X-Ray Structures of Chiral (Salen)manganese(III) Complexes: Proof of Pliability of the Salen Ligand

Ryo Irie, Takashi Hashihayata, Tsutomu Katsuki,* Munetaka Akita,† and Yoshihiko Moro-oka†
Department of Chemistry, Faculty of Science, Kyushu University, 33 Hakozaki, Higashi-ku, Fukuoka 812-8581
†*Research Laboratory of Resource Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503*

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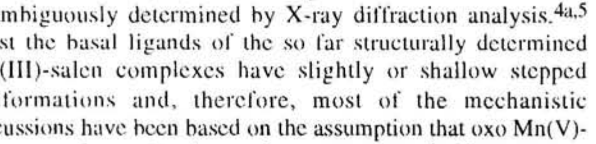
The structures of two cationic chiral (salen)manganese(III) complexes (**2** and **3**) have been unambiguously determined by X-ray diffraction analysis, demonstrating high pliability of the basal salen ligand of these complexes.

Recently we and others disclosed that well-designed chiral (salen)manganese(III) complexes (hereafter referred to as Mn(III)-salen complexes) are good catalysts for asymmetric epoxidation of conjugated olefins[1] but the mechanism of their asymmetric induction is still in controversy. Kochi et al. has proposed that epoxidation using Mn(III)-salen complexes proceeds through the corresponding oxo Mn(V)-salen complexes, which transfer one oxygen atom to olefins (Scheme 1).[2] The presence of oxo Mn(V)-salen complexes was recently proved by MS/MS study of μ-oxo Mn(IV)-salen species.[3] However, the attempts at isolating oxo Mn(V)-salen complexes have not met with success and no information on their structures is available to date. For this reason, discussions on the asymmetric induction have so far been made on the basis of the structures of Mn(III)-salen complexes[4] which have been unambiguously determined by X-ray diffraction analysis.[4a,5] Most the basal ligands of the so far structurally determined Mn(III)-salen complexes have slightly or shallow stepped conformations and, therefore, most of the mechanistic discussions have been based on the assumption that oxo Mn(V)-salen complexes also have planar structures.[4] However, we recently disclosed that some stereochemistries observed in salen-catalyzed epoxidation could be explained only by assuming that the basal salen ligand of oxo Mn(V)-salen complexes had a stepped conformation (non-planar structure) and that olefins approached from its side of the downward benzene ring (**A** in Figure 1).[6] To shed more light on the mechanism of asymmetric induction, we prepared two different single crystals (**2** and **3**) from cationic Mn(III)-salen complex (**1**) and determined their structures by X-ray diffraction.

Complex **1** was prepared in ethanol according to the reported procedure[7] and submitted to column chromatography on silica gel. Recrystallization of **1** from the appropriate solvents gave single crystals **2** $[\mathbf{1}\cdot(H_2O)_2]$ which carried two axial aqua ligands and **3** $[\mathbf{1}\cdot$(cyclopentene oxide)$\cdot H_2O]$ which carried axial cyclopentene oxide and aqua ligands. These crystals were subjected to X-ray diffraction analysis and the obtained structures were described in Figure 2.[8] Complexes **2** and **3** have several common structural features: i) The manganese ions of **2** and **3** take octahedral coordination and both the basal salen ligands are coordinated to the manganese ion in slightly distorted square planar geometry with stepped conformation. ii) The five-membered chelate rings including two imino nitrogen atoms take a half-chair conformation, in which two phenyl substituents take pseudo-equatorial orientation. iii) The phenyl substituents on C3- and C3'-naphthalene rings (**C** and **C'**) are not co-planar with these rings [9]



Scheme 1.

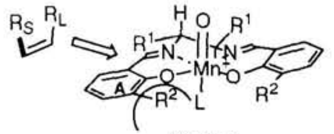


Figure 1.

However, there are differences in the structures **2** and **3**. Their naphthalene rings (**B** and **B'**) in the basal salen ligands are out of the plane of N_2Mn with one of the rings being downward and the other upward, but the deviation from the plane in **3** is larger than that in **2**.[10] Although these stepped conformations of the basal salen ligand are caused by the half-chair conformation of the five membered chelate ring, this structural difference in **2** and **3** may be attributed to the absence and presence of cyclopentene oxide ligand at their apical position. The cyclopentene oxide ligand in **3** locates in the close vicinity of the phenyl ring and the naphthalene ring (pointed by arrows 3 and 4). The short distances between the axial ligand and the substituents of the salen ligand (lesser than 3.8Å) indicate the presence of CH-π interaction between them, which may amplify the bend of the salen ligand. This suggests that the framework of basal salen ligands is pliable enough to be bent even by weak CH-π interaction.[9]

The structures of cationic oxo Cr(V)-salen complex and its pyridine *N*-oxide adduct have been determined unambiguously by X-ray diffraction study.[11a] Recently the structure of nitrido Mn(V)-salen complex was also determined by X-ray diffraction analysis.[11b] These are structurally related complexes and all their basal ligands take stepped conformation. However, the degree of the ligand-folding is not identical. The cationic oxo Cr(V) complex folds most deeply and the nitrido Mn(V) complex slightly. The ligand-fold becomes deep as the metal-$O_{equatorial}$ bond length gets short.[12] It is reasonable to assume that shortening of the M-ligand bond occurs as the oxidation state of the manganese ion in Mn-salen complex becomes higher and amplifies the non-planarity of its basal salen ligand, since the ligand is pliable. This suggests that the oxo Mn(V) salen complex derived from **2** or **3** have more deeply folded stepped conformation, supporting our proposal.

In conclusion, the present study demonstrates that the basal ligand of Mn(III)-salen complexes have high pliability and

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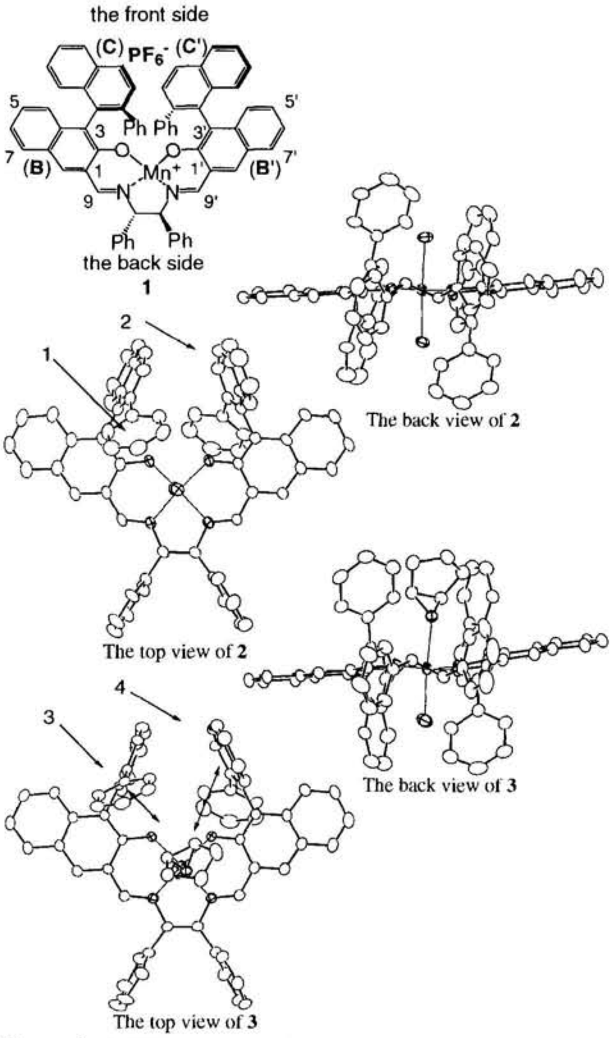

Figure 2. ORTEP diagrams for the top and back views of complexes **2** and **3** based on their crystal structures. Molecules such as solvent and water taken in the crystal lattice and the counter anion (PF_6^-) are omitted for clarity.

that the assumption of stepped conformation for oxo Mn(V)-salen structure[6] is reasonable.[13]

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7 R. Irie, Ph. D. thesis, Kyushu University, Fukuoka, Japan, December 1995. The crystals obtained from the reaction in ethanol gave the following elemental analysis. Found: H, 4.81; C, 71.17; N, 2.31%. Calcd. for $C_{68}H_{46}N_2O_2F_6MnP{\bullet}2C_2H_5OH$: H, 4.98; C, 71.22; N, 2.31%.

8 Crystallographic data for **2**: Recrystallized from $CHCl_3$-toluene, $C_{75}H_{65}N_2O_4F_6PCl_3Mn$ (**2**$\bullet CHCl_3\bullet$hexane), M = 1364.6, monoclinic, space group $P2_1$, a = 11.053(2) Å, b = 19.163(4) Å, c = 15.90(1) Å, β = 95.84(3)°, V = 3350(1) $Å^3$; Z = 2; D_C = 1.35 g cm^{-3}, μ(Mo-Kα) = 4.08 cm^{-1}, $R1$ = 0.088, $wR2$= 0.212 for 6656 reflections and 845 variables, GOF = 1.70. Crystallographic data for **3** (consisting of two independent molecules with essentially the same geometry of the cationic parts): Recrystallized from cyclopentene oxide-toluene-heptane, $C_{76.5}H_{63.66}N_2O_{5.83}F_6PMn$ [**3**$\bullet(H_2O)_{1.83}$(toluene)$_{1/2}$], M = 1304.2, monoclinic, space group $C2$, a = 44.630(6) Å, b = 11.070(1) Å, c = 26.482(6) Å, β = 103.074(5)°, V = 12744(4) $Å^3$; Z = 8; D_C = 1.36 g cm^{-3}, μ(Mo-Kα) = 3.06 cm^{-1}, $R1$ = 0.067, $wR2$= 0.170 for 14516 reflections and 1705 variables, GOF = 1.24. Data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα at -60 °C. Structural analysis was performed using the teXsan crystallographic software package. The structure was solved by the direct methods (SHELXS-86) and all non-hydrogen atoms were refined anisotropically (on F2) using SHELXL-97 linked to teXsan.

9 CH-π interaction between the phenyl ring (pointed by arrow 1 or 3) and the neighboring naphthyl group (by arrow 2 or 4) may stabilize this conformation. M. Nishio and M. Hirota, *Tetrahedron*, **45**, 7201 (1989). W. L. Jorgensen and D. L. Severance, *J. Am. Chem. Soc.*, **112**, 4768 (1990).

10 The coordination squares in **2** and **3** are slightly twisted as indicated by the dihedral angles between the planes defined by the atoms (N, Mn, N) and (O, Mn, O), 3° in **2** and 7° in **3**. The degree of the non-planarity of salen ligands is indicated by the dihedral angles between the mean planes [defined by atoms (N,C9,C1, C2,O) and by (N,C9',C1',C2',O)] and the plane [defined by atoms (N,N,O,O)]. The dihedral angles in **2** are ca. 9° and 6°, and those in **3** are ca. 13° and 7°, respectively. These values reflect the twisted coordination squares described above.

11 The analysis of the X-ray structures of Mn- and Cr-salen complexes taken from Cambridge Crystallographic database suggests that the five-membered chelate rings of some salen ligands take envelope-like conformation and also force their basal ligands to take stepped conformation. For example, see reference 5a and a) K. Srinivasan and J. K. Kochi, *Inorg. Chem.*, **24**, 4671 (1985). b) J. D. Bois, J. Hong, E. M. Carreira, and M. W. Day, *J. Am. Chem. Soc.*, **118**, 915 (1996).

12 For example, the lengths of M-$O_{equatorial}$ are *ca.* 1.81 Å [cationic Cr(V)], *ca.* 1.84 Å [Cr(V)-pyridine *N*-oxide adduct], and *ca.* 1.91 Å [nitrido Mn(V)]. The Mn-$O_{equatorial}$ bond lengths in **2** and **3** are 1.84-1.88 Å. On the other hand, change of the length of M-$N_{equatorial}$ bonds is small. The lengths of M-N bonds are *ca.* 1.98 Å [cationic Cr(V)], *ca.* 1.98 Å [Cr(V)-pyridine *N*-oxide adduct], and *ca.* 1.94 Å [nitrido Mn(V)] (references 11a and 11b).

13 The Mn(III)-salen epoxide adduct corresponds to the final stage of one oxygen atom transfer from oxo Mn(V)-salen complex to olefins. However, the orientation of the coordinated epoxide in complex **3** does not reflect the pathway of the incoming olefins in the epoxidation. Although the epoxide ring is *syn*-periplanar to one of the Mn-$O_{equatorial}$ bonds, this simply means that the *syn*-periplanar orientation is thermodynamically the most stable, probably due to the favorable CH-π interactions.