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Manganese(III) Complexes Containing Optically Active Tetradentate Schiff Base Ligands. Effect of Phenyl Substituents

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Manganese(III) complexes containing optically active tetradentate Schiff Base ligands have been prepared. The crystal structure of the complex [Mn{7-Phsal-(*SS*)-stien}Cl]·CH_2Cl_2, where 7-Phsal-(*SS*)-stien is the dianion of the product formed from the condensation of 2 mol of 2-hydroxybenzophenone and 1 mol of (*S,S*)-1,2-diphenylethylenediamine, has been established by the X-ray method. Crystal data: monoclinic, $P2_1$, a = 16.796(2) Å, b = 14.366(2) Å, c = 15.266(2) Å, β = 101.84(1)°, V = 3605.2(9) Å^3, Z = 4. The structure was refined to R = 0.058 and R_w = 0.063. The coordination polyhedron is a distorted square pyramid, the Schiff base ligand occupying the basal sites and the chloride the apical site. The two phenyl groups of the diamine moiety are in the axial positions, and the central chelate ring of the Schiff base ligand assumes a λ gauche conformation. On the basis of the circular dichroism spectral data for [Mn{7-Phsal-(*SS*)-stien}Cl] and related complexes, the preferred conformation of the central chelate ring in solution is assigned. The effects of phenyl substituents on the Mn(III)/Mn(II) and Mn(IV)/Mn(III) redox potentials are discussed in terms of the conformational behavior of the Schiff base ligands. The manganese(III) complexes with axial phenyl groups offer great opposition to oxidation.

Introduction

In the previous papers, we reported that oxovanadium(IV) and titanium(IV) complexes containing optically active tetradentate Schiff base ligands catalyze the asymmetric oxidation of methyl phenyl sulfide (ee ≤ 60%).[1−4] Very recently, the enantioselective epoxidation of unfunctionalized olefins catalyzed by related manganese(III) complexes was reported by two groups.[5,6] In order to elucidate the asymmetric catalytic reaction mechanism and to improve the enantioselectivity, it is important to have detailed knowledge regarding the conformation of the ligands in the complex catalysts. It has been shown that the enantioselectivity is closely related to the conformational chirality of the complex catalysts.[3,4] Moreover, in asymmetric catalytic reactions, the importance of the orientation of the phenyl groups has been pointed out.[7,8] Thus, it is relevant to study the steric and electronic effects of the phenyl substituents of Schiff base ligands.

Here, we report the preparation and characterization of manganese(III) complexes containing optically active Schiff base ligands with phenyl substituents, paying special attention to the orientation of the phenyl substituents and their effects on such properties as redox potentials. The crystal structure of a manganese(III) complex with the Schiff base ligand derived from 2-hydroxybenzophenone and (*S,S*)-1,2-diphenylethylenediamine is also reported.

Experimental Section

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

[Mn{7-Phsal-(*SS*)-stien}Cl]·CH_2Cl_2. To a suspension of H_2{7-Phsal-(*SS*)-stien} (0.57 g, 1 mmol) in ethanol (50 cm^3) was added $MnCl_2·4H_2O$ (0.99 g, 5 mmol) with stirring. A 0.5 M (1 M = 1 mol dm^{-3}) solution (2 cm^3) of NaOH in ethanol was added dropwise to the mixture, and the resulting dark brown solution was stirred in air for 3 h to form the Mn(III) chelate. A dark brown precipitate was collected by filtration and washed with ethanol and then with water. The product was dried over P_4O_{10} under vacuum to yield 0.65 g (92%) of [Mn{7-Phsal-(*SS*)-stien}Cl]·C_2H_5OH. Anal. Calcd for $C_{42}H_{36}ClMnN_2O_3$: C, 71.33; H, 5.13; N, 3.96. Found: C, 71.07; H, 4.77; N, 3.99.

This complex was dissolved in dichloromethane, and the solution was filtered. To the filtrate was added ethanol, and the resulting solution was left in a refrigerator to give prismatic crystals. The overall yield was 78%. Anal. Calcd for $C_{41}H_{32}Cl_3MnN_2O_2$ = [Mn{7-Phsal-(*SS*)-stien}Cl]·CH_2Cl_2: C, 66.01; H, 4.32; N, 3.76. Found: C, 66.35; H, 4.29; N, 3.55. A piece of the crystal was used for the X-ray crystal structure determination.

[Mn{7-Phsal-(*SS*)-stien}I]. To a solution of H_2{7-Phsal-(*SS*)-stien} (0.286 g, 0.5 mmol) in dichloromethane (5 cm^3) was added an ethanol solution (5 cm^3) of $Mn(CH_3COO)_2·4H_2O$ (0.245 g, 1 mmol) with stirring, and the resulting dark brown solution was stirred for 1 h. After filtration, an ethanol solution (5 cm^3) of NaI (0.225 g, 1.5 mmol) was added, and the mixture was stirred for additional 3.5 h. The resulting dark brown precipitate was isolated by filtration and washed with cold

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(1) Nakajima, K.; Kojima, M.; Fujita, J. *Chem. Lett.* **1986**, 1483.

(2) Nakajima, K.; Sasaki, C.; Kojima, M.; Aoyama, T.; Ohba, S.; Saito, Y.; Fujita, J. *Chem. Lett.* **1987**, 2189.

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

(4) Sasaki, C.; Nakajima, K.; Kojima, M.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1318.

(5) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801.

(6) Irie, R.; Noda, K.; Ito, Y.; Matsumoto. N.; Katsuki, T. *Tetrahedron Lett.* **1990**, *31*, 7345.

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

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

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

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

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

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

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

(14) Boucher, L. J. *J. Inorg. Nucl. Chem.* **1974**, *36*, 531.

(15) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063.

(16) Baudry, M.; Etienne, S.; Bruce, A.; Palucki, M.; Jacobsen, E.; Malfroy, B. *Biochem. Biophys. Res. Commun.* **1993**, *192*, 964.

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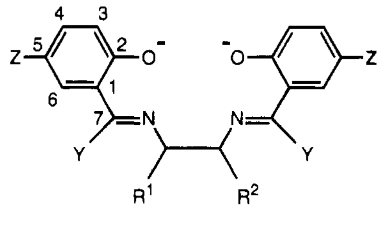
Chart 1



R^1	R^2	Y	Z	
H	H	H	H	salen
Ph	H	H	H	sal-(*R*)-pen
Ph	Ph	H	H	sal-(*SS*)-stien
Ph	Ph	H	H	sal-(*meso*)-stien
H	H	Ph	H	7-Phsalen
Ph	H	Ph	H	7-Phsal-(*R*)-pen
Ph	Ph	Ph	H	7-Phsal-(*SS*)-stien
(CH$_2$)$_4$		H	H	sal-(*RR*)-chxn
H	H	Me	Me	5-Me-7-Mesalen
Me	H	H	*s*-Bu	5-*s*-Busal-(*S*)-pn

dichloromethane and then with ethanol. Yield: 0.043 g (11%). Anal. Calcd for $C_{40}H_{30}IMnN_2O_2$: C, 63.84; H, 4.02; N, 3.72. Found: C, 64.23; H, 3.90; N, 3.52.

[Mn{7-Phsal-(*SS*)-stien}]ClO$_4$. This dark brown complex was prepared by the same method as for [Mn{7-Phsal-(*SS*)-stien}Cl] except that $Mn(ClO_4)_2{\cdot}6H_2O$ was used instead of $MnCl_2{\cdot}4H_2O$. Yield: 64%. Anal. Calcd for $C_{40}H_{30}ClMnN_2O_6$: C, 66.26; H, 4.17; N, 3.86. Found: C, 66.23; H, 4.05; N, 3.66.

[Mn{7-Phsal-(*R*)-pen}Cl]. To a solution of H_2{7-Phsal-(*R*)-pen} (0.349 g, 0.7 mmol) in dichloromethane (7 cm^3) was added a solution of $MnCl_2{\cdot}4H_2O$ (0.277 g, 1.4 mmol) in ethanol (14 cm^3). A 0.5 M solution (1.4 cm^3) of NaOH in ethanol was added to the mixture, and the resulting dark brown solution was stirred for 6 h. A dark brown precipitate was collected by filtration and washed with ethanol. The crude product was recrystallized from dichloromethane–ethanol. Yield: 0.204 g (50%). Anal. Calcd for $C_{34}H_{26}ClMnN_2O_2$: C, 69.81; H, 4.48; N, 4.79. Found: C, 69.87; H, 4.70; N, 4.76.

[Mn{sal-(*meso*)-stien}Cl]·1.5H$_2$O. The same procedure as for [Mn{7-Phsal-(*R*)-pen}Cl] was used. Recrystallization was carried out from dichloromethane–ethanol. Yield: 48%. Anal. Calcd for $C_{28}H_{25}ClMnN_2O_{3.5}$: C, 62.75; H, 4.70; N, 5.23. Found: C, 62.29; H, 4.57; N, 4.96.

[Mn(7-Phsalen)Cl]·C$_2$H$_5$OH·H$_2$O. The same procedure as for [Mn{7-Phsal-(*R*)-pen}Cl] was used. Recrystallization was carried out from dichloromethane–ethanol. Yield: 79%. Anal. Calcd for $C_{30}H_{30}ClMnN_2O_4$: C, 62.89; H, 5.28; N, 4.89. Found: C, 63.13; H, 5.56; N, 4.53.

[Mn{sal-(*R*)-pen}Cl]. A racemic compound of this complex has already been prepared.[17] The optically active complex was synthesized by another procedure. To a hot solution of H_2{sal-(*R*)-pen} (0.343 g, 1 mmol) in ethanol (10 cm^3) was added an ethanol solution (10 cm^3) of $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.490 g, 2 mmol) with stirring, and the resulting dark brown solution was refluxed for 1 h. An ethanol solution (10 cm^3) of LiCl (0.128 g, 3 mmol) was then added, and the mixture was refluxed for additional 0.5 h. After filtration, the reaction mixture was cooled, and the resulting dark brown precipitate was isolated by filtration and washed with ethanol. The crude product was recrystallized from dichloromethane–ethanol (2:1). Yield: 0.261 g (61%). Anal. Calcd for $C_{22}H_{18}ClMnN_2O_2$: C, 61.05; H, 4.19; N, 6.47. Found: C, 60.84; H, 4.29; N, 6.41.

Physical Measurements. CD spectra were recorded on a JASCO J-500A or a J-720 spectropolarimeter. Visible–UV absorption spectra were recorded with a JASCO Ubest-30 or a Hitachi U-3400 spectrophotometer. Cyclic voltammetric measurements were performed on acetonitrile solutions containing Bu_4NBF_4 (0.1 M) as a supporting electrolyte using a FUSO HECS 321B potential sweep unit 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$^+$. Rotating disk electrode voltammetric measurements were also performed on the same solutions at a rotation rate of 2000 rpm and a scan rate of 0.01 V s^{-1}. High-performance liquid chromatography analysis was performed with a CrestPac C18S column for the analysis of [VO{sal-(*R*)-pen}].[18] The sample was eluted with CH_3CN-H_2O (42:58 v/v) at a flow rate of 1.0 cm^3 min^{-1}, and the isomers were detected at 260 nm.

Table 1. Crystallographic Data for [Mn{7-Phsal-(*SS*)-stien}Cl]·CH$_2$Cl$_2$

formula	$C_{41}H_{32}Cl_3MnN_2O_2$	V, Å^3	3605.2(9)
fw	745.98	Z	4
crystal system	monoclinic	D_{calcd}, g cm^{-3}	1.37
space group	$P2_1$ (No. 4)	λ, Å	0.710 73
a, Å	16.796(2)	μ(Mo Kα), cm^{-1}	6.12
b, Å	14.366(2)	R [a]	0.058
c, Å	15.266(2)	R_w [b]	0.063
β, deg	101.84(1)		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma_{count}^2 + (0.015|F_o|)^2]^{-1}$.

Collection and Reduction of X-ray Data for [Mn{7-Phsal-(*SS*)-stien}Cl]·CH$_2$Cl$_2$. A prismatic brown crystal of approximate dimensions of 0.2 × 0.2 × 0.5 mm^3 was used for the measurement. The crystal data are given in Table 1. Diffraction data were collected on a Rigaku AFC-5S diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) and a $\theta-2\theta$ scan mode (scan range (1.21 + 0.50 tan θ)°). Lattice parameters were obtained by least-squares refinement of the angular settings of 25 reflections in the range $25° < 2\theta < 29°$. Crystallographic parameters are given in Table 1. Three standard reflections were monitored every 150 reflections and showed no significant variation during the data collection. All the calculations were carried out using Xtal3.2. The location of manganese was determined by direct methods using SHELXS-86,[19] and the other non-hydrogen atoms were found by the usual Fourier methods. Structure determination and refinement were carried out using 7452 unique reflections with $|F_o| > 6\sigma(|F_o|)$. The final least-squares refinement converged to $R = 0.058$ and $R_w = 0.063$. The atomic parameters of non-hydrogen atoms are listed in Table 2.

Results and Discussion

Crystal Structure of [Mn{7-Phsal-(*SS*)-stien}Cl]·CH$_2$Cl$_2$. The X-ray analysis of [Mn{7-Phsal-(*SS*)-stien}Cl]·CH$_2$Cl$_2$ disclosed that two independent molecules, **A** and **B**, exist in a unit cell. Selected bond distances, bond angles, and the other geometric data are listed in Table 3. Figure 1 shows the perspective views. The coordination geometry around each manganese atom can be described as a distorted square pyramid. The tetradentate Schiff base ligand lies in the equatorial plane, and the chloro ligand occupies the apical position. The central N–N chelate ring of the 7-Phsal-(*SS*)-stien ligand takes a λ gauche conformation, and the phenyl groups are axially oriented to reduce the steric interactions with the phenyl substituents on the 7-positions. However, one phenyl group in the N–N chelate ring cannot occupy the fully axial position because of the steric repulsion between the phenyl group and the chloro ligand. This repulsion is implicated in the two different structures, **A** and **B**. The Mn(1)–Cl(1) bond length (2.391(3) Å) in **A** is longer than Mn(2)–Cl(2) (2.313(3) Å) in **B**, while the dihedral angles of N–C–C–N are 37.4(7)° (**A**) and 45.5(7)° (**B**). Also, the manganese center in each isomer is displaced by 0.387(1) Å

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(17) Nakamura, M.; Shimokawa, S.; Miyanaka, Y.; Huang, H.; Kai, F. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1692.

(18) Pasini, A.; Gullotti, M. *J. Coord. Chem.* **1974**, *3*, 319.

(19) Sheldrick, G. M. SHELXS 86: Program for the Solution of Crystal Structures. University of Göttingen, Germany, 1986.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [Mn{7-Phsal-(*SS*)-stien}Cl]·CH_2Cl_2

atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$	atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$
Mn(1)	0.60187(7)	0.42260	0.94867(8)	0.0386(4)	C(34)	0.6372(4)	0.3413(5)	0.7880(5)	0.036(3)
Mn(2)	0.90387(7)	−0.18632(8)	0.55097(8)	0.0378(4)	C(35)	0.7194(5)	0.3946(5)	0.7858(5)	0.046(3)
Cl(1)	0.4702(1)	0.3839(2)	0.9746(2)	0.070(1)	C(36)	0.7359(5)	0.4821(6)	0.8166(6)	0.058(4)
Cl(2)	1.0249(1)	−0.1547(2)	0.5069(2)	0.0639(9)	C(37)	0.8087(6)	0.5284(6)	0.8109(7)	0.074(4)
Cl(3)	0.2580(2)	0.2225(2)	1.0360(3)	0.139(2)	C(38)	0.8636(6)	0.4911(7)	0.7679(7)	0.076(4)
Cl(4)	0.1731(3)	0.1365(3)	0.8770(3)	0.162(2)	C(39)	0.8495(5)	0.3887(7)	0.7347(7)	0.079(4)
Cl(5)	0.3206(3)	0.1122(3)	0.6059(3)	0.187(3)	C(40)	0.7757(5)	0.3484(6)	0.7439(5)	0.047(3)
Cl(6)	0.2357(2)	−0.0037(3)	0.4673(3)	0.158(2)	C(41)	1.0027(4)	−0.3085(5)	0.7222(5)	0.040(3)
O(11)	0.6651(3)	0.4423(3)	1.0642(3)	0.060(2)	C(42)	0.9724(4)	−0.3590(5)	0.6370(5)	0.039(3)
O(12)	0.5832(3)	0.5485(3)	0.9302(3)	0.050(2)	C(43)	0.9960(5)	−0.4440(5)	0.6257(5)	0.045(3)
O(21)	0.9169(3)	−0.3173(3)	0.5709(4)	0.049(2)	C(44)	1.0487(4)	−0.4911(5)	0.6930(5)	0.043(3)
O(22)	0.8393(3)	−0.2168(4)	0.4404(3)	0.056(2)	C(45)	1.0811(4)	−0.4465(5)	0.7719(6)	0.045(3)
N(11)	0.6577(3)	0.3023(4)	0.9437(4)	0.040(2)	C(46)	1.0559(5)	−0.3634(6)	0.7867(6)	0.052(3)
N(12)	0.5828(3)	0.4088(4)	0.8175(4)	0.033(2)	C(47)	0.9776(4)	−0.2191(5)	0.7427(5)	0.033(3)
N(21)	0.9386(3)	−0.1595(4)	0.6838(4)	0.034(2)	C(48)	0.9959(5)	−0.1907(6)	0.8414(5)	0.050(3)
N(22)	0.8306(3)	−0.0760(4)	0.5556(4)	0.037(2)	C(49)	1.0597(5)	−0.1275(5)	0.8676(6)	0.056(3)
C(1)	0.7177(4)	0.2913(5)	1.1060(5)	0.032(3)	C(50)	1.0730(6)	−0.0983(6)	0.9594(7)	0.086(5)
C(2)	0.7009(4)	0.3867(5)	1.1221(5)	0.040(3)	C(51)	1.0273(6)	−0.1426(7)	1.0185(6)	0.086(5)
C(3)	0.7273(6)	0.4197(7)	1.2123(6)	0.077(4)	C(52)	0.9705(6)	−0.2002(7)	0.9877(7)	0.082(5)
C(4)	0.7695(6)	0.3618(8)	1.2817(6)	0.083(5)	C(53)	0.9497(6)	−0.2332(7)	0.8979(6)	0.083(5)
C(5)	0.7859(5)	0.2661(6)	1.2619(5)	0.053(3)	C(54)	0.9042(4)	−0.0735(5)	0.7137(5)	0.038(3)
C(6)	0.7574(4)	0.2401(5)	1.1757(5)	0.038(3)	C(55)	0.9522(5)	0.0165(5)	0.7085(5)	0.044(3)
C(7)	0.7006(4)	0.2570(5)	1.1066(5)	0.036(3)	C(56)	1.0038(5)	0.0316(6)	0.6496(6)	0.055(3)
C(8)	0.7383(5)	0.1621(5)	0.9996(5)	0.044(3)	C(57)	1.0344(6)	0.1259(7)	0.6438(7)	0.080(5)
C(9)	0.6934(5)	0.0812(5)	1.0001(5)	0.049(3)	C(58)	1.0206(5)	0.1911(6)	0.6979(6)	0.060(4)
C(10)	0.7254(6)	−0.0050(6)	0.9907(6)	0.067(4)	C(59)	0.9734(6)	0.1768(5)	0.7551(6)	0.065(4)
C(11)	0.8023(5)	−0.0115(6)	0.9792(6)	0.068(4)	C(60)	0.9366(5)	0.0898(6)	0.7625(6)	0.056(4)
C(12)	0.8514(5)	0.0663(6)	0.9758(6)	0.063(4)	C(61)	0.7813(4)	−0.0623(5)	0.3995(5)	0.042(3)
C(13)	0.8196(5)	0.1569(5)	0.9866(5)	0.048(3)	C(62)	0.7998(5)	−0.1520(6)	0.3781(5)	0.053(3)
C(14)	0.6529(5)	0.2590(5)	0.8555(5)	0.043(3)	C(63)	0.7741(5)	−0.1865(6)	0.2904(5)	0.055(3)
C(15)	0.5861(5)	0.1863(5)	0.8294(5)	0.043(3)	C(64)	0.7367(6)	−0.1274(6)	0.2241(5)	0.062(4)
C(16)	0.5240(5)	0.1769(6)	0.8720(6)	0.055(3)	C(65)	0.7227(5)	−0.0364(6)	0.2420(6)	0.061(4)
C(17)	0.4679(6)	0.1054(7)	0.8482(7)	0.079(5)	C(66)	0.7419(5)	0.0040(6)	0.3297(5)	0.056(3)
C(18)	0.4774(7)	0.0372(7)	0.7787(8)	0.091(5)	C(67)	0.7921(4)	−0.0264(5)	0.4918(5)	0.032(3)
C(19)	0.5429(6)	0.0521(7)	0.7305(7)	0.081(5)	C(68)	0.7564(5)	0.0642(5)	0.5063(5)	0.042(3)
C(20)	0.6005(6)	0.1269(6)	0.7589(6)	0.072(4)	C(69)	0.8058(5)	0.1418(5)	0.5110(6)	0.056(3)
C(21)	0.5019(4)	0.5489(5)	0.7832(5)	0.037(3)	C(70)	0.7716(5)	0.2294(6)	0.5249(6)	0.064(4)
C(22)	0.5315(4)	0.5860(5)	0.8658(5)	0.038(3)	C(71)	0.6896(6)	0.2365(6)	0.5134(6)	0.072(4)
C(23)	0.5075(5)	0.6851(5)	0.8864(5)	0.043(3)	C(72)	0.6408(6)	0.1555(6)	0.5234(6)	0.067(4)
C(24)	0.4541(5)	0.7310(6)	0.8216(6)	0.061(4)	C(73)	0.6757(5)	0.0663(6)	0.5115(5)	0.059(4)
C(25)	0.4271(5)	0.6927(6)	0.7346(6)	0.060(4)	C(74)	0.8191(4)	−0.0590(5)	0.6518(5)	0.033(3)
C(26)	0.4458(4)	0.5962(5)	0.7144(6)	0.050(3)	C(75)	0.7565(4)	−0.1265(5)	0.6752(5)	0.036(3)
C(27)	0.5325(4)	0.4579(5)	0.7579(5)	0.040(3)	C(76)	0.7395(5)	−0.2139(6)	0.6352(6)	0.066(4)
C(28)	0.5144(4)	0.4293(6)	0.6642(5)	0.042(3)	C(77)	0.6825(6)	−0.2718(7)	0.6650(7)	0.079(5)
C(29)	0.4605(5)	0.3557(6)	0.6395(6)	0.059(4)	C(78)	0.6450(5)	−0.2392(6)	0.7321(6)	0.060(4)
C(30)	0.4409(6)	0.3292(7)	0.5483(7)	0.086(5)	C(79)	0.6631(5)	−0.1650(7)	0.7685(6)	0.070(4)
C(31)	0.4798(6)	0.3638(7)	0.4883(6)	0.076(4)	C(80)	0.7178(5)	−0.0971(6)	0.7395(6)	0.062(4)
C(32)	0.5348(6)	0.4428(7)	0.5099(6)	0.071(4)	C(01)	0.2703(8)	0.1672(9)	0.9430(9)	0.129(7)
C(33)	0.5490(4)	0.4687(6)	0.5995(5)	0.043(3)	C(02)	0.2296(7)	0.0817(8)	0.5473(9)	0.115(6)

^{a} $U_{eq} = {}^1/_3\{\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\boldsymbol{a}_i\boldsymbol{a}_j\}$.

(**A**) or 0.451(1) Å (**B**) toward the apical chloro ligand from the least-squares equatorial plane. Pecoraro and Butler suggest that the chloride ion is required to be approximately 2.7 Å from the N_2O_2 plane.[20] In [Mn(salen)Cl][20] and [Mn(5-Me-7-Mesalen)-Cl],[21] the Mn−Cl bond lengths are 2.461(1) and 2.391(2) Å, while the displacements of Mn are 0.19 and 0.305 Å, respectively. The sums of the Mn−Cl bond length and the displacement for [Mn(salen)Cl] and [Mn(5-Me-7-Mesalen)Cl] are 2.65 and 2.70 Å, respectively. On the other hand, the values for two isomers of [Mn{7-Phsal-(*SS*)-stien}Cl] are 2.78 Å in **A** and 2.76 Å in **B**, slightly longer than the above-mentioned values. The lengthening can be attributed to the steric repulsion between the chloro ligand and the axial phenyl group. The displacement of Mn from the N_2O_2 plane reflects the strain exerted by the ligand structure. Thus, in the [Mn{7-Phsal-(*SS*)-stien}Cl] complex, which contains a sterically hindered ligand, the Mn center is displaced more largely from the equatorial plane than in the other analogues.

CD and Absorption Spectra. The CD and absorption spectra of the Mn(III) Schiff base complexes were measured in dichloromethane, acetonitrile, and methanol solutions (Figures 2−5). The bands in the 14 000−20 000, 20 000−30 000, and 30 000−35 000 cm^{-1} regions can be assigned to the d−d, d−π^* (azomethine), and π−π^* (azomethine) transitions, respectively.[22−24] The remaining higher energy absorption bands may be attributed mainly to the π−π^* transitions within the phenyl rings.[22]

Although the complexes reported in this paper were prepared using diamines with different absolute configurations ((*S*,*S*)-1,2-diphenylethylenediamine, (*R*)-1-phenylethylenediamine, (*R*,*R*)-1,2-cyclohexanediamine), we have chosen to use the mirror images for the CD spectra of the species derived from the last two diamines. This allows us to most easily make significant comparisons between the conformations of these complexes.

The CD spectra of metal complexes containing optically

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(20) Pecoraro, V. L.; Butler, W. M. *Acta Crystallogr.* **1986**, *C42*, 1151.
(21) Oki, A. R.; Hodgson, D. J. *Inorg. Chim. Acta* **1990**, *170*, 65.
(22) Davis, T. S.; Fackler, J. P.; Weeks, M. J. *Inorg. Chem.* **1968**, *7*, 1994.
(23) Boucher, L. J.; Farrell, M. O. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3731.
(24) Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627.

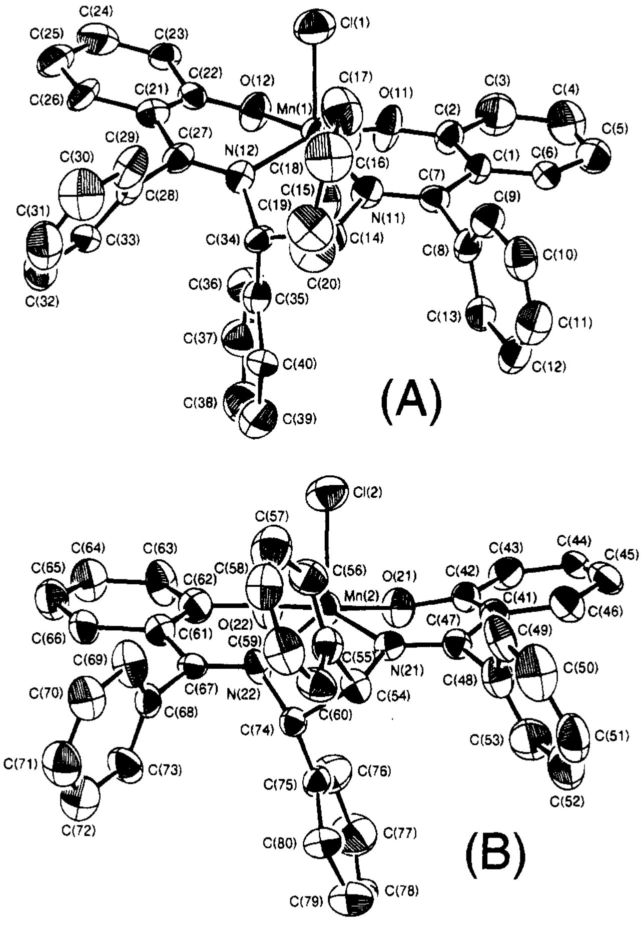


Figure 1. Perspective views of two structures of [Mn{7-Phsal-(*SS*)-stien}Cl].

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), Dihedral Angles (deg), and Distances (Å) from the Least-Squares Basal Plane

Bond Lengths			
Mn(1)-Cl(1)	2.391(3)	Mn(2)-Cl(2)	2.313(3)
Mn(1)-O(11)	1.883(5)	Mn(2)-O(21)	1.912(5)
Mn(1)-O(12)	1.847(5)	Mn(2)-O(22)	1.862(5)
Mn(1)-N(11)	1.976(6)	Mn(2)-N(21)	2.029(6)
Mn(1)-N(12)	1.972(6)	Mn(2)-N(22)	2.017(6)
Bond Angles			
Cl(1)-Mn(1)-O(11)	104.1(2)	Cl(2)-Mn(2)-O(21)	99.2(2)
Cl(1)-Mn(1)-O(12)	96.8(2)	Cl(2)-Mn(2)-O(22)	99.5(2)
Cl(1)-Mn(1)-N(11)	105.4(2)	Cl(2)-Mn(2)-N(21)	99.4(2)
Cl(1)-Mn(1)-N(12)	100.5(2)	Cl(2)-Mn(2)-N(22)	115.8(2)
O(11)-Mn(1)-O(12)	92.4(2)	O(21)-Mn(2)-O(22)	86.5(2)
O(11)-Mn(1)-N(11)	89.2(2)	O(21)-Mn(2)-N(21)	91.6(2)
O(11)-Mn(1)-N(12)	155.3(3)	O(21)-Mn(2)-N(22)	145.0(2)
O(12)-Mn(1)-N(11)	156.6(3)	O(22)-Mn(2)-N(21)	161.0(3)
O(12)-Mn(1)-N(12)	87.5(2)	O(22)-Mn(2)-N(22)	88.3(2)
N(11)-Mn(1)-N(12)	81.5(2)	N(21)-Mn(2)-N(22)	82.4(2)
Dihedral Angles			
N(11)-C(14)-C(34)-N(12)	37.4(7)		
N(21)-C(54)-C(74)-N(22)	45.5(7)		
Distances from the Least-Squares Basal Plane			
Mn(1)	0.387(1)	Mn(2)	0.451(1)

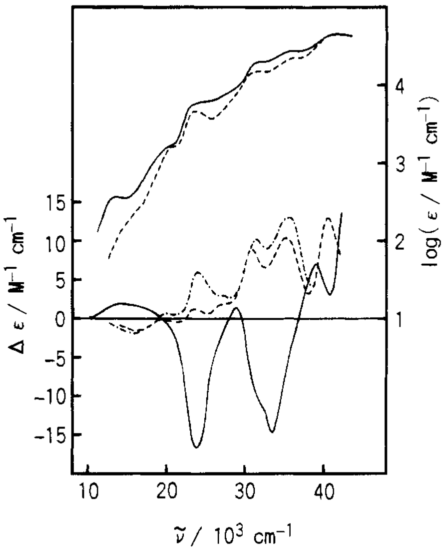
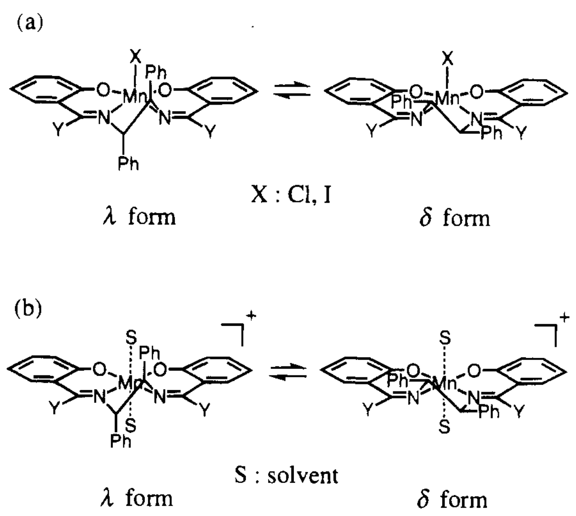


Figure 2. CD and absorption spectra in dichloromethane solution of [Mn{7-Phsal-(*SS*)-stien}Cl] (—) and [Mn{sal-(*SS*)-stien}Cl] (- - -) and CD spectrum in dichloromethane solution of [Mn{sal-(*SS*)-chxn}Cl] (– • –).

Scheme 1



active Schiff base ligands have been extensively studied for complexes with a variety of geometries.[25] The relationship between the CD pattern in the $\pi-\pi^*$(azomethine) band region and the absolute configuration of the metal Schiff base complexes has been well established.[24,25] In the [Mn{sal-(*SS*)-chxn}Cl] complex, the conformation of the central chelate ring is fixed to a δ gauche form, and the $\pi-\pi^*$(azomethine) transition shows a positive CD band (Figure 2). The assignment agrees with that reported by Boucher *et al.*[26,27] The [Mn{sal-(*SS*)-stien}Cl] complex in dichloromethane also shows a positive CD band in the $\pi-\pi^*$(azomethine) transition region (Figure 2), so the conformation of the N−N chelate ring can be assigned to a δ gauche form with the phenyl groups in the equatorial positions (Scheme 1a). This results from the repulsion between the axial chloro ligand and the phenyl group. In square planar complexes such as [Co{sal-(*SS*)-stien}] where no such repulsion exists, the N−N chelate ring has been shown to take a λ gauche conformation with the axially oriented phenyl groups.[25] It is to be noted that [Mn{7-Phsal-(*SS*)-stien}Cl] in dichloromethane exhibits a CD spectrum almost enantiomeric to that of [Mn{sal-(*SS*)-stien}Cl], despite the fact that both complexes have the same parent diamine, (*SS*)-stien (Figure 2). This finding shows that the central chelate ring of [Mn{7-Phsal-(*SS*)-stien}Cl] in solution takes a λ gauche conformation with the axial phenyl groups just as in the solid state and that the steric

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(25) Pasini, A.; Gullotti, M.; Ugo, R. *J. Chem. Soc., Dalton Trans.* **1977**, 346.

(26) Boucher, L. J.; Herrington, D. R. *Inorg. Chem.* **1974**, *13*, 1105.

(27) Boucher, L. J.; Coe, C. G. *Inorg. Chem.* **1976**, *15*, 1334.

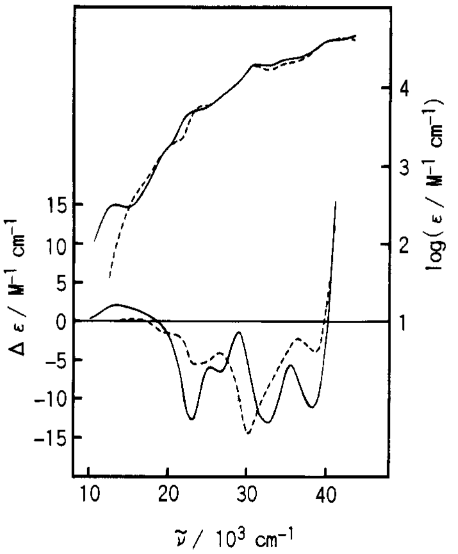


Figure 3. CD and absorption spectra in dichloromethane solution of [Mn{7-Phsal-(*SS*)-stien}I] (—) and [Mn{7-Phsal-(*SS*)-stien}]ClO$_4$ (- - -).

interaction between R and Y seems to play a major role in determining the structure of this complex. In the CD and absorption spectra of [Mn{7-Phsal-(*SS*)-stien}Cl], the d−d transition band shifts to a lower energy (14.2 × 10^3 cm^{-1}, CD; 13.6 × 10^3 cm^{-1}, absorption) than that of [Mn{sal-(*SS*)-stien}-Cl] (16.3 × 10^3 cm^{-1}, CD). [Mn{7-Phsal-(*SS*)-stien}]ClO$_4$ does not show CD appreciably in the same region (Figure 3). The d−d transition of [Mn{7-Phsal-(*SS*)-stien}I] is observed at lower energy (13.7 × 10^3 cm^{-1}, CD; 13.2 × 10^3 cm^{-1}, absorption) than that of [Mn{7-Phsal-(*SS*)-stien}Cl] (Figure 3). However, the difference is regarded as small in comparison with the change in the d−d transition band of [Mn{sal-(*SS*)-stien}Cl]. This result corresponds with the report that the frequency of this d−d transition band for analogues is insensitive to the axial anion.[28] The energy of this d−d transition band should be connected with the steric interaction in [Mn{7-Phsal-(*SS*)-stien}-Cl] and [Mn{7-Phsal-(*SS*)-stien}I]. A more crowded complex usually shows the d−d transition at lower energy. Also, the energy levels in the square pyramidal transition metal complex are dependent on the displacement of the central metal from the basal plane.[29]

In methanol, the coordinated chloride ion is displaced with a solvent molecule, giving a solvated cationic species, and the geometries of these complexes change from a five-coordinated square pyramid to a six-coordinated octahedron (Scheme 1b).[30,31] However, the sign of the CD band of [Mn{7-Phsal-(*SS*)-stien}-Cl] in the $\pi-\pi^*$(azomethine) transition region is the same as that in CH$_2$Cl$_2$ and opposite to that of [Mn{sal-(*SS*)-stien}Cl] (Figure 4). In addition, the spectral pattern of [Mn{7-Phsal-(*SS*)-stien}Cl] in methanol is similar to that of [Mn{7-Phsal-(*SS*)-stien}]ClO$_4$ in acetonitrile except that the intensity of the former is larger. Accordingly, in both cases the central chelate ring takes a λ gauche conformation and the stien phenyl groups preserve the axial orientation.

Four isomers are possible for [Mn{7-Phsal-(*S*)-pen}Cl] and [Mn{sal-(*S*)-pen}Cl] (Scheme 2). The CD spectrum of [Mn-{7-Phsal-(*S*)-pen}Cl] shows that the λ gauche conformation is dominant (Figure 5), and the **B**-λ isomer should be the most stable on steric grounds. [Mn{sal-(*S*)-pen}Cl] exhibits a CD pattern opposite to that of [Mn{7-Phsal-(*S*)-pen}Cl], and the major conformation of the central chelate ring is suggested to be a δ gauche form. This result is different from the case of [Mn{5-*s*-Busal-(*S*)-pn}Cl], which slightly favors the λ gauche conformation with an axially disposed methyl group.[27] A similar result to that for [Mn{sal-(*S*)-pen}Cl] has been reported for [VO{sal-(*S*)-pen}] and [Fe{sal-(*S*)-pen}Cl], and the **B**-δ isomer has been suggested to be dominant due to solvation.[25] However, we have obtained evidence that [VO{sal-(*S*)-pen}] consists of two isomers, **A** and **B**, by high-performance liquid chromatography. The ratio was about 1:1. The energy difference among **A**−δ, **B**-λ, and **B**-δ will be small, and we should also consider these isomers in cases other than the vanadium complex.

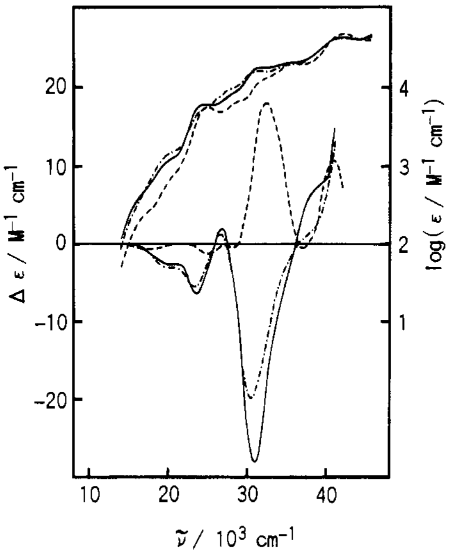
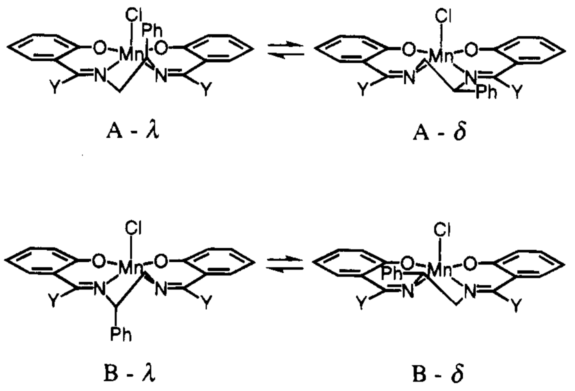


Figure 4. CD and absorption spectra in methanol solution of [Mn-{7-Phsal-(*SS*)-stien}Cl] (—) and [Mn{sal-(*SS*)-stien}Cl] (- - -) and in acetonitrile solution of [Mn{7-Phsal-(*SS*)-stien}]ClO$_4$ (— • —).

Scheme 2



Electrochemistry. Electrochemistry is useful for examining electronic effects of substituents on ligands in metal complexes. Figure 6 shows a cyclic voltammogram of [Mn{7-Phsal-(*SS*)-stien}Cl] in acetonitrile containing Bu$_4$NBF$_4$, and the data are summarized in Table 4, together with those for the related complexes. All the complexes exhibit a quasi-reversible redox process assignable to the Mn(III)/Mn(II) redox couple in a fairly small range (−0.60 to −0.47 V vs Ag/Ag$^+$). The data show that substitution of H with Ph on the azomethine carbon atoms or on the carbons in the N−N chelate ring does not exert a large effect on the Mn(III)/Mn(II) redox potential.

Although [Mn(salen)Cl], [Mn{sal-(*R*)-pen}Cl], [Mn{sal-(*SS*)-

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(28) Boucher, L. J.; Day, V. W. *Inorg. Chem.* **1977**, *16*, 1360.

(29) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(30) Van Der Bergen, A.; Murray, K. S.; O'Connor, M. J.; West, B. O. *Aust. J. Chem.* **1969**, *22*, 39.

(31) Nakamura, M.; Miyanaka, Y.; Ohmura, Y.; Sekine, S.; Huang, H.; Kai, F. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2846.

Table 4. Electrochemical Data for the Redox Couples Mn(IV)/Mn(III) and Mn(III)/Mn(II)[a]

	Mn(IV)/Mn(III)[b] $E^{\circ\prime}$/V (ΔE_p/mV)	Mn(IV)/Mn(III)[c] $E^{\circ\prime}$/V	Mn(III)/Mn(II)[b] $E^{\circ\prime}$/V (ΔE_p/mV)
[Mn(salen)Cl]	0.60 (165)	0.63	−0.55 (78)
[Mn{sal-(*R*)-pen}Cl]	0.62 (180)	0.67	−0.52 (75)
[Mn{sal-(*SS*)-stien}Cl]	0.62 (155)	0.65	−0.53 (65)
[Mn{sal-(*meso*)-stien}Cl]	*d*	0.90	−0.47 (85)
[Mn(7-Phsalen)Cl]	0.60 (185)	0.62	−0.60 (75)
[Mn{7-Phsal-(*R*)-pen}Cl]	0.78 (240)	0.87	−0.55 (90)
[Mn{7-Phsal-(*SS*)-stien}Cl]	*d*	1.04	−0.48 (95)

[a] Measured in CH_3CN with Bu_4NBF_4 (0.1 M) as a supporting electrolyte; all $E^{\circ\prime}$ values are given vs Ag/Ag^+. [b] Data from cyclic voltammetric measurements; scan rate is 0.1 V s^{-1}; $E^{\circ\prime}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = E_{pa} - E_{pc}$. [c] Data from rotating-disk-electrode voltammetric measurements; scan rate is 0.01 V s^{-1}; rotation rate is 2000 rpm. [d] No clear couple was observed.

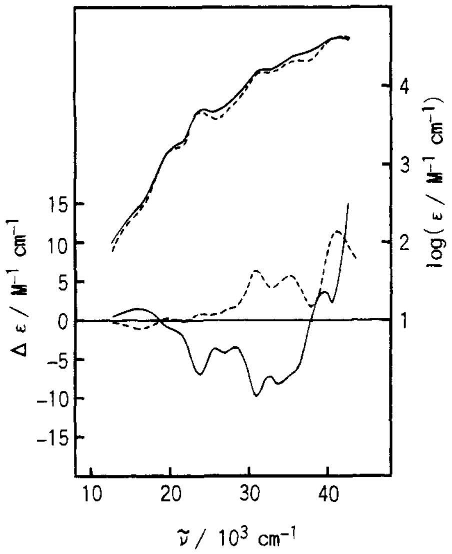

Figure 5. CD and absorption spectra in dichloromethane solution of [Mn{7-Phsal-(*S*)-pen}Cl] (—) and [Mn{sal-(*S*)-pen}Cl] (- - -).

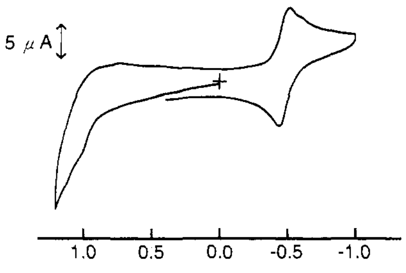

Figure 6. Cyclic voltammogram of a solution (5.0×10^{-4} M) of [Mn{7-Phsal-(*SS*)-stien}Cl] in CH_3CN (0.1 M Bu_4NBF_4).

stien}Cl], and [Mn(7-Phsalen)Cl] exhibit another quasi-reversible redox process at ca. 0.6 V assignable to the Mn(IV)/Mn(III) redox couple, no clear couple was observed up to 1.2 V for [Mn{7-Phsal-(*SS*)-stien}Cl] and [Mn{sal-(*meso*)-stien}Cl] in the cyclic voltammograms (Table 4 and Figure 6). Rotating-electrode voltammetric measurements show the Mn(IV)/Mn(III) couple for [Mn{sal-(*meso*)-stien}Cl], [Mn{7-Phsal-(*R*)-pen}Cl], and [Mn{7-Phsal-(*SS*)-stien}Cl] at a much more positive position than those of the other complexes. These findings may be understood by considering the difference in steric effects among the oxidized Mn(IV) species. It is to be noted that there is a large difference in $E^{\circ\prime}$ for the Mn(IV)/Mn(III) couple between a diastereomeric pair, [Mn{sal-(*SS*)-stien}Cl] and [Mn{sal-(*meso*)-stien}Cl]. The electronic contributions of the phenyl groups in the N−N chelate moiety should be comparable in the two complexes. Thus the difference in $E^{\circ\prime}$ can be solely attributed to the steric effects. In [Mn{sal-(*SS*)-stien}Cl], the two phenyl groups can take equatorial positions in the δ gauche conformation. On the other hand, [Mn{sal-(*meso*)-stien}Cl] has one axially disposed phenyl group irrespective of the conformation (λ or δ gauche). The axial phenyl group will cause strong steric repulsion with the additional ligand trans to the chloro ligand. A manganese (IV) complex has a strong tendency to take an octahedral structure compared with the corresponding manganese(III) complex. Thus a severe interaction occurs only for the oxidized form of the complex. The resulting destabilization of the tetravalent state causes 250 mV increase in $E^{\circ\prime}$ for the Mn(IV)/Mn(III) couple from 0.65 to 0.90 V. A similar argument can be applied to [Mn{7-Phsal-(*R*)-pen}Cl], which also has an axial phenyl group on the central chelate ring. The X-ray structure analysis of [Mn{7-Phsal-(*SS*)-stien}Cl] shows that the site trans to the chloro ligand is blocked by a phenyl group (Figure 1), and it is difficult for the complex to take an octahedral structure with the additional ligand. This results in a significant anodic shift. Actually, [Mn{7-Phsal-(*SS*)-stien}Cl] has the most positive $E^{\circ\prime}$ value among the seven complexes studied. We conclude that axial phenyl groups cause the manganese(III) complexes to be difficult to oxidize. We have reported that the corresponding cobalt(II) complex [Co{7-Phsal-(*rac*)-stien}] is also very difficult to oxidize.[32]

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research Nos. 05403009 and 06640720 from the Ministry of Education, Science and Culture of Japan.

Supporting Information Available: For [Mn{7-Phsal-(*SS*)-stien}Cl]·CH_2Cl_2, a stereo packing diagram and tables giving crystallographic data and experimental details, atomic coordinates and equivalent isotropic temperature factors for hydrogen atoms, anisotropic temperature factors for non-hydrogen atoms, and complete bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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(32) Hirotsu, M.; Kojima, M.; Nakajima, K.; Kashino, S.; Yoshikawa, Y. *Chem. Lett.* **1994**, 2183.