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Novel homogeneous Salen Mn(III) catalysts synthesized from dialdehyde or diketone with *o*-aminophenol for catalyzing epoxidation of alkenes

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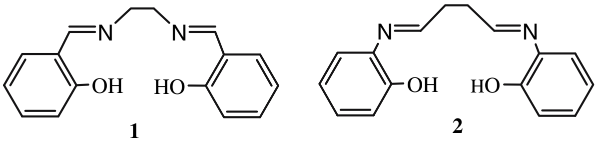
A series of novel non-salicylaldehyde based Salen ligands have been synthesized from the condensation of dialdehyde or diketone with *o*-aminophenol and the corresponding manganese(III) complexes prepared by further coordination of them with $Mn(OAc)_2 \cdot 2H_2O$. FT-IR, UV–Vis spectra, chemical analysis and the structure optimized by Hartree-Fork/3-21G+ all indicated that the qualities of these novel Mn complexes were relative to their molecular structures. More specifically, glyoxal based Mn complex 2c, which was similar to the traditional Mn(III)-salicylethylenediamine, had a short carbon chain and non geometrical constraint of the aliphatic bridge in the two *o*-aminophenol, and its quality was the best when compared to glutaraldehyde, 2,4-pentanedione and 1,3-cyclohexanedione based Salen Mn(III) complexes (3c, 4c and 5c). And it was also the excellent catalyst for the epoxidations of several non-functionalized alkenes with molecular oxygen/sacrificial-isobutyaldehyde, $PhI(OAc)_2$ or H_2O_2 as oxidant.

KEY WORDS: novel Salen(III) Mn complexes; dialdehyde; diketone; *o*-aminophenol; epoxidation of alkenes; molecular oxygen/isobutyaldehyde.

1. Introduction

Most of the known Salen ligands (see a typical salicylethylenediamine ligand 1 in Scheme 1) are usually synthesized by condensation of salicylaldehyde derivatives with diamines, and their complexes with transition metals can catalyze several kinds of organic reactions, such as epoxidation of non-functionalized alkenes [1, 2], oxidation [3, 4], cyclopropanation [5], trimethylsilylcyanation of aldehydes [6, 7], Diels–Alder reactions [8, 9], and so on. In particular, the typical Mn(III) complexes as high-efficient epoxidative catalysts have been extensively reported [10–15]. In recent years, several studies have been devoted to the syntheses of some special Salen ligands such as unsymmetrical ligands [16, 17], a pentadentate ligand [18] and ligands derived from inexpensive carbohydrates [19–21]. However, to the best of our knowledge, few people plough into creating non-salicylaldehyde based Salen ligands. It is believed that, by using condensation reaction of a diketone or a dialdehyde with 2 equivalent of *o*-aminophenol, a series of new non-salicylaldehyde based Salen ligands come into being. Such ligands, like the traditional Salen ligands, feature two covalent and two coordinate covalent sites situated in a planar array. As a result, this makes these ligands ideal for the equatorial coordination of transition metals, leaving the two axial sites open for ancillary ligands. Based on this designed idea, we first report on the condensation of *o*-aminophenol with glyoxal, glutaraldehyde, 2,4-pentanedione, or 1,3-cyclohexanedione to synthesize a series of novel N,N',O,O' tetradentate Salen ligands (see a typical glyoxal based ligand 2 in Scheme 1), and explore the catalytic performances of their corresponding manganese(III) complexes for the epoxidation of un-functionalized alkenes.



Scheme 1. General formula of ligand 1, novel ligands formula ligand 2.

2. Experimental

2.1. Materials and methods

All solvents were distilled prior to use. Distilled deionized water was used; Glyoxal, glutaraldehyde, 2,4-pentanedione, and 1,3-cyclohexanedione were purchased from Aldrich Chem., manganese acetate dihydrate and *o*-aminophenol were purchased from E. Merck and the Beijing Research Institute of Chemical Industry, respectively.

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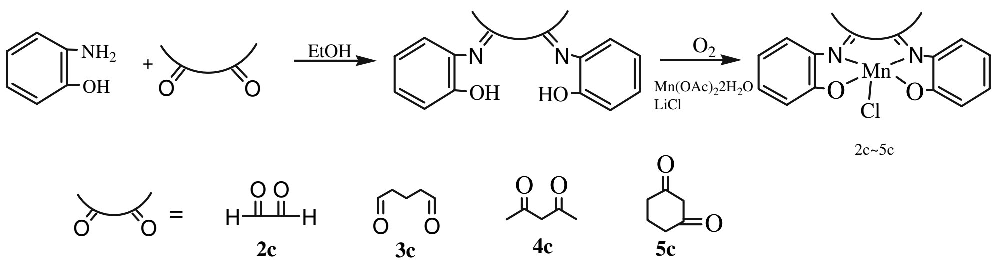


Scheme 2. Preparation procedure of Salen Mn(III) complexes.

2.2. Catalyst preparations

According to the preparation procedures of the traditional Mn(III)-Salen complexes [1], the novel Salen ligands were prepared by the standard procedure of refluxing ethanolic solution of dialdehyde (or diketone) and *o*-aminophenol at a 1:2 molar ratio. A standard run was described as follows (see scheme 2): Firstly, 10 mmol of dialdehyde (or diketone) was refluxed with 20 mmol of *o*-aminophenol in 85 ml of ethanol for 2–3 h. After that, the solution was cooled and then kept in the refrigerator overnight. The solid precipitated from the ethanolic solution was collected by filtration and dried under vacuum to obtain glyoxal based Salen ligand 2 (yield: 92%; m.p.: 204°C), glutaraldehyde based Salen ligand 3 (yield: 85%; m.p.: 173°C), 2,4-pentanedione based Salen ligand 4 (yield: 82%; m.p.: 194°C) or 1,3-cyclohexanedione based Salen ligand 5 (yield: 74%; m.p.: 218°C), respectively. Secondly, 6.0 mmol of manganese acetate dihydrate and 5.0 mmol of the ligand 2 (3, 4 or 5) obtained from the above manner in 70 ml of ethanol were refluxed for 3 h under N_2 atmospheres, followed by adding 6.0 mmol of LiCl, and then the mixture was continuously refluxed for 2 h in air. The resulting solution was concentrated and then cooled to room temperature. Finally, the solid precipitated from the ethanolic solution was filtrated off, washed and dried under vacuum to obtained catalysts 2c (yield: 84%; color: dark red), 3c (yield: 62%; color: dark brown), 4c (yield: 73%; color: dark brown) or 5c (yield: 67%; color: dark yellow), respectively. For comparison purposes, we also prepared salicylethylenediamine ligand 1 (yield: 89%) and its Mn(III) complex 1 c (yield: 83%) according to a standard method [1].

2.3. Catalyst characterizations

The UV–Vis and FT-IR spectra of these ligands and the corresponding Mn(III) complexes were recorded from 200 to 800 nm on a UV-3310 spectrophotometer (ethanol as a solvent) and from 400 to 4000 cm^{-1} on a Nicolet Nexus 510P FT-IR spectroscopy (using KBr pellets), respectively. The Mn contents of these novel Mn(III) complexes were measured by chemical analysis.

2.4. Catalytic testing

In a typical experiment, the desired amount of catalyst, 30 ml of acetonitrile, 5 mmol of substrate and 25 mmol of isobutylaldehyde were mixed in a 100 ml of three-neck round-bottomed flask equipped with magnetic stirrer, thermometer and water-cooled condenser, and then the constant gas flow pump was used to impel oxygen (stored in a gas storage container) to be cycled continuously inside the reactor at constant gas flow rate of 30 ml/min. The reaction was carried out at 35°C for 3–9 h. At the end of the reaction, the reaction mixture was cooled to room temperature. The products of E-stilbene epoxidation were analyzed by an Agilent 1100 high performance liquid chromatography (Eclipse C18, 4.6 mm × 250 mm, eluent methanol/water = 85/15, flow rate = 0.8 ml/min, UV detector $\lambda = 275$ and 290 nm), and the epoxidative products of styrene, α-pinene, β-pinene and cyclohexene were analyzed by an Agilent-6890N gas chromatograph (FID detector, HP-5 column 30 m × 0.32 mm × 0.25 μm). The identities of the products were further confirmed by Varian 3900 GC and Saturn 2100 MS.

3. Results and discussions

3.1. Characterizations

The UV–Vis and FT-IR spectra data of the novel Salen Mn(III) complexes are listed in table 1. It was evident that the broad intense band around ca. 430 nm region in the UV–Vis spectra of these complexes, which is associated with metal to ligand charge transfer (MLCT) transition [22], supplied a support for manganese(III) coordinated to these ligands. On the other hand, the *N*,*N′*,*O*,*O′* (donors of ligand functionalities) mode of metal coordination, which is similar to the traditional Salen Mn(III) complex 1c, was apparent from the red shift (ca. 10 cm^{-1}) of the $\upsilon(C=N)$ and the blue shift (ca. 10 cm^{-1}) of the $\upsilon(C–O)$ vibrations of the free ligand upon 2c. Further support for this coordination mode was provided by bands at ca. 566 and ca. 419 cm^{-1} due to the $\upsilon(Mn–O)$ and $\upsilon(Mn–N)$ of 2c, respectively. It is worthy of mentioning that, in the case of other complexes 3c, 4c and 5c, although the $\upsilon(C=N)$ bands of the three complexes gave rise to the red shift

Table 1
The Mn contents, FT-IR spectra (cm^{-1}) and UV–Vis spectra data λ (nm) of novel Salen Mn(III) complexes[a]

Catalysts	Mn contents ($mmol\ g^{-1}$)		UV–Vis spectra data λ (nm)			FTIR spectra[a] (cm^{-1})			
	Theoretical	Found				υ (Mn–N)	υ (C=N)	υ (C–O)	υ (Mn–O)
1c	2.789	2.432				1627 (1638)	1081 (1041)	593	463
2c	3.026	2.989	433	293 (293)	239 (236)	1601 (1611)	1028 (1018)	566	419
3c	2.685	2.409	430		237 (244)	1585 (1601)	– (1028)	–	–
4c	2.685	2.014	435	310 (321)	211	1596 (1602)	1027 (1027)	–	–
5c	2.601	2.024	434	291(300)		1594 (1607)	– (1037)	–	–

[a] UV–Vis and FT-IR spectra data of corresponding ligands were listed in parentheses.

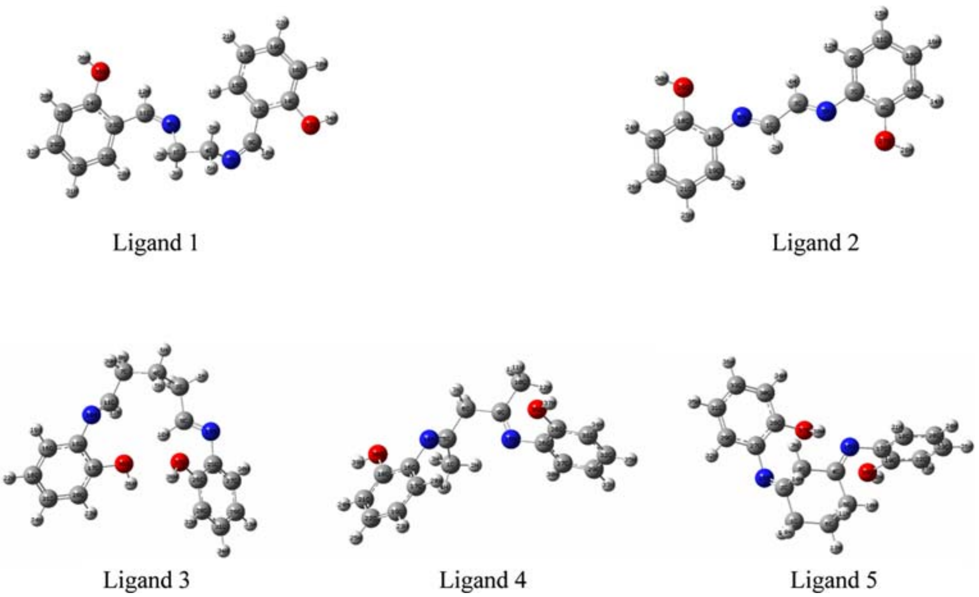
compared to the corresponding ligands, their υ(C–O) bands didn't give rise to the blue shift compared to their ligands. Moreover, the υ(Mn–O) and υ(Mn–N) bands were ambiguous in their IR spectra, proposing a weak *N*,*N′*,*O*,*O′* mode of Mn coordination for the three complexes.

The three dimensional structure modes of four non-salicylaldehyde based ligands (2, 3, 4 and 5) and the traditional salicylethylenediamine (Ligand 1) were established by Hartree-Fock/3–21G+ with Ganssian-03 software (see figure 1) and their O–H and C=N bond distances calculated from these modes are given in table 2. Clearly, the O–H and C=N bond distances of ligand 2, being nearly identical the traditional ligand 1, are obviously shorter than these of the other three ligands 3, 4 and 5, which indicating that glyoxal reacts more efficiently with *o*-aminophenol to form a stable ligand 2 in comparison with the other dialdehydes or diketones. A comparisons of their three dimensional structures may propose that ligand 2, which has a short carbon chain and weak geometrical constraint of the aliphatic bridge in the two *o*-aminophenol, should coordinate manganese(III) very easily when compared to the other three ligands, in accordance with the above-described IR results. Furthermore, a further proof for this conclusion was provided by the differences between the calculated theoretical Mn contents and measured actual Mn contents from these complexes (see table 2).

Table 2
Compared to the O–H and C=N bond distances of various Salen ligands

Ligands	O–H (1)[a] (Å)	O–H (2)[a] (Å)	C=N (1)[a] (Å)	C=N (2)[a] (Å)
1	0.96398	0.96386	1.25870	1.25690
2	0.96414	0.96414	1.25987	1.25992
3	0.98776	0.98836	1.27782	1.27825
4	0.98859	0.98852	1.27797	1.27797
5	0.99236	0.98810	1.27584	1.27878

[a] 1 and 2 in parentheses indicated the left and right O–H or C=N bond, respectively.



Ligand 1

Ligand 2

Ligand 3

Ligand 4

Ligand 5

Figure 1. The optimum three dimensional structures of various Salen ligands.

3.2. Catalytic tests

The epoxidation of E-stilbene with molecular oxygen/sacrificial-isobutyaldehyde was employed to evaluate the catalytic performances of the novel Salen Mn(III) complexes, and the obtained results are listed in table 3. It was evident that these novel Salen Mn(III) complexes were very active for this reaction, more specifically, an extremely high conversion of E-stilbene (ca. 96–100%) with a moderate selectivity for E-stilbene oxide (ca. 43.5–72.4%) was obtained upon them. Further comparisons of the turnover frequency (TOF) data of these novel complexes showed that, among them, 2c, like the traditional 1c, had the highest TOF value (ca. 119.1), the TOF values of 4c and 5c were about a quarter of 2c's, and 3c gave the lowest TOF value (ca. 13.6). This distinct difference in oxidative rate is just accordant with the above-described qualities of these Mn(III) complexes.

In the following experiments, the excellent 2c was employed to catalyze the epoxidations of other non-functionalized alkenes with oxygen/sacrificial-isobutyaldehyde, and the obtained results are listed in table 4. Seen from it, 2c was still very efficient for the epoxidations of α-pinene, styrene and especially β-pinene, but it gave a relative low conversion and high epoxidative selectivity for the epoxidation of cyclohexene. However, this catalyst was not active for the epoxidations of the functionalized alkenes such as cinnamic alcohol and cinnamic acid. These reaction results indicate that the novel complexes, similar to the traditional Salen Mn(III), are effective only to the epoxidations of the non-functionalized alkenes. Furthermore, among these epoxidations of the non-functionalized alkenes, they are more effective to the substrates with a cyclo-external C = C bond than cyclo-inner C = C bond.

Finally, we tested the effects of the other oxidants such as H_2O_2 and $PhI(OAc)_2$ for styrene epoxidation over 2c catalyst, and the obtained results are listed in table 5. As could be seen from it, $PhI(OAc)_2$ or especially H_2O_2 gave much lower epoxidative yield compared to O_2/sacrificial-isobutyaldehyde.

Table 4
The reaction results obtained from epoxidations of various alkenes with O_2/isobutylaldehyde over Salen Mn(III) complex 2c

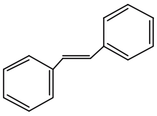
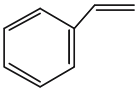
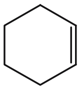
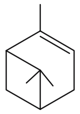
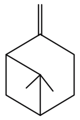
Substrates	Time (h)	Conversion (%)	Selectivity (%)
	2	100.0	43.5
	6	87.3	64.6
	8	48.0	80.6
	6	70.3	47.0
	6	96.7	63.9

Table 5
Epoxidative results of styrene with various oxidants over Salen Mn(III) complex 2c

Entry	Oxidant	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)
1	O_2	6	87.3	64.6	56.4
2	H_2O_2[a]	24	21.7	100.0	21.7
3	$PhI(OAc)_2$[b]	24	57.0	57.7	32.9

[a] Reaction conditions: Styrene: 2 mmol, 30% H_2O_2: 6 mmol, $NaHCO_3$: 0.2 mmol, catalyst: 0.05 mmol and temperature: 0°C.

[b] Reaction conditions: Styrene: 0.5 mmol, $PhI(OAc)_2$: 1 mmol, bromobenzene: 0.5 mmol, catalyst 0.025 mmol, CH_3CN: 5 ml, and temperature 25°C.

Table 3
The reaction results obtained from the epoxidation of E-stilbene with O_2/isobutylaldehyde over novel Salen Mn(III) complexes

Mn complexes (amount/mol%)	Aldehyde/alkene (molar ratio)	Time (h)	Conversion (%)	Selectivity[a] (%)	TOF[b] (h^{-1})
1c (0.25%)	2.5	2	97.6	41.8	159.6
2c (0.25%)	2.5	2	100.0	43.5	119.1
3c (1.00%)	5.0	9	100.0	72.4	13.6
4c (0.50%)	5.0	9	100.0	59.9	29.0
5c (0.50%)	5.0	9	96.1	56.4	27.7

[a] Except E-stilbene, benzaldehyde as a main by-product was also detected by GC-MS.

[b] Turnover frequency (TOF) was calculated from E-stilbene amount (mmol) × its conversion (%)/(catalyst amount (g) × Mn loading (mmol g^{-1}) × reaction time (h)).

4. Conclusions

A series of novel Salen manganese(III) complexes have been successfully prepared *via* the condensation of diketones or dialdehydes with *o*-aminophenol following the coordination with manganese(III). IR and UV–Vis spectra, chemical analysis and the structure optimized by Hartree-Fork/3-21G+ all indicate that the qualities of these Salen Mn(III) complexes are relative to their molecular structures. Glyoxal based Mn complex 2c has the best quality, so that it is also the excellent catalyst for the epoxidations of several non-functionalized alkenes containing a cyclo-external C=C bond such as styrene, β-pinene and especially E-stilbene with molecular oxygen as an oxidant in the presence of sacrificial-isobutyaldehyde. The molecular design and synthesis of these non-salicylaldehyde based chiral Salen Mn(III) complexes are in progress.

Acknowledgments

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