(2)	0.582(2)	0.1185(4)	5.2(8)
C31	0.470(2)	0.513(2)	0.0810(3)	2.8(5)
C32	0.282(2)	0.449(2)	0.0902(5)	4.6(6)
C33	0.246(3)	0.571(3)	0.1171(5)	5.6(8)
C34	0.207(2)	0.279(2)	0.1130(5)	5.4(7)

(0.34 g, 4 mmol) and cobalt(II) acetate tetrahydrate (0.49 g, 2 mmol), and the mixture was stirred at 60 °C for 2 h and allowed to stand overnight at ambient temperature. The resulted red crystals were recrystallized from ethanol.

Found: C, 70.84; H, 5.51; N, 5.54%. Calcd for $C_{30}H_{28}CoN_2O_2$: C, 71.00; H, 5.52; N, 5.56%.

Single-Crystal X-Ray Analyses. Single crystals of [Co(sal-ment)$_2$] were grown by the slow crystallization from a chloroform–ethanol (3 : 1 in volume) mixture, and a crystal with approximate dimensions of 0.4×0.4×0.2 mm was used for the study. Intensities and lattice parameters were obtained on a Rigaku AFC-5 automated four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at 20±1 °C. Lattice parameters and their estimated standard deviations were obtained from a least-squares fit to 25 2θ values in the range $15° < 2\theta < 30°$. For the intensity data collections, the ω–2θ scan mode was used at a scan rate of 6° min^{-1}. The octant measured was $+h$, $+k$, $+l$. Three standard reflections were monitored every 100 reflections and their intensities showed a good stability. The intensity data were corrected for Lorentz-polarization effects but not for absorption. The crystal data of [Co(sal-ment)$_2$] are summarized in Table 1.

The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. Atomic scattering factors were taken from Ref. 12. Hydrogen atoms were included in their calculated positions and held fixed. All the calculations were carried out on a FACOM M-780 computer in the Computer Center of Kyushu University by the use of local version of the UNICS-III and ORTEP programs.[13,14] The final positional parameters for [Co(sal-ment)$_2$] are given in Table 2. The F_o–F_c tables, thermal parameters, H-atom parameters, and full bond distances and angles are deposited as Document No. 8958 at the Office of the Editor of Bull. Chem. Soc. Jpn.

[Cu(sal-ment)$_2$] was found to be isomorphous to [Co(sal-ment)$_2$]: Formula=$CuO_2N_2C_{34}H_{48}$, F.W.=580.31, trigonal, space group=$P3_1$, a=8.874(3), c=34.645(9) Å, V=2365(2) Å^3, Z=3, D_x=1.22 g cm^{-3}.

[Co(sal-Rmb)$_2$] was also found to be isostructural with [Zn(sal-Rmb)$_2$]: Formula=$Co_2O_4N_4C_{60}H_{54}$, F.W.=1012.98, space group=$P2_12_12_1$, orthorhombic, a=17.771(3), b=29.681(9), c=9.892(6) Å, V=5218(3) Å^3, Z=4, D_x=1.28 g cm^{-3}.

Molecular Mechanics Calculations. The molecular mechanics calculations were carried out by the use of the MM2 program.[15] The most stable structure of [Co(sal-ment)$_2$] was obtained by the procedures as described as follows. As the first step the complex was divided into two parts, the *l*-menthyl part and the rest, and their most stable structures were calculated for imaginal "*l*-menthylmethane" (1-isopropyl-2,4-dimethylcyclohexane) and tetrahedral bis(salicylideneaminato)cobalt(II) [Co(sal-ment)$_2$], respectively. As the second step the initial steric energy of [Co(sal-ment)$_2$] was calculated for both Δ and Λ forms every 30° by rotating the *l*-menthyl groups with respect to the N–C(menthyl) bond, while maintaining the most stable structures of the constituents obtained in the first step. Finally, the conformer with the lowest steric energy was used in the energy minimization to obtain the most stable structure of the whole complex molecule. Since the parameters of sp^2 nitrogen atom and cobalt atom are lacking, the parameters of sp^2 carbon atom were used for the sp^2 nitrogen and the four donor atoms and the six atoms attached to the donor atoms were fixed at the positions determined from the crystal structure analysis. In other words, the cobalt atom was not included in the energy minimization. The MM2 calculational data are deposited as supplementary materials (Table S5—S10).

Results and Discussion

Crystal Structures of [Co(sal-ment)$_2$] and [Cu(sal-ment)$_2$]. These complexes are isomorphous (see Table 1). The crystal structure of the cobalt complex is described here. Its perspective view is given in Fig. 2, together with the numbering system. Relevant bond lengths and angles are listed in Table 3.

The deprotonated form of the Schiff base functions as a bidentate ligand to form a nearly tetrahedral surrounding about the cobalt ion. The dihedral angle between the plane defined by Co, N(1), and O(1) and the plane defined by Co, N(2), and O(2) is 82.5°. We analyzed the molecular structure by taking into account the established configuration of the *l*-menthyl group and found the dextral disposition of two ligands along the C$_2$ axis, i.e. Δ configuration.

The cyclohexane ring of the *l*-menthyl group assumes a chair form and the salicylideneamine moiety is equatorially bonded to the cyclohexane ring. The conformation with respect to the N(1)–C(8) bond is such that the hydrogen attached to C(8) is eclipsed to the hydrogen attached to C(7). This conformation must be the most preferred one. In any other conformations a large interligand steric repulsions is expected between the azomethine hydrogen and *l*-menthyl group.

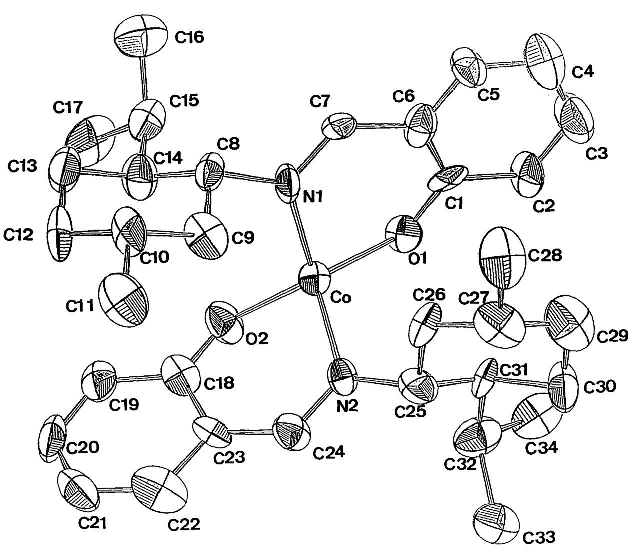

Fig. 2. ORTEP view of [Co(sal-ment)$_2$] with numbering system.

Table 3. Relevant Bond Distances and Angles of [Co(sal-ment)$_2$]

Bond distances (Å)	
Co-O1	1.91(1)
Co-O2	1.90(1)
Co-N1	1.98(1)
Co-N2	2.02(1)
Bond angles (deg)	
O1-Co-O2	125.0(3)
O1-Co-N1	95.5(5)
O1-Co-N2	112.3(4)
O2-Co-N1	112.5(4)
O2-Co-N2	94.9(5)
N1-Co-N2	118.6(4)
Distances between non-bonded atoms (Å)	
O1-C31	3.26(2)
O2-C14	3.31(2)

In the crystal the C(14) of the *l*-menthyl group is in a close proximity of the phenolic oxygen O(2) of the adjacent chelate ring with the interatomic distance of 3.31(2) Å. Similarly the C(31)–O(1) interatomic distance is 3.26(2) Å. Even taking the C–H–O angles into consideration, those short distances suggest the presence of the hydrogen bonding between these atoms.

[Co(sal-Rmb)$_2$]. The X-ray study has shown that the crystal of this complex is isomorphous to that of [Zn(sal-Rmb)$_2$]. This zinc complex assumes a nearly tetrahedral environment about the metal ion and the absolute configuration is Λ. The detailed structure of this complex has been reported in our recent paper.[9]

Molecular Mechanics Results. *l*-Menthylmethane. This molecule assumes a chair structure.[16] In our calculations only the rotation of the isopropyl group with respect to C(cyclohexane)–C(isopropyl) bond was considered. The result indicates that the isopropyl group is subjected to a severe steric effect from the adjacent methyl group. The most preferred conformation is such that the isopropyl hydrogen ($-\text{C}\underline{\text{H}}(\text{CH}_3)_2$) is eclipsed to the adjacent methyl group and the two methyl groups of the isopropyl moiety are thrust away to the opposite side.

[Co(sal-ment)$_2$]. The most stable structure of [Co(sal-ment)$_2$] obtained by molecular mechanics calculations is shown in Fig. 3. This structure is essentially the same as the molecular structure determined by the single crystal X-ray method (see Fig. 2). The bond distances and bond angles determined by the two methods agree within 0.1 Å and 4°, respectively, except for those of the aromatic part.

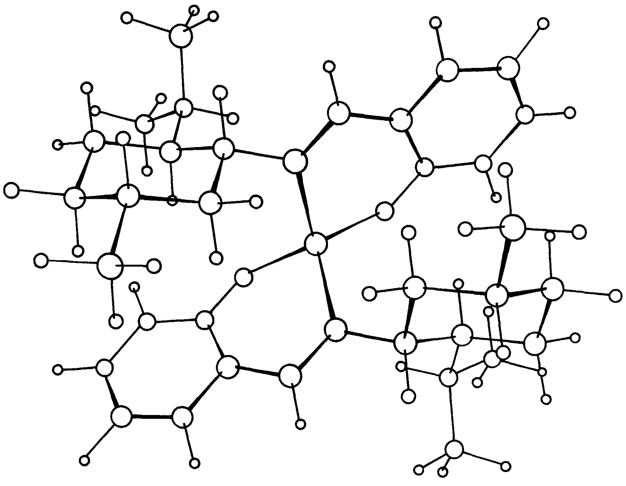

Fig. 3. The most stable structure of [Co(sal-ment)$_2$] obtained by the molecular mechanics calculation.

The ligand moiety in the complex molecule retains the most stable structure of free (sal-ment)$^-$, in which the conformation about the N–C(menthyl) bond is such that the hydrogen on the asymmetric carbon attached to the nitrilo nitrogen is eclipsed to the azomethine carbon so as to reduce the steric repulsion between the *l*-menthyl group and the aromatic part. A large rotational barrier about the N–C(menthyl) bond is probably the cause to retain this conformation even in the complex molecule. The Λ form is possible if the *l*-menthyl group is rotated by ca. 180° about the N–C(menthyl) bond from the most stable conformation of the free ligand, but this form is unfavorable because of a steric repulsion between the aromatic ring and *l*-menthyl group.

Factors Responsible for Stereoselectivity. Though the structurally well-characterized, tetrahedral or pseudo-tetrahedral complexes of salicylideneamines with a chiral N-substituent are still limited, their stereochemistries are significantly diversed, depending upon the nature of the central metal ion and the Schiff base ligand. In this study we have aimed to deduce dominant factors responsible for the stereochemistry in each complex. Four factors can be considered here: (A) the preferred configuration of the central metal ion, (B) the preferred conformation of salicylideneamines mainly due to the intraligand steric repulsion, (C) an interligand steric repulsion between ligands, and (D) an interligand noncovalent attracting interaction.

The preferred configurations for four-coordinate cobalt(II) and zinc(II) ions are tetrahedral whereas that for copper(II) ion is planar.[17,18] The most stable structures of (sal-ment)$^-$ and (sal-Rmb)$^-$ are such that the N-substituent and the aromatic part are disposed as far as possible because of the steric repulsion. With respect to the rotational barrier due to the steric repulsion, (sal-Rmb)$^-$ is more flexible than (sal-ment)$^-$.

(1) [M(sal-ment)$_2$] (M=Co, Cu). The tetrahedral surrounding has been proved for both complexes. Because of the interligand steric repulsion tetrahedral configuration is preferable rather than square planar configuration. This configuration is also preferable to cobalt(II) but not to copper(II). The ligand moiety retains the most stable conformation in the complexes because of the rotational barrier due to the intraligand steric repulsion. If two (sal-ment)$^-$ ligands maintaining the most stable conformation were disposed planarly about a metal ion, a severe interligand steric hinderance would occur. Thus, such a steric effect is the cause for the tetrahedral distortion of the copper complex. The stereoselectivity to afford Δ configuration about the central metal may also be attributed to an interligand steric repulsion between the two chiral ligands.

(2) [Cu(sal-Rmb)$_2$]. In this complex the dihedral angle around the metal ion is rather small (39.5°).[10] This is because the steric requirement of the copper(II) to prefer a planar configuration is larger than the intraligand steric repulsion in each ligands. The ligand conformation is significantly altered from the most stable free-ligand conformation so as to reduce the interligand steric repulsion. It is also obvious that the hydrogen bonding between the asymmetric carbon and the phenolic oxygen of the neighboring chelate ring is cotributing to the stabilization. The difference of the steric hindrance between the methyl group and the phenyl group gives rise to the stereoselectivity to afford the Δ configuration.

(3) [M(sal-ment)$_2$] (M=Co, Cu). (3) [M(sal-Rmb)$_2$ (M=Co, Zn). Both the cobalt(II) and zinc(II) complexes assume a tetradedral structure which is preferable to both metal ions. Since this configuration causes little interligand steric hindrance, the ligand retains essentially its most stable form of the free ligand. The stereoselectivity of those complexes to afford Λ configuration about the metal ion should be attributed to the intramolecular interligand interaction between the N-substituent and the chelate ring of another ligand of the complex.

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