Bull. Chem. Soc. Jpn., ***69***, *2549—2557 (1996)*

Stereochemistry and Electrochemistry of Cobalt(II) and Cobalt(III) Complexes Containing Optically Active Tetradentate Schiff Base Ligands

Masakazu Hirotsu,* Masaaki Kojima,* Kiyohiko Nakajima,† Setsuo Kashino, and Yuzo Yoshikawa††

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700

†Department of Chemistry, Aichi University of Education, Igaya, Kariya 448

††Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444

(Received March 5, 1996)

Cobalt(II) complexes containing tetradentate Schiff base ligands with phenyl substituents, [Co(Schiff base)], have been prepared and the electrochemical properties are reported. The crystal structure of [Co{7-Phsal-(*rac*)-stien}], where the Schiff base ligand was derived from 2-hydroxybenzophenone and (*rac*)-1,2-diphenylethylenediamine, has been determined by X-ray structure analysis. Crystal data: monoclinic, $P2_1/n$, $a=13.956(2)$, $b=14.703(2)$, $c=17.808(3)$ Å, $\beta=112.21(1)^\circ$, $V=3383.0(9)$ Å^3, $Z=4$, and $R=0.052$ and $R_w=0.039$ for 3976 unique reflections with $I>3\sigma(I)$. The two phenyl groups in the N–N chelate moiety are in the axial positions and block the apical sites. In this complex, the redox potential of the Co(III)/Co(II) couple is 0.20 V vs. Ag/Ag$^+$ in acetonitrile and becomes more positive by *ca.* 300 mV than that for [Co(salen)]. This large positive shift is attributed to the steric effect of the two axially disposed phenyl groups. The redox potentials of the analogous cobalt(II) Schiff base complexes, where (*meso*)-1,2-diphenylethylenediamine and (*R*)-1-phenylethylenediamine were used as a diamine, are also explained in terms of the steric effect of the phenyl substituents. The corresponding cobalt(III) Schiff base complexes with two additional axial ligands, [Co(Schiff base)(L)$_2$]ClO$_4$ (L = imidazole (im), 1-methylimidazole (Meim)), have been prepared. The steric interaction between the phenyl groups on the N–N chelate moiety and the axial ligands is discussed based on the X-ray structure, the circular dichroism (CD) spectra, and the ^{1}H NMR spectra. The crystal structure determination of [Co{sal-(*meso*)-stien}(Meim)$_2$]ClO$_4$ has been performed. Crystal data: monoclinic, $P2_1/c$, $a=10.789(2)$, $b=20.512(3)$, $c=15.330(2)$ Å, $\beta=99.88(1)^\circ$, $V=3342.3(8)$ Å^3, $Z=4$, and $R=0.051$ and $R_w=0.049$ for 3414 unique reflections with $I>3\sigma(I)$. In order to study the steric effect of the phenyl substituents, the [Co(Schiff base)(L)$_2$]ClO$_4$ complexes have been prepared using (*R*)-1,2-propanediamine as a diamine. The different behavior shows that the interaction between the phenyl groups is sensitive to the orientation.

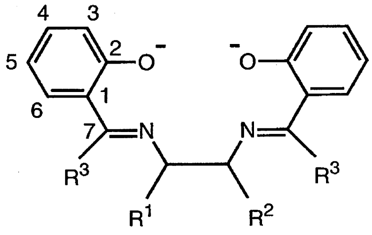
Cobalt(II) Schiff base complexes are useful as catalysts for the oxygenation reactions of organic molecules.[1)] The reversibility of oxygenation of the cobalt(II) complexes is closely related to the redox potential of the Co(III)/Co(II) couple.[2)] In asymmetric catalytic reactions using other metal Schiff base complexes, both the geometry and the redox potential affect the enantioselectivity.[3,4)] On the other hand, it has been pointed out that the orientation of phenyl groups plays an important role in those reactions.[5,6)] In a previous paper,[7)] we reported that the phenyl substituents on both the azomethine carbon atoms and the ethylene backbone control the structure of the cobalt(II) Schiff base complexes and affect the electrochemical properties. It has been deduced that the steric interaction between the phenyl substituents and additional donors at the apical sites contribute to the redox potentials. The axially disposed phenyl groups of the cobalt(II) Schiff base complexes effectively block the apical site, and make it difficult to oxidize to cobalt(III). This phenomenon is affected by the orientation of the phenyl groups. Thus, it is useful to investigate the structures of the hexacoordinated cobalt(III) Schiff base complexes with axial ligands.

In this paper, we report on the preparation and characterization of cobalt(II) and cobalt(III) complexes containing optically active Schiff base ligands with phenyl substituents. Furthermore, in order to contrast the phenyl–phenyl and methyl–phenyl interactions, we also studied the complexes containing the methyl substituent. The interaction between the substituents of the Schiff base ligands and the axial ligands in cobalt(III) Schiff base complexes is discussed based on the CD spectra, the ^{1}H NMR spectra, and the crystal structures.

Experimental

Abbreviations of the Schiff base ligands are represented in Chart 1. (*S*,*S*)-1,2-diphenylethylenediamine ((*SS*)-stien),[8)] *meso*-1,2-diphenylethylenediamine ((*meso*)-stien),[9)] (*R*)-1-phenylethylenediamine ((*R*)-pen),[10)] (*R*)-1,2-propanediamine ((*R*)-pn),[11)] and (*R*,*R*)-1,2-cyclohexanediamine ((*RR*)-chxn)[12)] were prepared by the published methods. Schiff bases were prepared by the method of Gullotti et al.[13)] [Co(salen)],[14)] [Co{sal-(*R*)-pen}],[15)] [Co{sal-(*SS*)-stien}],[15)] [Co{sal-(*meso*)-stien}],[15)] [Co(7-Phsalen)],[16)] and [Co{7-Phsal-(*R*)-pn}][17)] have already been reported.

[Co{7-Phsal-(*SS*)-stien}]·0.5H$_2$O. The ligand H$_2${7-Phsal-(*SS*)-stien} (1.145 g, 2 mmol) was dissolved in dichloromethane–ethanol (1 : 1, 30 cm^3), and the solution was refluxed under a nitrogen atmosphere. Upon the addition of Co(CH$_3$COO)$_2$·4H$_2$O



R^1	R^2	R^3	
H	H	H	salen
Ph	H	H	sal-(*R*)-pen
Ph	Ph	H	sal-(*SS*)-stien
Ph	Ph	H	sal-(*meso*)-stien
H	H	Ph	7-Phsalen
Ph	H	Ph	7-Phsal-(*R*)-pen
Ph	Ph	Ph	7-Phsal-(*SS*)-stien
Me	H	H	sal-(*R*)-pn
Me	H	Ph	7-Phsal-(*R*)-pn
(CH$_2$)$_4$		H	sal-(*RR*)-chxn
Me	Me	H	sal-(*SS*)-bn

Chart 1.

(0.498 g, 2 mmol), the yellow solution turned red. The reaction mixture was refluxed for 20 min. The resulting solution was cooled and concentrated on a rotary evaporator. A red precipitate was collected by filtration and washed with ethanol. Recrystallization was carried out twice from dichloromethane–ethanol. The product was dried over P_4O_{10} under vacuum. Yield: 1.178 g (93%). Anal. Found: C, 75.24; H, 4.89; N, 4.17%. Calcd for $C_{40}H_{31}CoN_2O_{2.5}$: C, 75.23; H, 4.89; N, 4.39%.

[Co{7-Phsal-(*rac*)-stien}]·C$_2$H$_5$OH·H$_2$O. The same procedure as for [Co{7-Phsal-(*SS*)-stien}] was used. Yield: 81%. Anal. Found: C, 72.79; H, 5.24; N, 3.92%. Calcd for $C_{42}H_{38}CoN_2O_4$: C, 72.72; H, 5.52; N, 4.04%.

[Co{7-Phsal-(*R*)-pen}]. The same procedure as for [Co{7-Phsal-(*SS*)-stien}] was used. Yield: 69%. Anal. Found: C, 73.42; H, 4.82; N, 4.75%. Calcd for $C_{34}H_{26}CoN_2O_2$: C, 73.78; H, 4.73; N, 5.06%.

[Co{sal-(*meso*)-stien}(Meim)$_2$]ClO$_4$·0.5C$_2$H$_5$OH·H$_2$O. To a suspension of the ligand H$_2${sal-(*meso*)-stien} (0.421 g, 1 mmol) and 1-methylimidazole (0.247 g, 3 mmol) in ethanol (15 cm^3) was added Co(CH$_3$COO)$_2$·4H$_2$O (0.249 g, 1 mmol). The reaction mixture was stirred for 18 h to give a deep reddish brown solution. NaClO$_4$·H$_2$O (0.351 g, 2.5 mmol) was then added and the mixture was stirred for 1 h. The resulting reddish brown precipitate was collected by filtration and washed with ethanol. Recrystallization was carried out from dichloromethane–ethanol. The product was dried over P_4O_{10} under vacuum. Yield: 0.670 g (86%). Anal. Found: C, 56.71; H, 4.89; N, 10.84%. Calcd for $C_{37}H_{39}ClCoN_6O_{7.5}$: C, 56.82; H, 5.03; N, 10.74%.

[Co{7-Phsal-(*R*)-pen}(im)$_2$]ClO$_4$. This brown complex was prepared by the same method as for [Co{sal-(*meso*)-stien}(Meim)$_2$]ClO$_4$ except that imidazole was used instead of 1-methylimidazole. Yield: 69%. Anal. Found: C, 60.76; H, 4.43; N, 10.60%. Calcd for $C_{40}H_{34}ClCoN_6O_6$: C, 60.88; H, 4.34; N, 10.65%.

[Co{sal-(*R*)-pen}(im)$_2$]ClO$_4$. This brown complex was prepared by the same method as for [Co{sal-(*meso*)-stien}(Meim)$_2$]ClO$_4$ except that imidazole was used instead of 1-methylimidazole. Yield: 73%. Anal. Found: C, 52.59; H, 4.23; N, 12.85%. Calcd for $C_{28}H_{26}ClCoN_6O_6$: C, 52.80; H, 4.11; N, 13.19%.

[Co{7-Phsal-(*R*)-pn}(Meim)$_2$]ClO$_4$. To a solution of [Co{7-Phsal-(*R*)-pn}] (0.392 g, 0.8 mmol) in dichloromethane (30 cm^3) was added an ethanol solution (20 cm^3) of 1-methylimidazole (0.206 g, 2.5 mmol). The resulting deep purple solution was stirred for 10 h. An ethanol solution (10 cm^3) of NaClO$_4$·H$_2$O (0.421 g, 3 mmol) was then added with stirring. The solution was concentrated by rotatory evaporation and stirred. A brown precipitate was collected by filtration, washed with ethanol, and then recrystallized twice from dichloromethane-ethanol. Yield: 0.305 g (50%). Anal. Found: C, 58.85; H, 4.77; N, 11.22%. Calcd for $C_{37}H_{36}ClCoN_6O_6$: C, 58.85; H, 4.81; N, 11.13%.

[Co{sal-(*R*)-pn}(Meim)$_2$]ClO$_4$. To an ethanol solution (15 cm^3) containing H$_2${sal-(*R*)-pn} (2 mmol, 0.567 g) and 1-methylimidazole (6 mmol, 0.493 g) was added a 0.5 M (1 M = 1 mol dm^{-3}) solution (5 cm^3) of NaOH in ethanol and then Co(CH$_3$COO)$_2$·4H$_2$O (2 mmol, 0.498 g). The reaction mixture was stirred for 4 h to give a purple solution. An ethanol solution (20 cm^3) of NaClO$_4$·H$_2$O (5 mmol, 0.702 g) was then added and the mixture was stirred for 1 h. The resulting purple precipitate was collected by filtration and washed with ethanol. Recrystallization was carried out twice from dichloromethane–ethanol. Yield: 0.944 g (78%). Anal. Found: C, 49.73; H, 4.70; N, 13.85%. Calcd for $C_{25}H_{28}ClCoN_6O_6$: C, 49.80; H, 4.68; N, 13.94%.

[Co{sal-(*RR*)-chxn}(Meim)$_2$]ClO$_4$. The same procedure as for [Co{sal-(*R*)-pn}(Meim)$_2$]ClO$_4$ was used. Yield: 59%. Anal. Found: C, 52.17; H, 5.24; N, 12.70%. Calcd for $C_{28}H_{32}ClCoN_6O_6$: C, 52.30; H, 5.02; N, 13.07%.

Physical Measurements. Cyclic voltammetric measurements were performed using a Fuso HECS 321B potential sweep unit with acetonitrile or dichloromethane solutions containing Bu$_4$NBF$_4$ (0.1 M) as a supporting electrolyte at a scan rate of 0.1 V s^{-1}. The electrochemical cell was a three-electrode system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/Ag$^+$ (Ag/0.01 M AgNO$_3$) reference electrode. As an external standard, the Fc/Fc$^+$ (Fc = ferrocene) couple was observed at 0.085 V vs. Ag/Ag$^+$ in acetonitrile and 0.195 V vs. Ag/Ag$^+$ in dichloromethane. CD spectra were recorded on a J-720 spectropolarimeter. Visible-UV absorption spectra were recorded with a JASCO Ubest-30 or a Hitachi U-3400 spectrophotometer. ^{1}H NMR spectra were measured at 270 MHz on a JOEL EX-270 spectrometer.

Collection and Reduction of X-Ray Data. [Co{7-Phsal-(*rac*)-stien}]·CH$_3$CN. Suitable crystals of [Co{7-Phsal-(*rac*)-stien}]·CH$_3$CN were obtained by slow evaporation of a dichloromethane–acetonitrile solution at room temperature. A red prismatic crystal (0.40×0.33×0.58 mm) was mounted on a Rigaku AFC-5R diffractometer at the X-ray Laboratory of Okayama University. The cell parameters were obtained by a least-squares refinement of the angular settings of 25 reflections in the range of $22° < 2\theta < 23°$. Data collections were carried out using graphite-monochromated Mo $K\alpha$ radiation to a maximum 2θ value of 50.0°. The intensities of three standard reflections were measured after every 97 reflections and showed no significant reduction during the data collection. An empirical absorption correction based on ψ scans of three reflections was applied. Crystallographic data are given in Table 1. All calculations were carried out using the TEXSAN[18] crystallographic software package on a Silicon Graphics IRIS Indigo workstation. The structure was solved by heavy-atom Patterson methods[19] and

Table 1. Crystallographic Data for [Co{7-Phsal-(*rac*)-stien}]·CH_3CN and [Co{sal-(*meso*)-stien}(Meim)$_2$]ClO_4

	[Co{7-Phsal-(*rac*)-stien}]·CH_3CN	[Co{sal-(*meso*)-stien}(Meim)$_2$]ClO_4
Formura	$C_{42}H_{33}CoN_3O_2$	$C_{36}H_{34}ClCoN_6O_6$
Fw	670.67	741.09
Crystall system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	13.956(2)	10.789(2)
b/Å	14.703(2)	20.512(3)
c/Å	17.808(3)	15.330(2)
β/deg	112.21(1)	99.88(1)
V/Å^3	3383.0(9)	3342.3(8)
Z	4	4
D_{calcd}/g cm^{-3}	1.317	1.481
λ/Å	0.7107 (Mo$K\alpha$)	0.7107 (Mo$K\alpha$)
μ/cm^{-1}	5.49	6.55
T/°C	18	23
No. of total deta collected	6169	7727
No. of unique data	5962	7470
No. of observations	3976 ($I > 3\sigma(I)$)	3414 ($I > 3\sigma(I)$)
No. of variables	434	563
R[a)]	0.052	0.051
R_w[b)]	0.039	0.049

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, $w=4F_o^2/\sigma^2(F_o^2)$.

expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by a full-matrix least-squares procedure. Hydrogen atoms were included except for those of the acetonitrile molecule, but not refined, and were placed at fixed distances from bonded carbon atoms of 0.95 Å. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.81 and −0.66 e Å^{-3}, respectively. The atomic parameters of non-hydrogen atoms are listed in Table 2.

[Co{sal-(*meso*)-stien}(Meim)$_2$]ClO_4. Suitable crystals of [Co{sal-(*meso*)-stien}(Meim)$_2$]ClO_4 were obtained by slow evaporation of a dichloromethane–ethanol solution at room temperature. A red prismatic crystal (0.17×0.13×0.42 mm) was mounted on an Enraf–Nonius CAD-4 diffractometer at Institute for Molecular Science. The cell parameters were obtained by a least-squares refinement of the angular settings of 20 reflections in the range of $20° < 2\theta < 42°$. Intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation to a maximum 2θ value of 53.9°. A 3.99% decay in the intensities of three standard reflections monitered after every two hours was observed during the data collection. The data were scaled to correct for this effect. An empirical absorption correction based on ψ scans of three reflections was applied. Crystallographic data are given in Table 1. The structure was solved by direct methods[20)] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by a full-matrix least-squares procedure. Hydrogen atoms were refined isotropically except for those of the two *N*-methyl groups. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.54 and −0.54 e Å^{-3}, respectively. The atomic parameters of non-hydrogen atoms are listed in Table 3.

For [Co{7-Phsal-(*rac*)-stien}]·CH_3CN and [Co{sal-(*meso*)-stien}(Meim)$_2$]ClO_4, full crystallographic data, experimental details, atomic coordinates and equivalent isotropic temperature factors for hydrogen atoms, anisotropic temperature factors for non-hydrogen atoms, complete bond distances and angles, and tables of observed and calculated structure factors are deposited as Document No. 69051 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Structure of [Co{7-Phsal-(*rac*)-stien}]·CH_3CN. The crystal structure of [Co{7-Phsal-(*rac*)-stien}]·CH_3CN shows that the cobalt metal center is in a square planar environment with the tetradentate Schiff base ligand (Fig. 1). The acetonitrile molecule does not coordinate to the cobalt. Selected bond distances and angles are given in Table 4. The Co–N and Co–O distances are close to those of related complexes.[21,22)] A slight tetrahedral distortion from an ideal square planar structure is found. The mean deviation of the coordinating atoms (N(1), N(2), O(1), and O(2)) from the N_2O_2 least-squares plane is 0.10 Å, which is comparable to those of the related complexes.[21,22)]

The most striking feature of this complex is that the two phenyl groups on the ethylene backbone (R^1 and R^2, Scheme 1a) occupy positions axial to the plane of the Schiff base ligand. The *gauche* conformation with the axial phenyl groups will be due to the steric repulsion with the phenyl groups on the azomethine carbon atoms (R^3).

Pasini et al. have extensively studied the conformation of the N–N chelate moiety of the related cobalt(II) Schiff base complexes based on the CD spectra.[23)] They reported that [Co{sal-(*S*)-pn}], [Co{sal-(*SS*)-bn}], [Co{sal-(*S*)-pen}], and [Co{sal-(*SS*)-stien}] show a negative CD band in the 25000—30000 cm^{-1} region; the dominant conformation of the central chelate ring has been assigned to the λ *gauche* form. Thus, the substituents on the N–N chelate ring are in the axial positions. The CD spectral pattern of [Co{7-Phsal-(*SS*)-stien}] in acetonitrile is similar (ν_{max}, $\Delta\epsilon$: 20000 cm^{-1}, −3.81 M^{-1} cm^{-1}; 28100 cm^{-1}, −10.42 M^{-1} cm^{-1}) to those of the above-mentioned complexes. Thus, the two phenyl groups on the N–N chelate ring are in the axial positions in the solution (Scheme 1a).

Table 2. Atomic Coordinates and B_{eq} for [Co{7-Phsal-(*rac*)-stien}]·CH_3CN

Atom	x	y	z	$B_{eq}/Å^2$ [a)]
Co	0.19701(5)	0.23541(4)	−0.02235(4)	3.58(1)
O(1)	0.1551(2)	0.1212(2)	−0.0070(2)	4.83(9)
O(2)	0.0602(2)	0.2607(2)	−0.0790(2)	4.43(8)
N(1)	0.3370(2)	0.2060(2)	0.0267(2)	3.3(1)
N(2)	0.2389(3)	0.3554(2)	−0.0259(2)	3.0(1)
N(3)	−0.3584(5)	0.2643(6)	−0.2916(4)	9.9(2)
C(1)	0.2118(4)	0.0538(3)	0.0346(3)	3.7(1)
C(2)	0.1593(3)	−0.0261(3)	0.0400(3)	4.9(1)
C(3)	0.2110(4)	−0.1002(3)	0.0811(3)	4.7(1)
C(4)	0.3177(4)	−0.0995(3)	0.1186(3)	4.4(1)
C(5)	0.3712(3)	−0.0224(3)	0.1148(3)	3.9(1)
C(6)	0.3210(3)	0.0560(3)	0.0727(2)	3.2(1)
C(7)	0.3815(3)	0.1340(3)	0.0672(3)	3.0(1)
C(8)	0.4975(3)	0.1282(3)	0.1091(3)	3.1(1)
C(9)	0.5434(4)	0.1541(3)	0.1881(3)	4.8(1)
C(10)	0.6494(5)	0.1464(4)	0.2282(3)	6.3(2)
C(11)	0.7083(4)	0.1119(4)	0.1886(4)	6.4(2)
C(12)	0.6637(4)	0.0863(3)	0.1101(4)	5.4(2)
C(13)	0.5575(4)	0.0947(3)	0.0695(3)	4.0(1)
C(14)	0.3993(3)	0.2774(3)	0.0084(3)	3.7(1)
C(15)	0.4016(3)	0.2621(3)	−0.0763(3)	3.7(1)
C(16)	0.4540(4)	0.3239(3)	−0.1063(3)	4.8(1)
C(17)	0.4651(4)	0.3059(4)	−0.1805(3)	5.7(2)
C(18)	0.4251(4)	0.2288(5)	−0.2226(3)	6.3(2)
C(19)	0.3730(4)	0.1680(4)	−0.1933(4)	6.2(2)
C(20)	0.3611(4)	0.1846(3)	−0.1212(3)	4.9(1)
C(21)	0.0175(3)	0.3379(3)	−0.1101(3)	3.6(1)
C(22)	−0.0893(4)	0.3373(3)	−0.1581(3)	4.3(1)
C(23)	−0.1410(3)	0.4146(4)	−0.1914(3)	4.8(1)
C(24)	−0.0890(4)	0.4979(3)	−0.1780(3)	4.9(1)
C(25)	0.0140(4)	0.5000(3)	−0.1326(3)	4.3(1)
C(26)	0.0714(3)	0.4214(3)	−0.0982(2)	3.1(1)
C(27)	0.1808(3)	0.4269(3)	−0.0548(2)	3.1(1)
C(28)	0.2276(3)	0.5204(3)	−0.0418(3)	3.2(1)
C(29)	0.2313(3)	0.5692(3)	0.0247(3)	4.3(1)
C(30)	0.2666(4)	0.6575(3)	0.0352(3)	5.3(2)
C(31)	0.2963(4)	0.6973(3)	−0.0227(4)	5.4(2)
C(32)	0.2924(4)	0.6503(4)	−0.0893(3)	4.9(2)
C(33)	0.2586(3)	0.5609(3)	−0.0984(3)	4.3(1)
C(34)	0.3520(3)	0.3665(3)	0.0164(3)	3.7(1)
C(35)	0.3861(4)	0.3890(3)	0.1070(3)	4.3(1)
C(36)	0.3256(4)	0.3740(3)	0.1519(3)	4.9(1)
C(37)	0.3636(5)	0.3914(4)	0.2351(4)	6.2(2)
C(38)	0.4634(6)	0.4214(4)	0.2747(3)	7.5(2)
C(39)	0.5239(5)	0.4357(4)	0.2311(4)	8.1(2)
C(40)	0.4855(4)	0.4201(4)	0.1490(4)	6.2(2)
C(41)	−0.4284(7)	0.2743(8)	−0.3555(7)	12.9(4)
C(42)	−0.5090(6)	0.2913(8)	−0.4208(4)	14.4(3)

a) $B_{eq}=(8/3)\pi^2[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$.

Table 3. Atomic Coordinates and B_{eq} for [Co{sal-(*meso*)-stien}$(Meim)_2$]ClO_4

Atom	x	y	z	$B_{eq}/Å^2$ [a)]
Co	0.29556(7)	0.03737(4)	0.70585(5)	2.22(2)
Cl	0.9434(2)	0.26004(9)	0.2887(1)	4.16(5)
O(1)	0.4453(3)	0.0879(2)	0.7330(3)	2.87(10)
O(2)	0.3746(3)	−0.0011(2)	0.6175(3)	2.65(9)
O(3)	0.9078(7)	0.2341(7)	0.3602(6)	21.9(5)
O(4)	1.0750(5)	0.2533(3)	0.2995(4)	7.6(2)
O(5)	0.8821(8)	0.2227(3)	0.2235(7)	16.2(3)
O(6)	0.9040(7)	0.3209(3)	0.2760(6)	13.5(3)
N(1)	0.2184(4)	0.0753(2)	0.7952(3)	2.3(1)
N(2)	0.1424(4)	−0.0114(2)	0.6763(3)	2.3(1)
N(3)	0.3766(4)	−0.0283(2)	0.7881(3)	2.5(1)
N(4)	0.2257(4)	0.1053(2)	0.6208(3)	2.5(1)
N(5)	0.4395(5)	−0.1218(3)	0.8513(3)	3.8(1)
N(6)	0.1531(5)	0.2000(2)	0.5637(4)	3.4(1)
C(1)	0.4604(5)	0.1391(3)	0.7849(4)	2.7(1)
C(2)	0.5746(7)	0.1744(3)	0.7925(5)	3.5(2)
C(3)	0.5960(8)	0.2284(4)	0.8442(5)	4.3(2)
C(4)	0.5064(8)	0.2511(4)	0.8900(5)	4.6(2)
C(5)	0.3972(8)	0.2187(4)	0.8873(5)	4.2(2)
C(6)	0.3711(5)	0.1611(3)	0.8361(4)	2.5(1)
C(7)	0.2581(6)	0.1265(3)	0.8414(4)	2.9(2)
C(8)	0.3324(5)	−0.0505(3)	0.5673(4)	2.3(1)
C(9)	0.4111(6)	−0.0764(3)	0.5109(4)	2.7(1)
C(10)	0.3704(7)	−0.1265(3)	0.4540(4)	3.5(2)
C(11)	0.2512(7)	−0.1533(3)	0.4491(4)	3.6(2)
C(12)	0.1730(7)	−0.1291(3)	0.5022(4)	3.6(2)
C(13)	0.2095(5)	−0.0771(3)	0.5615(4)	2.6(1)
C(14)	0.1195(6)	−0.0538(3)	0.6137(4)	2.7(1)
C(15)	0.0994(5)	0.0427(3)	0.8103(4)	2.6(1)
C(16)	0.1280(5)	−0.0026(3)	0.8907(4)	2.7(1)
C(17)	0.1467(6)	−0.0686(4)	0.8875(5)	3.7(2)
C(18)	0.1786(7)	−0.1061(5)	0.9642(7)	5.2(2)
C(19)	0.1939(8)	−0.0747(6)	1.0448(7)	6.1(3)
C(20)	0.1754(8)	−0.0092(6)	1.0511(6)	5.7(3)
C(21)	0.1407(6)	0.0267(4)	0.9741(5)	4.1(2)
C(22)	0.0401(5)	0.0175(3)	0.7185(4)	2.3(1)
C(23)	−0.0834(5)	−0.0195(3)	0.7151(4)	2.3(1)
C(24)	−0.0962(6)	−0.0859(3)	0.7270(4)	3.2(2)
C(25)	−0.2149(7)	−0.1143(4)	0.7240(5)	3.9(2)
C(26)	−0.3216(6)	−0.0751(4)	0.7109(5)	3.7(2)
C(27)	−0.3102(6)	−0.0093(4)	0.7005(5)	3.7(2)
C(28)	−0.1922(6)	0.0186(3)	0.7024(4)	3.1(2)
C(29)	0.3694(7)	−0.0920(4)	0.7821(5)	3.6(2)
C(30)	0.4960(7)	−0.0730(4)	0.9049(5)	4.3(2)
C(31)	0.4585(7)	−0.0167(4)	0.8654(5)	3.9(2)
C(32)	0.4510(9)	−0.1934(3)	0.8678(5)	6.6(2)
C(33)	0.1824(6)	0.1631(3)	0.6375(5)	3.5(2)
C(34)	0.1815(7)	0.1623(4)	0.4959(5)	3.9(2)
C(35)	0.2251(7)	0.1051(4)	0.5309(4)	3.5(2)
C(36)	0.1010(8)	0.2674(3)	0.5582(5)	6.0(2)

a) $B_{eq}=(8/3)\pi^2[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$.

Electrochemistry. Cyclic voltammograms of the cobalt(II) Schiff base complexes containing the phenyl substituents were measured in acetonitrile with Bu_4NBF_4 as a supporting electrolyte. The measurement of [Co{7-Phsal-(*R*)-pn}] was done in dichloromethane because of the low solubility in acetonitrile, and the result was compared with those of [Co{7-Phsal-(*R*)-pen}] and [Co{7-Phsal-(*SS*)-stien}] in dichloromethane. The redox potentials of the Co(III)/Co(II) couple are summarized in Table 5. All complexes show almost reversible one-electron waves. The redox potentials range from −0.11 to 0.20 V vs. Ag/Ag^+ in acetonitrile solutions. The substituents in the N–N chelate moiety have little elec-

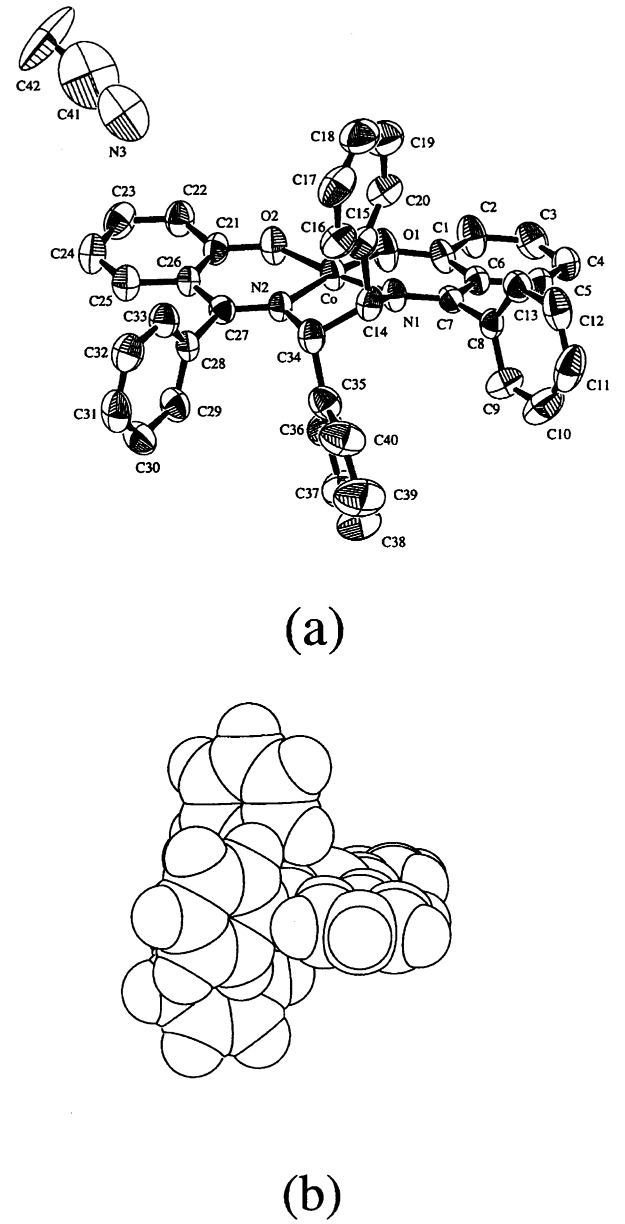
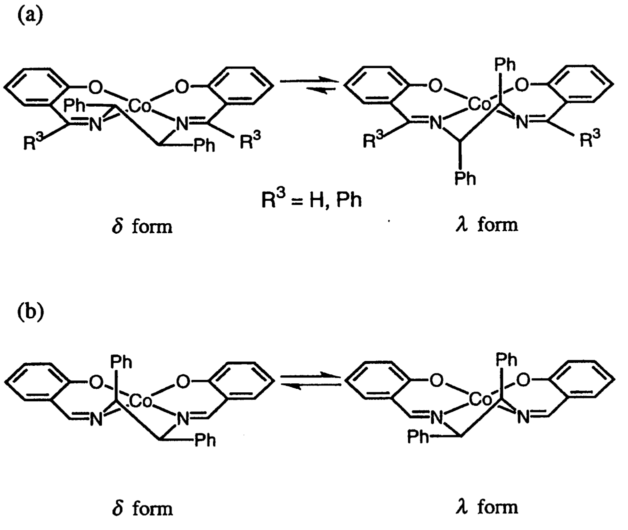


Fig. 1. Molecular structure of [Co{7-Phsal-(*rac*)-stien}]·CH_3CN: (a) ORTEP diagram (50% probability thermal ellipsoids); (b) space-filling diagram.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Co{7-Phsal-(*rac*)-stien}]·CH_3CN (See Fig. 1)

Co–O(1)	1.833(3)	Co–N(1)	1.864(3)
Co–O(2)	1.829(3)	Co–N(2)	1.867(3)
O(1)–Co–O(2)	86.7(1)	O(2)–Co–N(1)	174.9(1)
O(1)–Co–N(1)	93.1(1)	O(2)–Co–N(2)	93.7(1)
O(1)–Co–N(2)	173.1(1)	N(1)–Co–N(2)	87.1(1)



Scheme 1.

Table 5. Redox Potentials for the Co(III)/Co(II) Couple[a)]

	$E^{\circ\prime}$/V (ΔE_p/mV)[b)]
[Co(salen)]	−0.10 (77)
[Co{sal-(*R*)-pen}]	−0.07 (76)
[Co{sal-(*SS*)-stien}]	−0.05 (80)
[Co{sal-(*meso*)-stien}]	0.07 (76)
[Co(7-Phsalen)]	−0.11 (81)
[Co{7-Phsal-(*R*)-pen}]	0.01 (73), 0.36 (84)[c)]
[Co{7-Phsal-(*SS*)-stien}]	0.20 (73), 0.53 (89)[c)]
[Co{7-Phsal-(*R*)-pn}]	0.34 (84)[c)]

a) Cyclic voltammograms were measured in CH_3CN with Bu_4NBF_4 (0.1 M) as a supporting electrolyte; scan rate is 0.1 V s^{-1}; all $E^{\circ\prime}$ values are given vs. Ag/Ag^+. b) $E^{\circ\prime}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = \Delta E_{pa} - \Delta E_{pc}$. c) Measured in CH_2Cl_2 with Bu_4NBF_4 (0.1 M) as a supporting electrolyte.

tronic effect on the Co(III)/Co(II) couple as shown by copper Schiff base complexes.[24)] In addition, the substitution of H on the azomethine carbon atoms (R^3) for C_6H_5 gives only a small electronic contribution because [Co(salen)] and [Co(7-Phsalen)] give closely similar $E^{\circ\prime}$ values (−0.10 and −0.11 V, respectively). Therefore, the extensive range of the redox potentials for these complexes is attributed to steric effect.

First, as the most obvious examples, we select the three complexes, [Co{sal-(*SS*)-stien}], [Co{sal-(*meso*)-stien}], and [Co{7-Phsal-(*SS*)-stien}]. [Co{sal-(*SS*)-stien}] and [Co{sal-(*meso*)-stien}] are diastereomers, and the electronic contributions of the two phenyl groups (R^1 and R^2) in the N–N chelate moiety should be the same. For [Co{7-Phsal-(*SS*)-stien}], only a small electronic effect is expected from the phenyl groups at the 7-positions. However, the redox potentials of these complexes in acetonitrile are −0.05, 0.07, and 0.20 V vs. Ag/Ag^+, respectively.

The [Co{sal-(*meso*)-stien}] complex has one axially disposed phenyl group irrespective of the conformation (λ or δ *gauche*) of the N–N chelate ring (Scheme 1b). The axial phenyl conformation is markedly destabilized by an interaction between the phenyl group and the apical donors in the corresponding cobalt(III) complex, since cobalt(III) complexes have a strong tendency to take a 6-coordinate octahedral structure. Square planar cobalt(II) complexes interact weakly with donors in the apical positions in solutions.

Thus, repulsion is significant only for the oxidized form of the complex. In the [Co{sal-(*SS*)-stien}] complex, the phenyl groups (R^1 and R^2) take predominantly axial positions in the λ *gauche* conformation (Scheme 1a). When the complex is oxidized to cobalt(III), the conformation of the central chelate ring can change to the δ form to reduce the interaction between the phenyl groups and the apical donors. Neither the cobalt(II) nor the cobalt(III) complex of sal-(*SS*)-stien involves a severe steric interaction. Therefore, the trivalent state for the sal-(*meso*)-stien complex is destabilized compared with that for the sal-(*SS*)-stien complex and causes a 120 mV increase in $E^{\circ\prime}$ for the Co(III)/Co(II) couple from -0.05 to 0.07 V. It has been reported that the *t*-butyl groups on the aromaitc rings of the salen ligand in [Co(salen)] derivatives make the redox potential of the Co(III)/Co(II) couple in DMF more positive, indicating the steric repulsions with solvent molecules.[25] In our case, the anion of the supporting electrolyte also serves as the apical ligand, because on using Bu_4NCl instead of Bu_4NBF_4, the $E^{\circ\prime}$ value for [Co{sal-(*SS*)-stien}] changes from -0.05 to -0.45 V.

Next, we compare [Co{7-Phsal-(*SS*)-stien}] with [Co{sal-(*SS*)-stien}]. One should note that the conformational change between λ and δ is difficult in [Co{7-Phsal-(*SS*)-stien}] because of steric interaction between the phenyl groups on the N–N chelate ring and the phenyl groups on the azomethine carbon atom (R^3). The two axially disposed phenyl groups on the N–N chelate ring more effectively obstruct the approach of the ligands to form a 6-coordinate octahedral structure. Therefore, the $E^{\circ\prime}$ value of [Co{7-Phsal-(*SS*)-stien}] is more positive than that of [Co{sal-(*SS*)-stien}] by 250 mV.

The redox potentials of the [Co{7-Phsal-(*R*)-pen}] and [Co{sal-(*R*)-pen}] complexes are similarly accounted for. However, the difference in the $E^{\circ\prime}$ values (80 mV) of these complexes is smaller than that between [Co{Phsal-(*SS*)-stien}] and [Co{sal-(*SS*)-stien}] (250 mV). An apparent factor is the decrease in the number of the axially disposed phenyl groups. Moreover, considering the difference between 80 and 250 mV, the phenyl groups of [Co{7-Phsal-(*SS*)-stien}] may be more strongly fixed to the axial positions than that of [Co{7-Phsal-(*R*)-pen}]. The behavior of the phenyl groups on the N–N chelate moiety can be more clearly demonstrated and visualized by the examination of the cobalt(III) complexes corresponding to [Co^{II}(Schiff base)].

The cobalt(III) Schiff base complexes were prepared in the presence of an additional ligand such as imidazole and 1-methylimidazole under aerobic conditions. However, the [Co{7-Phsal-(*SS*)-stien}] complex was not oxidized under the same conditions. This fact reflects that the [Co{7-Phsal-(*SS*)-stien}] complex has the most positive $E^{\circ\prime}$ value of all the complexes. To elucidate the characteristics of the phenyl group, the [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]ClO_4 and [Co{sal-(*R*)-pn}$(Meim)_2$]ClO_4 complexes, containing a methyl group on the N–N chelate moiety, were prepared and compared with the (*R*)-pen analogues; i.e., the differences between the phenyl–phenyl and methyl–phenyl interactions were examined.

Structure of [Co{sal-(*meso*)-stien}$(Meim)_2$]ClO_4. Figure 2 shows a perspective view of the complex cation, [Co{sal-(*meso*)-stien}$(Meim)_2$]$^+$. Selected bond distances and angles are given in Table 6. The cobalt(III) ion is coordinated by the tetradentate Schiff base ligand and two 1-methylimidazole ligands in an octahedral environment. The sal-(*meso*)-stien anion forms the N_2O_2 equatorial plane, and 1-methylimidazole molecules occupy the axial positions. Although the electrochemical data for [Co{sal-(*meso*)-stien}] show the repulsive interaction between the phenyl group and the axial ligand, the geometric data around the cobalt center are comparable to those of the analogues.[26]

The two phenyl groups at the N–N chelate moiety take a different orientation. One phenyl group is in an axial position and the other equatorial. The axial phenyl group is almost parallel with the 1-methylimidazole ligand to reduce the steric repulsion. However, a slight deviation is caused by the repulsion with the adjacent equatorial phenyl group. The dihedral angle between the least-squares planes of these axial aromatic rings is 29.6°.

CD, Absorption, and ^{1}H NMR Spectra of Cobalt(III) Schiff Base Complexes. Figures 3 and 4 show the CD and absorption spectra of the cobalt(III) Schiff base com-

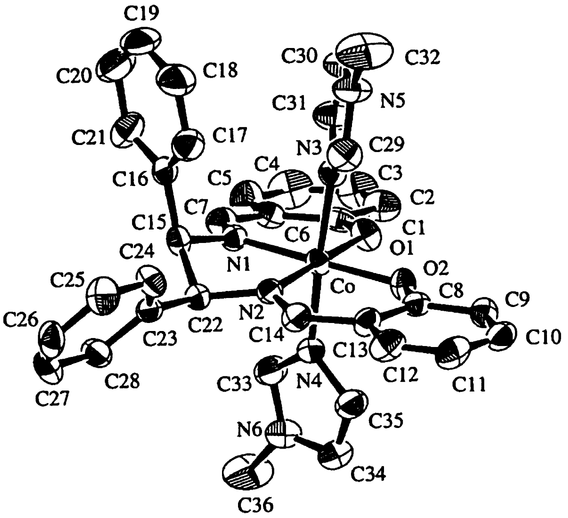


Fig. 2. ORTEP diagram of [Co{sal-(*meso*)-stien}$(Meim)_2$]$^+$ (50% probability thermal ellipsoids).

Table 6. Selected Bond Lengths (Å) and Angles (deg) for [Co{sal-(*meso*)-stien}$(Meim)_2$]ClO_4 (See Fig. 2)

Co–O(1)	1.904(4)	Co–N(2)	1.918(4)
Co–O(2)	1.892(4)	Co–N(3)	1.946(4)
Co–N(1)	1.888(4)	Co–N(4)	1.967(4)
O(1)–Co–O(2)	85.1(2)	O(2)–Co–N(4)	89.3(2)
O(1)–Co–N(1)	94.6(2)	N(1)–Co–N(2)	85.2(2)
O(1)–Co–N(2)	178.3(2)	N(1)–Co–N(3)	91.1(2)
O(1)–Co–N(3)	88.0(2)	N(1)–Co–N(4)	91.3(2)
O(1)–Co–N(4)	88.5(2)	N(2)–Co–N(3)	93.7(2)
O(2)–Co–N(1)	179.3(2)	N(2)–Co–N(4)	89.8(2)
O(2)–Co–N(2)	95.1(2)	N(3)–Co–N(4)	175.9(2)
O(2)–Co–N(3)	88.2(2)		

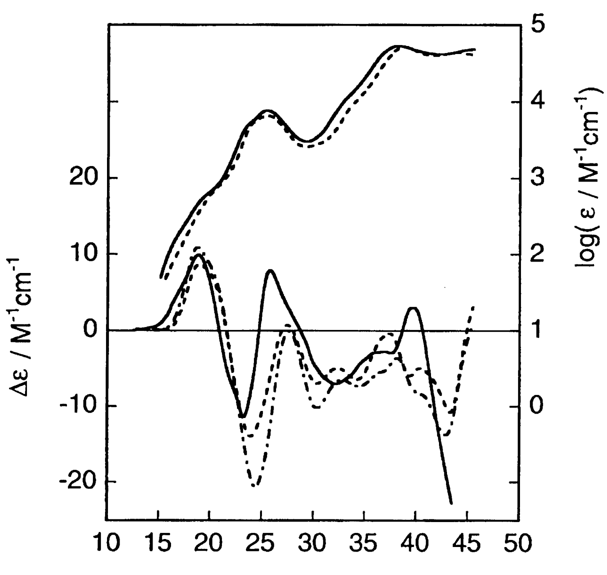


Fig. 3. CD and absorption spectra of $[Co\{7\text{-}Phsal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ (——) and $[Co\{sal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ (- - -) in acetonitrile and CD spectrum of $[Co\{sal\text{-}(RR)\text{-}chxn\}(Meim)_2]ClO_4$ (– • –) in acetonitrile.

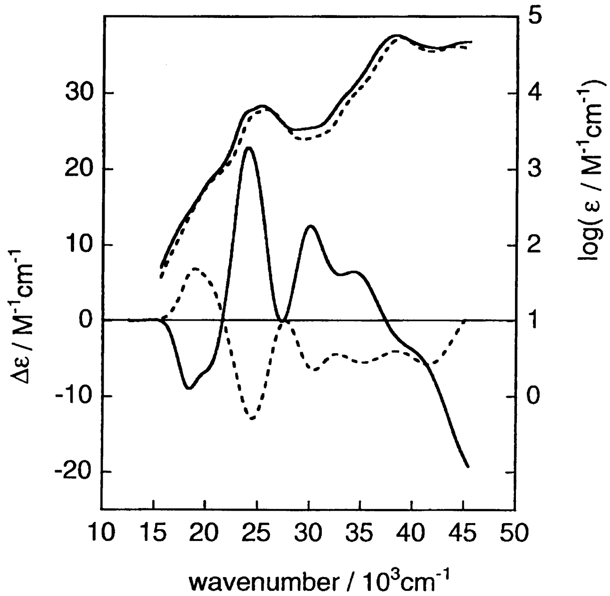
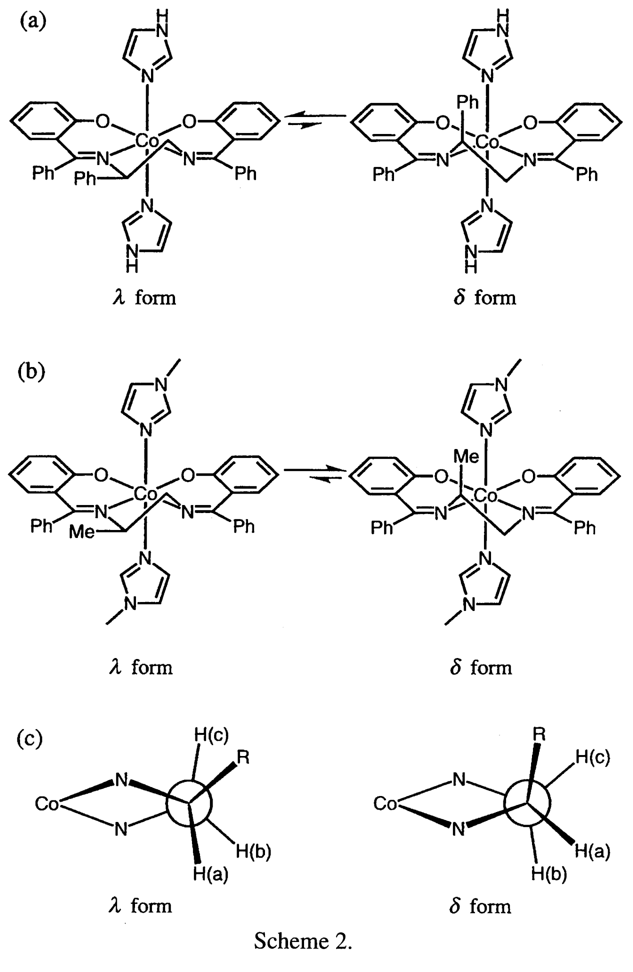


Fig. 4. CD and absorption spectra of $[Co\{7\text{-}Phsal\text{-}(R)\text{-}pn\}(Meim)_2]ClO_4$ (——) and $[Co\{sal\text{-}(R)\text{-}pn\}(Meim)_2]ClO_4$ (- - -) in acetonitrile.

plexes containing the axial, 1-methylimidazole or imidazole ligands, in acetonitrile. The CD spectra of the various metal complexes containing Schiff base ligands have been extensively investigated.[23] The relationship between the CD spectral pattern and the conformation of the central chelate ring has been well established. The absorption in the region of 16000—22000 cm^{-1} is assigned to the d–d transition. The higher energy transition band (22000—27000 cm^{-1}) can be assigned as the charge transfer transitions.

The CD spectrum of $[Co\{sal\text{-}(RR)\text{-}chxn\}(Meim)_2]ClO_4$ is represented in Fig. 3. The sign of the d–d transition band is positive, and the higher energy transition (22000—27000 cm^{-1}) indicates a negative CD band. In this complex, the conformation of the N–N chelate moiety is fixed to a λ *gauche* form because of the fused cyclohexane ring.

On the other hand, for the $[Co\{7\text{-}Phsal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ and $[Co\{sal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ complexes, two conformations (*δ gauche* and *λ gauche*) are possible. Figure 3 shows the CD spectra of these complexes, and the d–d transition bands represent the same positive sign as that of $[Co\{sal\text{-}(RR)\text{-}chxn\}(Meim)_2]ClO_4$. Thus the dominant conformation of $[Co\{7\text{-}Phsal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ and $[Co\{sal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ is *λ gauche*, and the phenyl group is in the equatorial position (Scheme 2a). The assignment of $[Co\{sal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ is in agreement with the structure of $[Co\{sal\text{-}(rac)\text{-}pen\}(py)_2]^+$ determined by X-ray analysis.[26] In $[Co\{7\text{-}Phsal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$, the phenyl group on the central chelate ring repulsively interacts with the axial imidazole ligand and the phenyl group on the azomethine carbon atom. The *λ gauche* conformation of $[Co\{7\text{-}Phsal\text{-}(R)\text{-}pen\}(im)_2]ClO_4$ suggests that the repulsion with the axial ligand is larger than that with the 7-positioned phenyl group. In general, aromatic rings are oriented parallel to each other to reduce the steric repulsion. In the *λ gauche* conformation, the equatorially disposed phenyl group on the central chelate ring should be parallel to the 7-positioned



Scheme 2.

phenyl group. However, in the δ *gauche* conformation, if the axially disposed phenyl group is oriented parallel to the axial imidazole ligand, the steric repulsion can be similarly reduced. Probably, such a conformation generates another repulsive interaction between the phenyl group (R^1) and the nearby 7-positioned phenyl group (R^3). This can be examined by the complex with a methyl group instead of the phenyl group on the central chelate ring, The axial methyl group, which is small and spherical, will not interact with the 7-positioned phenyl group.

Figure 4 shows the CD spectra of the [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]ClO_4 and [Co{sal-(*R*)-pn}$(Meim)_2$]ClO_4 complexes. The CD pattern for [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]-ClO_4 is opposite to those for [Co{sal-(*R*)-pn}$(Meim)_2$]ClO_4 and [Co{sal-(*RR*)-chxn}$(Meim)_2$]ClO_4. Thus, the dominant conformation of [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]ClO_4 is δ *gauche*, and the methyl group is in the axial position (Scheme 2b). This conformation is different from that of [Co{7-Phsal-(*R*)-pen}$(im)_2$]ClO_4. These assignments are supported by the ^{1}H NMR spectra which were obtained in acetonitrile-d_3. The chemical shifts and coupling constants of the central chelate ring are as follows: [Co{7-Phsal-(*R*)-pen}$(im)_2$]ClO_4, δ_a=5.30, δ_b=3.78, δ_c=3.37, J_{ab}=6.6 Hz, J_{ac}=10.2 Hz, J_{bc}=14.5 Hz; [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]-ClO_4, δ_a=4.09, δ_b=3.42, δ_c=3.15, J_{ab}=6.6 Hz, J_{ac}=1.7 Hz, J_{bc}=15.2 Hz. The meanings of the subscripts are represented in Scheme 2c. On the basis of Karplus equations, the large J_{ac} value of [Co{7-Phsal-(*R*)-pen}$(im)_2$]ClO_4 indicates that this complex takes a λ *gauche* form, while the small J_{ac} value of [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]ClO_4 indicates a δ *gauche* form.[27,28] Obviously, in [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]ClO_4, the repulsion of the methyl group with the 7-positioned phenyl group is larger than that with the axial ligand. The situation is different in [Co{7-Phsal-(*R*)-pen}$(im)_2$]ClO_4. As a result, the methyl group of [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]ClO_4 favors the axial position rather than does the phenyl group of [Co{7-Phsal-(*R*)-pen}$(im)_2$]ClO_4. The redox potentials of [Co{7-Phsal-(*R*)-pen}] and [Co{7-Phsal-(*R*)-pn}] in CH_2Cl_2 are 0.36 and 0.34 V, respectively; we therefore presume that the repulsive interactions in [Co{7-Phsal-(*R*)-pen}$(im)_2$]-ClO_4 and [Co{7-Phsal-(*R*)-pn}$(Meim)_2$]ClO_4 are almost the same. In the crystal structure of $[Co(salcppn)(py)_2]^+$, where salcppn is *N*,*N*′-2-(*p*-chlorophenyl)propane-1,2-bis(salicylideneaminate) and does not include the 7-positioned phenyl group, the *p*-chlorophenyl group is in the axial position and the methyl group is in the equatorial position.[26] That is, although the phenyl–phenyl interaction and the methyl–phenyl interaction are similar in terms of the extent of the steric repulsion, the former is more sensitive to the orientation of the phenyl group.

In conclusion, two steric factors affect the redox potential of the Co(III)/Co(II) couple for the [Co(Schiff base)] complexes. One is the repulsive interaction of the substituents on the N–N chelate ring with the 7-positioned phenyl groups; the other is that with the additional axial ligands. In both factors, the orientation of the phenyl group is important. In [Co{7-Phsal-(*SS*)-stien}], two phenyl groups on the N–N chelate ring are crowded out from the equatorial positions. However, in the axial positions, these phenyl groups cannot dodge the approaching donors to axial sites because of the 7-positioned phenyl groups. Inspection of the space-filling diagram of [Co{7-Phsal-(*rac*)-stien}] shows that the two axially disposed phenyl groups cannot rotate to accommodate the axial ligands (Fig. 1b). Thus, this complex is the most difficult to oxidize among the complexes used in this study.

The present work was supported by Grants-in-Aid for Scientific Research Nos. 05403009, 06640720, and 07640753 from the Ministry of Education, Science, Sports and Culture.

References

1) E. C. Niederhoffer, J. H. Timmons, and A. E. Martell, *Chem. Rev.*, **84**, 137 (1984).

2) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).

3) K. Nakajima, K. Kojima, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 2620 (1990).

4) E. N. Jacobsen, W. Zhang, and M. L. Güler, *J. Am. Chem. Soc.*, **113**, 6703 (1991).

5) B. Bosnich and N. K. Roberts, *Adv. Chem. Ser.*, **196**, 337 (1982).

6) J. M. Hawkins and K. B. Sharpless, *Tetrahedron Lett.*, **28**, 2825 (1987).

7) M. Hirotsu, M. Kojima, K. Nakajima, S. Kashino, and Y. Yoshikawa, *Chem. Lett.*, **1994**, 2183.

8) K. Saigo, N. Kubota, S. Takebayashi, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **59**, 931 (1986).

9) H. Irving and R. M. Parkins, *J. Inorg. Nucl. Chem.*, **27**, 270 (1965).

10) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 2691 (1981).

11) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959); "Shin-Zikken Kagaku Koza," Maruzen, Tokyo (1977), Vol. 8, p. 1429.

12) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1429 (1965).

13) M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazz. Chim. Ital.*, **102**, 855 (1972).

14) B. O. West, *J. Chem. Soc.*, **1954**, 395.

15) C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, **1973**, 754.

16) E. G. Samsel and J. K. Kochi, *J. Am. Chem. Soc.*, **108**, 4790 (1986).

17) C. J. Hipp and W. A. Baker, Jr., *J. Am. Chem. Soc.*, **92**, 792 (1970).

18) "TEXSAN: Single Crystal Structure Analysis Software, Version 1.6," Molecular Structure Corp., The Woodlands, TX 77381 (1993).

19) PATTY: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, and C. Smykalla, "The DIRDIF Program System," Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1992).

20) SIR-88: M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, and D. Viterbo, *J. Appl. Crystallogr.*, **22**, 389 (1989).

21) M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc.*,

Dalton Trans., **1973**, 419.

22) W. Hiller, A. Nishinaga, T. Tsutsui, and A. Rieker, *Acta Crystallogr., Sect. C*, **C49**, 1357 (1993).

23) A. Pasini, M. Gullotti, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, **1977**, 346.

24) S. Maeda, M. Nakamura, T. Shinmyozu, H. Ōkawa, and S. Kida, *Mem. Fac. Sci. Kyusyu Univ., Ser. C*, **15**, 71 (1985).

25) A. Nishinaga, K. Tajima, B. Speiser, E. Eichhorn, A. Rieker, H. Ohya-Nishiguchi, and K. Ishizu, *Chem. Lett.*, **1991**, 1403.

26) E. Kitaura, Y. Nishida, H. Ōkawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1987**, 3055.

27) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

28) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 3184 (1969).