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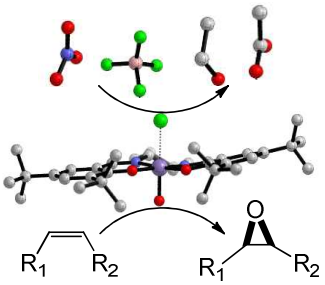
Graphical abstract:

The axial anions influence the electronic structure, steric configuration, and enantioselectivity of the chiral Mn(III) salen complexes.



Journal Name

ARTICLE

Structure and asymmetric epoxidation reactivity of chiral Mn(III) salen catalysts modified by different axial anions

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A series of chiral Mn(III) catalysts [salen-Mn(III)][X] (X^-=Cl^-, OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$, $OCH_2CH_3^-$) were synthesized by ion exchange. The influence of the axial anion on both the electronic structure and steric configuration of [salen-Mn(III)][X] were carefully investigated. Besides, the reactivity and enantioselectivity of these catalysts were explored in the asymmetric epoxidation of olefins. The obtained results indicate that the axial anions have influences on both electronic structure and steric configuration of the chiral Mn(III) salen complexes. Controlling the reactivity and enantioselectivity of these chiral Mn(III) salen complexes can be achieved by changing the axial anions.

Introduction

The asymmetric epoxidation of olefins is an extremely important and powerful reaction for the synthesis of chiral intermediates in the pharmaceutical and agrochemical fields[1-7]. Jacobsen et al. had reported that the chiral Mn(III) salen complexes with chloride ion connecting to the mental center could efficiently catalyze the asymmetric epoxidation of olefins[8-14]. As a kind of homogeneous catalysts, the chiral Mn(III) salen complexes show quite good catalytic activity and enantioselectivity.

In order to further improve their activity and enantioselectivity, intense efforts have been made to modify the chiral metal (Cr, Mn, Co, or Cu) salen complexes. Among the various methods that have been reported, modifying the salicylidene rings of the metal-salen catalysts with functional group is considered as an effective method to produce compounds with high enantioselectivity[15-20]. The most established one is introducing different substituents at the 3,3'- and 5,5'-positions of the salen unit, such as bulked triethylaminomethyl, methylimidazolium[15], triphenyl phosphine[18]. Moreover, an increasing number of studies have been focusing on the substituent of the cyclohexyl on the structure of the metalsalen complexes[21-25]. Besides, macrocyclic chiral metal salen complexes possessing achiral and chiral linkers were introduced for enantioselective reactions to obtain higher catalytic activity and enantioselectivity relative to the monomeric counterparts[4,26-28].

An exciting new progress is that asymmetric counterion-directed catalysis (ACDC) is used as a general strategy for asymmetric synthesis and it has been revealed that a chiral counterion could induce a preference for enantiomorphic conformations[29-37]. These findings suggest the strong ability of counterion with big bulk to influence the asymmetric catalysis. Most of the chiral metal (Cr, Mn, Co, or Cu) salen complexes, including the well-known Jacobsen catalyst, have quite small counterion (such as Cl^-, OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$, and $CH_3CH_2O^-$)[8-14,18,38-41]. The influence of these small counterions on the electronic structure has received much research attention[8-14,18,38-42]. What is the influence of these axial anions on the reactivity and enantioselectivity of chiral salen catalysts? Recently, Kurahashi et al. found that the small axial anions could obviously change the steric configuration of chiral salen-Mn(IV) compound[43,44]. However, it still remained unclear about the influence of these small counterions on the structure of Mn^V=O active intermediate and the enantioselectivity of the chiral salen catalysts[19-21,44-46].

Herein, the influence of the axial anions on the electronic structure and steric configuration of [salen-Mn(III)][X] and its Mn^V=O active intermediate were investigated. Besides, the reactivity and enantioselectivity of these catalysts were explored in the asymmetric epoxidation of olefins.

Results and discussion

Influence of axial anions on the structure of chiral Mn(III) salen catalysts

The chiral Mn(III) salen compounds were synthesized according to the well-known procedures[8-14] and catalysts with different anions were obtained by ion exchange (Scheme 1). These compounds were characterized by FT-IR, MS, elemental analysis and UV-vis spectroscopy.

As we know, the IR frequency and UV-vis absorption band can be used as an indicator for the slight change of electronic structure. The C=N groups in different [salen-Mn(III)][X], which participate in coordination with manganese, have different IR

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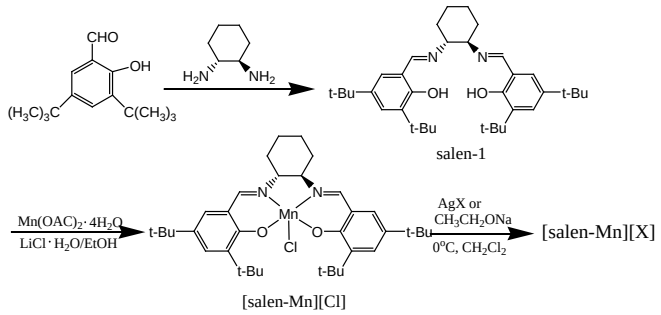

Scheme 1. Synthetic of [salen-Mn(III)][X](X^-=OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$ and $CH_3CH_2O^-$)

Table 1. Some of the typical spectroscopy parameters

Axial anions	$V_{C=N}$(cm^{-1})[a]	V_{C-O}(cm^{-1})[a]	λ_{max} (nm)[b]		$[\alpha]_D^{20}$ [c]
Cl^-	1608	1251	435.6	496.8	-1038
OAc^-	1609	1251	431.8	492.6	-1268
NO_3^-	1612	1252	437.6	491.2	-954
BF_4^-	1613	1252	431.5	489.8	-536
$CF_3SO_3^-$	1620	1252	438.6	486.6	-456
$CH_3CH_2O^-$	1608	1251	434.4	491.6	-890
None[d]	1611	1251	421.6	481.4	-640

[a] The typical vibration frequency measured as KBr pellets. [b] The main absorbed peak of UV-vis in CH_2Cl_2. [c] The specific rotation of 0.0005 g/ml [salen-Mn][X](X^-=Cl^-, OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$ and $CH_3CH_2O^-$) in CH_2Cl_2. [d] Compound without axial anion was synthesized according to the method reported in ref. 46.

vibration frequencies (ranging from 1607.9 to 1619.8 cm^{-1}) (Table 1). Similarly, the C-O vibration frequencies also differ from each other. Moreover, the UV-vis absorption band for the d-d transition of Mn salen complex[4], ranges from 486.6 to 496.8nm for different catalysts. Comparing with compound without axial anion, the coordinated anion obviously increase the λ_{max} values. These FT-IR and UV-vis differences suggest that the axial anions directly influence the electronic distribution of the active site Mn.

Besides the influence on the electronic structure of the active center, axial anion also brings remarkable steric configuration variation of [salen-Mn(III)][X]. It is well-known that specific rotatory power is an inherent property to rotate the plane of incident polarized light, which is related to the steric configuration of the chiral compound. The specific rotator power of different [salen-Mn(III)][X] was measured on the same conditions. It was found that these values ranged from -456 to -1268. Comparing with compound without axial anion, week coordinated anion BF_4^- and $CF_3SO_3^-$ decrease the values of specific rotation whereas the other stronger coordinated anion increase this value. It indicated the axial anion had an obvious influence on the steric configuration of the chiral Mn(III) salen, which agreeswith the crystal results of double axial anion [salen-Mn(IV)][$X]_2$[43].

Table 2. Structural parameters for complexes [Mn^V=O(salen)][X] (X^-=Cl^-, OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$ and $CH_3CH_2O^-$)[a].

	X=Cl	X=AcO	$X=NO_3$	$X=BF_4$	$X=CH_3CH_2O$
SD_{Mn}[b]	3.099	2.622	2.647	2.597	3.125
	(2.757)	(2.772)	(2.643)	(2.621)	(2.982)
SD_O[b]	-0.870	0.632	0.596	0.587	-0.852
	(0.870)	(0.892)	(0.824)	(0.751)	(1.024)
Q_O[c]	-0.099	-0.589	-0.584	-0.506	-0.150
	(-0.216)	(-0.313)	(-0.331)	(-0.370)	(-0.038)
$R_{Mn=O}$[d]	1.751	1.649	1.645	1.637	1.776
	(1.723)	(1.715)	(1.685)	(1.664)	(1.828)
R_{Mn-X}[d]	2.361	2.106	2.225	2.227	1.869
	(2.405)	(2.023)	(2.114)	(2.167)	(1.872)
$\angle MnN_1$	32.9	35.3	44.4	37.5	38.1
O_1C_1[e]	(17.6)	(11.5)	(14.7)	(18.7)	(36.8)
$\angle MnN_1$	13.6	17.7	14.9	23.1	14.6
O_1C_4[e]	(9.7)	(11.8)	(13.3)	(17.2)	(10.7)
$\angle MnO_2$	-33.0	-27.2	-11.3	-23.0	-36.1
N_2C_2[e]	(-28.5)	(-35.1)	(-31.6)	(-28.5)	(-39.1)
$\angle MnO_2$	-11.9	-6.7	-6.2	-1.3	-16.5
N_2C_3[e]	(-3.6)	(-1.9)	(0.1)	(4.8)	(-17.3)
ΔE[f]	1.4	17.8	9.2	5.7	-11.4

[a] Structural parameters of triplet (quintuplet). [b] The absolute value of spin density carried by Mn and O. [c] The charge carried by Mn and O. [d] The Mn=O and Mn-X bond lengths in Å. [e] Dihedral angle. [f] The energy difference between triplet and quintuplet ($E_{triplet}$ - $E_{quintuplet}$).

Influence of axial anions on the Mn^V=O active intermediate

It has been widely accepted that Mn^V=O(salen) complex is the active intermediate in the asymmetric epoxidation using Mn(III) salen as catalyst[45-49]. Though steric configuration of [salen-Mn(IV)][$X]_2$ (X^-=Cl^-, NO_3^-, N_3^- and $CF_3CH_2O^-$) have been well established basing on crystal research[43], it is still quite difficult to explore the steric structure of these active Mn^V=O(salen) intermediates by experimental methods. Herein, theoretical calculations based on density functional theory were used to investigate the influence of axial anions on Mn^V=O active intermediate. It is worth noting that this theoretical method is accurate enough to reproduce the crystal structures[43] or predict experimental results[50-52].

It has been found that the spin density (SD) and charge (Q) carried by the active metal and oxygen are good indicators for the reactivity of catalysts and there exists a linear relationship between SD/Q values and reaction barrier[51,53]. For the [Mn^V=O(salen)][X] system, it is not surprising that the axial anion has an obvious influence on the SD/Q values of Mn and O atoms (Table 2). Hence, these catalysts should have quite different catalytic abilities.

The steric configuration of Mn salen complex plays a significant role in determining the enantioselectivity of th

catalytic process[1-7,45]. It is interesting to find that, though the volumes of these anions (Cl^-, AcO^-, NO_3^-, BF_4^-, and $CH_3CH_2O^-$)

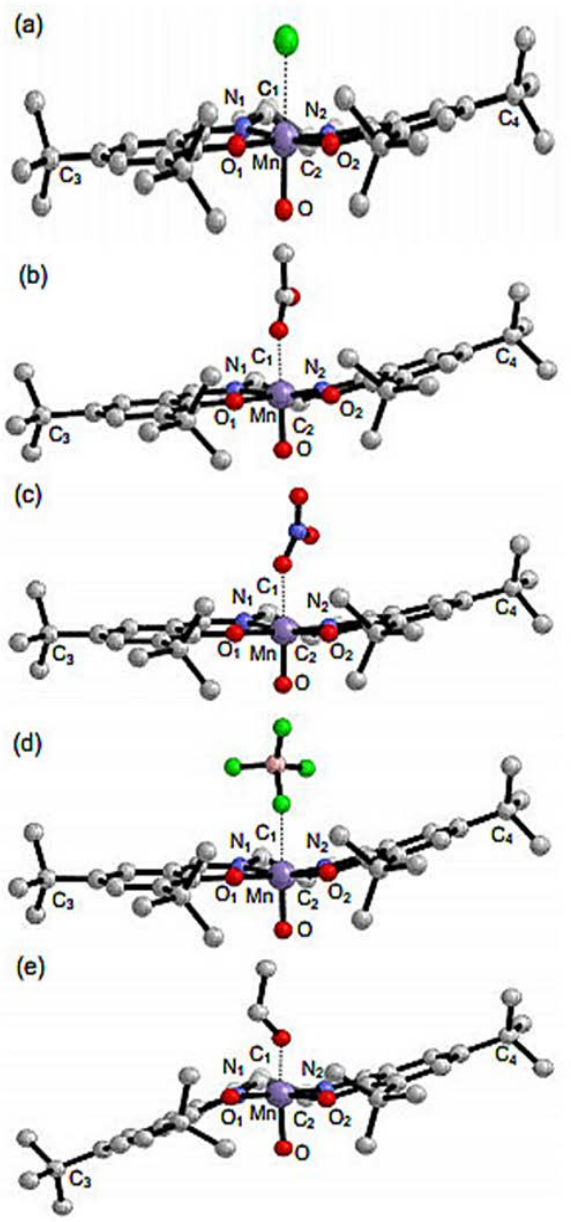

Fig. 1. The optimized structures of [Mn^V=O(salen)][X], (a) X^-=Cl^-, (b) X^-=OAc^-, (c) X^-=NO_3^-, (d) X^-=BF_4^-, (e) X^-= $CH_3CH_2O^-$

are quite small compared with those used in ACDC[29-37], they have an undeniable effect on the steric configuration of Mn salen complex. Being similar to [salen Mn(IV)][X]$_2$[43,44], these active Mn^V=O(salen) intermediates also adopt a stepped conformation with one of two salicylidene rings pointing upward and the other downward (Fig. 1). The values of dihedral angle $\angle MnN_1O_1C_1$, $\angle MnN_1O_1C_4$, $\angle MnO_2N_2C_2$, and $\angle MnO_2N_2C_3$ were used to describe steric configuration distortion of these catalysts (Table 2). For the quintuplet structure, the values of $\angle MnO_2N_2C_3$ and $\angle MnO_2N_2C_2$ range from 4.8 to -17.3 and -28.5 to -39.1 respectively.

Though it is found that the catalysts with different structure characteristics can be obtained by introducing different counterion, we still can not find out the relationship between the specific rotation and the degree of configuration distortion

Table 3. Asymmetric epoxidation of different olefins catalyzed by [salen-Mn][X] (X^-=Cl^-, OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$ and $CH_3CH_2O^-$)[a]

Entry	Axial anion[b]	Substrate	Con.(%)[c]	ee(%)[d]	TOF (h^{-1})[e]
1	Cl^-	Styrene	99.1	34.7	198.2
2	AcO^-		99.5	40.7	199.0
3	NO_3^-		98.6	37.1	197.2
4	BF_4^-		93.0	45.8	186.0
5	$CF_3SO_3^-$		93.8	28.6	184.0
6	$CH_3CH_2O^-$		90.2	33.5	199.6
7	Cl^-	Indene	96.1	78.7	192.2
8	AcO^-		93.2	90.6	186.4
9	NO_3^-		89.7	93.1	179.4
10	BF_4^-		96.4	57.7	192.8
11	$CF_3SO_3^-$		93.0	64.9	186.0
12	$CH_3CH_2O^-$		99.8	48.9	199.6
13	Cl^-	Acenaphthylene	29.7	94.2	59.4
14	AcO^-		34.2	97.7	68.4
15	NO_3^-		36.5	91.1	73.0
16	BF_4^-		49.2	94.4	98.4
17	$CF_3SO_3^-$		30.7	97.2	61.4
18	$CH_3CH_2O^-$		28.5	95.1	57.0

[a] Reaction conditions: substrate (1mmol), m-CPBA (2mmol), NMO (5mmol) in CH_2Cl_2, T=0℃. [b] Catalyst was 1 mol% of substrate. [c] Conversion % of substrate determined by GC. [d] Ee is the enantiomeric excess, which determined by GC with RESTEK RT-BetaDEXse chiral column. [e] Turnover Frequency (TOF) is calculated by expression of [product]/[catalyst]×time (h^{-1}).

of these complexes. Based on the results presented in Table 1 and Fig. 1, what we can safely state is that the degree of configuration distortion diversifies with different axial anion obviously. Controlling the enantioselectivity by changing the axial anions should be possible.

Reactivity of chiral Mn(III) salen with different axial anions

Though above spectral and theoretic results have demonstrated that the axial anions have an undeniable effect on the electronic and steric configuration of Mn salen complex, Table 4. The effect of solvent on the epoxidation of indene catalyzed by different catalysts [a].

Entry	Catalyst [b]	Solvent [c]	Time (h)	Con. (%) [d]	ee (%) [e]	TOF (h^{-1}) [f]
1	X=Cl^-	DCM	0.5	96.1	78.7	192.2
2		CH_3CN	0.5	98.6	71.1	197.2
3		DMF	0.5	23.6	55.7	47.2
4	X=NO_3^-	DCM	0.5	89.7	93.1	179.4
5		CH_3CN	0.5	93.8	80.7	187.6
6		DMF	0.5	8.6	59.5	17.2
7	X=BF_4^-	DCM	0.5	96.4	57.7	192.8
8		CH_3CN	0.5	97.3	86.8	194.6
9		DMF	0.5	6.8	41.0	13.6

[a] Reaction conditions: indene (1mmol), m-CPBA (2mmol), NMO (5mmol) in different solvent, T=0℃. [b] Catalyst was 1 mol% of indene. [c] DCM: dichloromethane; CH_3CN: acetonitrile; DMF: N,N-dimethylformamide. [d] Conversion % of indene determined by GC. [e] Ee is the enantiomeric excess, which determined by GC with RESTEK RT-BetaDEXse chiral column. [f] Turnover Frequency (TOF) is calculated by expression of [product]/[catalyst]×time (h^{-1}).

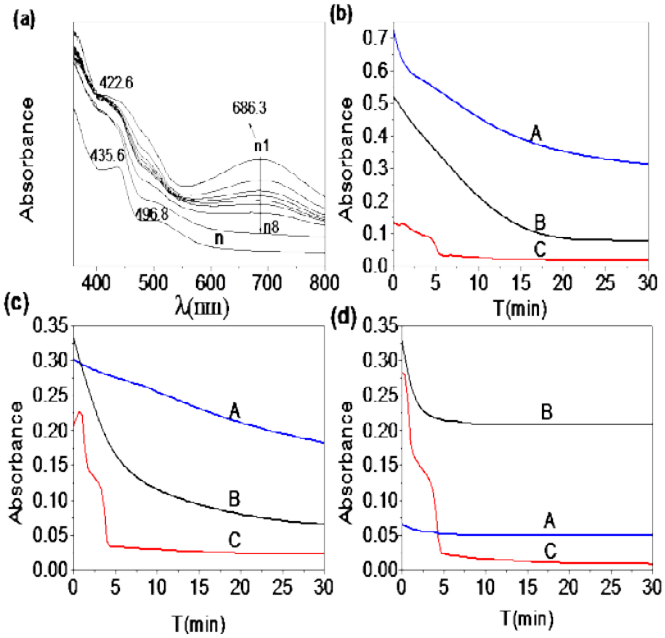

Fig. 2. (a) UV-vis spectra of [salen-Mn(III)][Cl], [salen-Mn(III)][Cl]+m-CPBA in CH_2Cl_2 (0.1mM) in dependence of time (every 20mins from the top down n1-n6, n7, 6h, n8, 8h). (b-d) The changing curves of Mn^V=O absorbance of [salen-Mn(III)][Cl], [salen-Mn(III)][NO_3] and [salen-Mn(III)][BF_4] with time in A: DCM, B: CH_3CN, C: DMF.

a careful experimental research on the catalytic process shows that the influence of axial anion is dependent on the reactio substrate and solvent.

The asymmetric epoxidation of olefins with different steric hindrance (styrene, indene, and acenaphthylene) we e investigated (Table 3). No matter what axial anion is used, the epoxidation of styrene can be finished within 0.5 hour. But, the enantioselectivities are all poor and the corresponding ee values only vary in a narrow range (28.6~45.8). Though axial anions have brought an obvious difference in the steric configuration distortion of these catalysts, the steric hindrance of styrene is too small to clearly distinguish the variation induced by the axial anions.

Increasing the steric hindrance of the reactant makes the diversity induced by axial anions more clear. In the asymmetric epoxidation of indene, the ee values range from 48.9 to 93.1 (Entries 7~12, Table 3). The catalyst with NO_3^- as axial anio gives the highest ee value whereas the one with CH_3CH_2C gives the lowest ee value. At the same time, high conversion can be achieved in 0.5 h for all catalysts. Compared with the methods which introduce functional groups on salicylidene rings of the metal-salen catalysts[15-20], changing the axial anion provides a much easier, but also effective, method to control the reactivity of the traditional Jacobsen catalysts [salen-Mn(III)][Cl].

Further increasing the steric hindrance of the substrate results in lower discrimination in the influence of the axial anion. In the asymmetric epoxidation of acenaphthylene (Entries 13~18, Table 3), though good enantioselectivities are obtained for all catalysts, the corresponding ee values vary in an extremely narrow range (91.1~97.7).

It should be noticed that even though the steric configuration of Mn salen complex plays a significant role i determining the enantioselectivity of the asymmetric epoxidation of olefins, many other factors also have noticeable influences on the enantioselectivity values. Jacobsen et al. discovered and studied the influence of electronic effects of substituents on the asymmetric epoxidation in detail. They found that the enantioselectivity could be improved when the electron-donating group at the 5,5'- positions of the salen unit[9]. Jacobsen also found that the structure of substrates had great influences on the enantioselectivity of the reaction[1,1-4,9], and cis-di-substituted olefins had high enantioselectivity values[1]. Besides that, oxidant[4,5], additives[9,6], and reaction temperature[9] also affect the enantioselectivity values.

Herein we found that the solvent can cooperate with the axial anion to influence the reaction. The asymmetric epoxidation of indene catalyzed by [salen-Mn(III)][X] (X=Cl^-, NO_3^-, and BF_4^-) were further investigated in solvents with different polarity (DCM, CH_3CN and DMF). For all catalysts, reactions performed in DMF gave poor conversion and enantioselectivity (Table 4). As we known, even though ther is no olefin in the reaction system, the Mn^V=O acti e intermediate can also decompose in solution (Fig. 2a)[54]. For [salen-Mn(III)][Cl], full decomposition takes 8 hours in DCI I. However, this decomposition becomes quite fast in DMF for all catalysts investigated here. It is probably because that the e

exists a competition between the active oxygen of Mn=O and the oxygen of DMF. This competition will accelerate the release of active oxygen and enhance the possibility of olefin oxidation by the released oxygen rather than by the active oxygen of Mn=O. Thus, the steric configuration of Mn salen complex has a poor influence on the reaction and a poor enantioselectivity was obtained in DMF. When the axial anions were Cl^- or NO_3^-, reactions performed in DCM gave better enantioselectivity, whereas the enantioselectivity was better in CH_3CN when the axial anion was BF_4^-. Correspondingly, we can find that the decomposition of the Mn^V=O active intermediate is slower in DCM than that in CH_3CN for [salen-Mn(III)][X] (X^-=Cl^- and NO_3^-). However, this decomposition is slower in CH_3CN than that in DCM for [salen-Mn(III)][BF_4].

Conclusions

The structure and reactivity of a series of chiral Mn(III) catalysts [salen-Mn(III)][X] (X^-= Cl^-, OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$, and $CH_3CH_2O^-$) were investigated. The obtained results indicate that a simply changing on the axial anions can result in obvious variation in not only the electronic structure, but also the steric configuration of [salen-Mn(III)][X] and its MnV=O active intermediate. It can further lead to different reactivity and enantioselectivity in the asymmetric epoxidation of olefins. Besides, the axial anions can also change the decomposition rate of the Mn^V=O active intermediate. However, the influence of axial anion is dependent on the substrate and the solvent.

Previous research has revealed that, based on the two-state-reactivity model, the singlet, triplet, and quintet spin states of Mn-salen complexs are all accessible during the reaction processes[55]. Hence, to fully understand the effect of these counterions on the enantioselectivity, a theoretic investigation on the whole reaction process is necessary. Our theoretic on this topic is on progress, including reaction catalyzed by singlet, triplet, and quintet spin states of Mn-salen complexs with different counterions.

Experimental

Synthesis of catalysts and characterizations

The NMR spectra were detected by Bruker ARX 500MHz instrument, using $CDCl_3$ as solvents and TMS as the internal standard. Elemental analysis was taken on an Elementar vario EL II. Optical rotations of chiral complexes were recorded on a WZZ-2A automatic polarimeter instrument. FT-IR spectra were obtained from KBr pellets on a Bruker APEX-III spectrometer in 400-4000cm^{-1} region and UV-vis spectra on a UV-vis SPECORD 200 spectrophotometer. No any data treatment were adopted on the spectra measurements. Mass spectra were performed on an LCMS-2020 mass spectrometer. The products of epoxidation reaction were monitored by GC5890C gas chromatograph equipped with a flame ionization detector using high-purity nitrogen as the carrier gas. Conversions and ee values were determined by GC with a chiral capillary column (RESTEK RT-BetaDEXse, 30m×0.25mm×0.25μm). The reagents and solvents were pure analytical grade materials purchased from commercial sources and used without further purification unless otherwise indicated.

Synthesis of salen-1: (1R,2R)-(-)-1,2-Diaminocyclohexane (3.42g, 30mol) was mixed with potassium carbonate (3.78g, 27mol) in 20ml distilled water at 80 ℃ for 0.5h. When the solid was completely dissolved, 50ml ethanol was added to the solution at reflux for 1h. Then 3,5-di-tert-Butyl salicylaldehyde (5.86g, 25mol) was added dropwise to the mixture within 1h which was dissolved in ethanol (100ml). The reaction mixture was heated at 80 ℃ for an additional 3h and then cooled at the ice-water bath. The yellow solid which was precipitated out was separated by filtration. The preliminary product was dissolved in dichloromethane (80ml) and then washed sequentially with distilled water (2×40ml) and saturated brine (2×30ml). The organgic layer was dried over anhydrous $MgSO_4$ overnight and the solvent was evaporated under reduced pressure to get bright yellow product. Yield: 74.8%; $[\alpha]_D^{20}$= -347.75 (c=0.02, CH_2Cl_2); m.p. 207.6~208.6 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ, ppm: 13.67 (s, 2H; Ar-OH), 8.33 (s, 2H; CH=N), 7.31 (d , 2H; Ar-H), 6.98 (d, 2H; Ar-H), 3.36 (s, 2H; N-CH), 2.0-1.4(m, 8H; CH_2), 1.43(s, 18H; CH_3), 1.26 (s, 18H; CH_3). ^{13}C NMR ($CDCl_3$, 500MHz) δ, ppm: 165.87, 158.04, 139.91, 136.39, 126.76, 126.07, 117.91, 72.46, 34.99, 34.06, 33.30, 32.22, 31.46, 29.49, 24.40; FT-IR (KBr, *v*/cm^{-1}): 3418.6, 2961.9, 2871.8, 1630.6, 1594.4, 1467.3, 1361.3, 1269.7, 1173.6, 1134.9, 1084.9, 1037.2, 878.8, 827.8, 772.4, 711.0, 644.0; UV-vis (CH_2Cl_2, λ_{max} /nm): 232, 262, 331; MS(m/z): Calcd for $C_{36}H_{55}N_2O_2$: 547.43 $[M+H]^+$; found: 547.25; Elemental analysis Calcd (%) for $C_{36}H_{54}N_2O_2$: C, 79.07; H, 9.95; N, 5.12; Found: C, 78.77; H, 9.93; N, 5.03.

Synthesis of [salen-Mn][Cl]: The ligand Salen-1 (4.92g, 9mmol) dissolved in toluene (60ml) was added dropwise to 3 equivalent of $Mn(OAc)_2{\cdot}4H_2O$ (6.62g, 27mmol) in ethanol (75 ml). The reaction mixture was stirred at reflux for 3h. Then the LiCl (27mol, 1.63g) was added and the resulted mixture was further heated to reflux at 80 ℃ for 2h. After 1.5h, the cold solution was washed with distilled water (2×40ml), and the orangic layer was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation under reduced pressure. The residue was purified by recrystallizing from CH_2Cl_2 (20ml) and pentane (80ml). After filtered and dried in vacuum, brown powdery [salen-Mn][Cl] was obtained. Yield: 79.7%; $[\alpha]_D^{20}$= -1038.0 (c=0.0005, CH_2Cl_2); m.p.>300°C; FT-IR (KBr, *v*/cm^{-1}): 2948.7, 2865.8, 1607.9, 1535.7, 1461.1, 1432.5, 1388.5, 1312.2, 1251.2, 1175.5, 1031.4, 837.0, 780.8, 749.2, 566.8, 543.4, 483.7; LC-MS(m/e): Calcd for $[C_{36}H_{52}ClMnN_2O_2]^{+\cdot}$: 634.31; found: 634.25; MS(ESI, m/z): calcd for $[salen\text{-}Mn]^+$: 599.34; found: 599.83 ;Elemental analysis Calcd (%) for $C_{36}H_{52}ClMnN_2O_2$: C, 68.07; H, 8.25; N, 4.41; Found: C, 68.25; H, 8.40; N, 4.08.

Synthesis of [salen-Mn][X] (X= OAc, NO_3, BF_4, CF_3SO_3)**:** 5 equivalent of AgX (X^-=OAc^-, NO_3^-, BF_4^-, $CF_3SO_3^-$) (1mmol) was respectively added to the [Salen-Mn][Cl] (0.127g, 0.2 mmol) in CH_2Cl_2 (5ml) at 40 ℃ below. The mixture was stirred for 5h. Then the cold solution was filtered to remove silver salts.

Anhydrous pentane (50ml) was added to the filtration to give a light brown precipate. Collected by filtration and washed with pentane, the residue was dried in vacuum. Then recrystallization from CH_2Cl_2 (2ml) and pentane (20ml) at 20 ℃ below, the pure solid [salen-Mn][X] was obtained.

[salen-Mn][OAc]: Yield: 52.3%; $[\alpha]_D^{20}$= -1268.0 (c=0.0005, CH_2Cl_2); FT-IR (KBr, ν/cm^{-1}): 3405.5，2946.5, 2865.6, 1609.3, 1536.9, 1434.4, 1388.0, 1308.1, 1250.7, 1175.9, 1031.6, 836.0, 780.9, 748.8, 567.5, 543.2, 483.7; LC-MS(m/e): calcd for $[C_{38}H_{55}MnN_2O_4]^{+\cdot}$: 658.35; found: 658.30; MS(ESI, m/z): calcd for [salen-Mn]$^+$: 599.34; found: 599.83; Elemental analysis Calcd (%) for $C_{38}H_{55}MnN_2O_4\cdot0.5H_2O$: C, 68.34; H, 8.45; N, 4.19; Found: C, 68.22; H, 8.46; N, 4.06.

[salen-Mn][NO$_3$]: Yield: 46.8%; $[\alpha]_D^{20}$= -954.0 (c=0.0005, CH_2Cl_2); FT-IR (KBr, ν/cm^{-1}): 3419.3, 2952.1, 2866.6, 1612.4, 1535.6, 1463.0, 1432.6, 1390.1, 1310.9, 1251.8, 1175.2, 1115.5, 1028.4, 836.9, 780.2, 748.8, 567.6, 543.3, 484.0; LC-MS(m/e): calcd for $[C_{36}H_{52}MnN_3O_5]^{+\cdot}$: 661.33; found: 661.25; MS(ESI, m/z): calcd for [salen-Mn]$^+$: 599.34; found: 599.92; Elemental analysis calcd (%) for $C_{36}H_{52}MnN_3O_5\cdot0.5H_2O$: C, 64.46; H, 7.96; N, 6.26. Found: C, 64.35; H, 8.05; N, 6.07.

[salen-Mn][BF$_4$]: Yield: 47.5%; $[\alpha]_D^{20}$= -536.0 (c=0.0005, CH_2Cl_2); FT-IR (KBr, ν/cm^{-1}): 2954.0, 2867.3, 1613.1, 1536.6, 1463.5, 1433.7, 1392.0, 1311.6, 1251.9, 1175.8, 1059.5, 1029.4, 837.2, 780.7, 749.4, 572.4, 544.0, 485.9; LC-MS(m/e): calcd for $[C_{36}H_{52}BF_4MnN_2O_2]^{+\cdot}$: 686.34; found: 686.30; MS(ESI, m/z): calcd for [salen-Mn]$^+$: 599.34; found: 599.83; Elemental analysis Calcd (%) for $C_{36}H_{52}BF_4MnN_2O_2$: C, 62.98; H, 7.63; N, 4.08; Found: C, 62.87; H, 7.63; N, 4.13.

[salen-Mn][CF$_3$SO$_3$]: Yield: 66.2%; $[\alpha]_D^{20}$= -456.0 (c=0.0005, CH_2Cl_2); FT-IR (KBr, ν/cm^{-1}): 3471.0, 2955.6, 2868.4, 1619.8, 1536.2, 1434.1, 1389.9, 1313.1, 1252.4, 1174.4, 1031.9, 837.7, 780.9, 750.2, 635.1, 574.9, 544.8, 487.9; LC-MS(m/e): calcd for $[C_{37}H_{52}F_3MnN_2O_5S]^{+\cdot}$: 748.29; found: 748.25; MS(ESI, m/z): calcd for [salen-Mn]$^+$: 599.34; found: 599.83; Elemental analysis Calcd (%) for $C_{37}H_{52}F_3MnN_2O_5S\cdot H_2O$: C, 57.95; H, 7.10; N, 3.65; Found: C, 58.19; H, 7.00; N, 3.68.

Synthesis of [salen-Mn][OCH$_2$CH$_3$]: 2 equivalents of CH_3CH_2O-Na (0.4mmol, 0.0272g) was added to the [Salen-Mn][Cl] (0.127g, 0.2 mmol) in CH_2Cl_2 (10ml) at 40 ℃ below. After the mixture was stirred for 2h, the solvent was removed by rotary evaporation. The resulting solid was dissolved in CH_2Cl_2 (5ml) and the solution was filtered in vacua. The rest of process was similar as above. Finally, the pure yellowish-brown powder [salen-Mn][OCH_2CH_3] was obtained.

[salen-Mn][OCH$_2$CH$_3$]: Yield: 37.8%; $[\alpha]_D^{20}$= -890.0 (c=0.0005, CH_2Cl_2); FT-IR (KBr, ν/cm^{-1}): 3448,1, 2949.8, 2866.1, 1607.9, 1534.8, 1432.2, 1388.6, 1312.7, 1251.4, 1175.1, 1031.7, 837.1, 780.7, 749.2, 566.6, 543.5, 483.6; LC-MS(m/e): calcd for $[C_{38}H_{57}MnN_2O_3]^{+\cdot}$: 644.37; found: 644.35; MS(ESI, m/z): calcd for [salen-Mn]$^+$: 599.34; found: 599.83; Elemental analysis Calcd (%) for $C_{38}H_{57}MnN_2O_3\cdot H_2O$: C, 68.86; H, 8.97; N, 4.23; Found: C, 68.56; H, 8.40; N, 4.37.

General epoxidation reaction procedure

A typical asymmetric epoxidation reaction was performed as follows. The catalysts [salen-Mn][X] (0.01mmol, 1mol% based on Mn element) and N-methylmorpholine-N-oxide (NMMO) (5mmol as an axial additive) were dissolved in CH_2Cl_2 containing olefins (styrene, indene, diphenylethene, acenaphthylene as substrates, 1mmol) at 0 °C. The mixed solution was stirred for 10minutes. Then 3-chloroperoxybenzoic acid (m-CPBA) (2mmol) as an oxidant was added in 4 equal portions in 2 minutes. Gas chromatograph was employed to determine the conversions and ee values of the reaction. Each ee value was measured three times. Hence, these data should be statistically reliable. Except dichloromethane, acetonitrile and N,N-dimethylformamide (DMF) were used as reactive solvent in the epoxidation of indene catalyzed by [salen-Mn][Cl], [salen-Mn][NO_3] and [salen-Mn][BF_4].

Computational Methods

The B3LYP method has been widely used in the calculation of metallorganic complexes. For this reason, we optimized all the structures by the B3LYP method. 6-31+G* basis set was generally used for these atoms except for transition metal. LANL2DZ was used for Mn. Geometric configuration optimization, energy calculation, frequency calculation, and zero-point energy correction were performed by using the same basis set. All calculations were performed with the Gaussian 03 suite of programs.

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