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Epoxidation catalyzed by iron(III) and manganese(III) pyridine-2-carboxamido complexes

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Abstract

A series of Fe(III) and Mn(III) complexes containing N_4 non-porphyrin pyridine-2-carboxamido ligands have been synthesized. Their catalytic abilities in epoxidation and the effects of reaction conditions such as temperature, solvent have been studied, leading to the highest yield of 92% for 4-methoxystyrene by using [Mn(bbpc)Cl(DMF)] (H_2bbpc = 1,2-bis(4′-*tert*-butylpyridine-2′-carboxamido)-4,5-dichlorobenzene) as catalyst.
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Keywords: Pyridine-2-carboxamido; Iron; Manganese; Catalytic epoxidation

1. Introduction

Design of metal catalysts to mimic bio-oxidative activity of P-450 has continued to be an active area of research [1]. There have been numerous reports on the catalytic oxidation of organic substrates by porphyrin complexes [2,3]. Due to the difficulties in modification, preparation of other planar tetradentate ligands, especially Schiff base [4,5] and amido ligands [6–9], is highly desirable. Pyridine-2-carboxamido complex, on the other hand, seems to be a good candidate for catalytic oxidation studies because of its stability to resist oxidation. Furthermore, being a good σ donor after deprotonated to form stable complex with transition-metal ion in high oxidation states [10], pyridine-2-carboxamido ligand could be relatively inexpensive and easy to prepare and modify. Thus, investigations have been carried out to study the structures of the complexes formed by H_2bpb (1,2-bis(pyridine-2′-carboxamido)-benzene) and some transition metal ions such as Cr(III) [10], Mn(III) [10], Fe(III) [11], Os(III) [12] and Ru(III) [13] in recent years. However, there have been few reports concerning catalysis partially because of their low solubilities in normal organic solvents. Continuing of our studies on catalysis by N_4 non-porphyrin complexes [14,15], herein is reported the synthesis of a series of iron(III) and manganese(III) complexes containing substituted pyridine-2-carboxamido ligands (Scheme 1) as well as their applications in catalytic epoxidation of olefins.

2. Experimental

2.1. Materials

Solvents and substrates were purchased from Aldrich or Lancaster and purified by standard procedures before use [16]. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate with sodium hydroxide solution [17]. Sodium cyanide was dried in vacuum at 120 °C. Pyridine-2-carboxylic acids were prepared by hydrolysis of 2-cyanopyridine in hydrochloric acid or sodium hydroxide solution according to the methods described in literatures [13,18,19].

2.2. Instrumentation/analytical procedures

All melting points were measured using a micro-melting apparatus and uncorrected. Ultraviolet and visible (UV–vis) spectra were recorded on a HP 8453 spectrometer. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker

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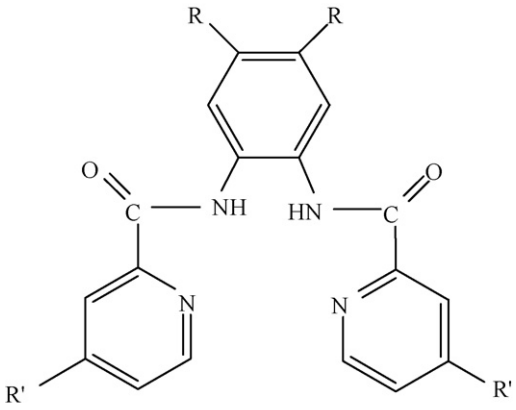


1	R=R'=H		H_2bpb
2	R=H	R'=CH_3	H_2bmpb
3	R=H	R'=Cl	H_2bcpb
4	R=Cl	R'=H	H_2bpc
5	R=Cl	R'=CH_3	H_2bmpc
6	R=Cl	R'=Cl	H_2bcpc
7	R=Cl	R'=*t*-Bu	H_2bbpc

Scheme 1.

DPX 300 spectrometer. Chemical shifts were reported relative to tetramethylsilane. Gas chromatography (GC) measurements were carried out on a HP 5890 series II chromatograph equipped with a flame ionization detector. Mass spectra data were recorded on a Finnigan MAT 4510 spectrometer. Elemental analysis were performed on a Carlo Erba 1106 instrument. IR spectra were performed on a NEXUS-670 FT-IR spectrophotometer in the 4000–400 cm^{-1} region.

2.3. General preparation of the ligands

H_2bpb, H_2bpc, H_2bbpc were synthesized according to the literature procedures [8,10,13]. The other new ligands were prepared by a similar method: to a hot solution of 2-pyridine acid (2 mmol) and triphenylphosphite (2 mmol) in 20 mL of pyridine was added a solution of diamine (1 mmol). After 5 h at 100 °C, the mixture was allowed to stand overnight. Brown oil or solid was obtained after removal of solvent. The pure product was recrystallized from ethyl acetate or ethanol.

1,2-bis(4′-Methylpyridine-2′-carboxamido)-benzene (H_2bmpb). Yield: 138 mg (40%). m.p.: 165–167 °C. Selected IR data (KBr, cm^{-1}): 3337 (s, N–H), 3052 (m), 2920 (m), 1704 (s), 1687 (amide I band, s), 1606 (amide II band, s), 1598 (s), 1537 (m), 1501 (s), 1459 (s), 1287 (w), 1180 (w), 989 (w), 743 (w). ^{1}H NMR ($CDCl_3$) (ppm): δ 10.25 (s, 2H, NH), 8.41 (d, J = 4.8 Hz, 2H, Ar–H), 8.13 (s, 2H, Ar–H), 7.87 (m, 2H, Ar–H), 7.31 (m, 4H, Ar–H), 2.45 (s, 6H, CH_3). EI-MS: *m/z* 346 (M^+).

1,2-bis(4′-Chloropyridine-2′-carboxamido)-benzene (H_2bcpb). Yield: 174 mg (45%). m.p.: 163–165 °C. Selected IR data (KBr, cm^{-1}): 3308 (s, N–H), 3082 (m), 2921 (m), 1688 (s), 1651 (amide I band, s), 1592 (amide II band, s), 1574 (s), 1524 (s), 1478 (s), 1472 (s), 1300 (m), 1097 (w), 990 (w), 751 (s), 692 (w). ^{1}H NMR ($CDCl_3$) (ppm): δ 10.14 (s, 2H, NH), 8.48 (d, J = 5.25 Hz, 2H, Ar–H), 8.31 (s, 2H, Ar–H), 7.80 (m, 2H, Ar–H), 7.47 (m, 2H, Ar–H), 7.32 (m, 2H, Ar–H). EI-MS: *m/z* 386 (M^+).

1,2-bis(4′-Methylpyridine-2′-carboxamido)-4,5-dichloro-benzene (H_2bmpc). Yield: 141 mg (34%). m.p.: 232–234 °C. Selected IR data (KBr, cm^{-1}): 3274 (s, N–H), 2922 (m), 2843 (m), 1686 (s), 1589 (amide I band, s), 1524 (amide II band, s), 1488 (s), 1446 (m), 1383 (m), 1133 (m), 1079 (m), 990 (w), 757 (w), 638 (w). ^{1}H NMR ($CDCl_3$) (ppm): δ 10.22 (s, 2H, NH), 8.3 (d, J = 4.86 Hz, 2H, Ar–H), 8.1 (m, 2H, Ar–H), 8.08 (s, 2H, Ar–H), 7.28 (m, 2H, Ar–H), 2.46 (s, 6H, CH_3). EI-MS: *m/z* 414 (M^+).

1,2-bis(4′-Chloropyridine-2′-carboxamido)-4,5-dichloro-benzene (H_2bcpc). Yield: 192 mg (42%). m.p.: 294–296 °C. Selected IR data (KBr, cm^{-1}): 3332 (s, N–H), 3081 (m), 2920 (m), 1711 (s), 1651 (amide I band, s), 1585 (amide II band, s), 1515 (s), 1489 (m), 1382 (s), 1227 (m), 1126 (w), 989 (w), 774 (w), 578 (w). ^{1}H NMR ($CDCl_3$) (ppm): δ 9.72 (s, 2H, NH), 8.48 (d, J = 6.0 Hz, 2H, Ar–H), 8.27 (d, J = 2.07 Hz, 2H, Ar–H), 7.68 (s, 2H, Ar–H), 7.52 (m, 2H, Ar–H). EI-MS: *m/z* 456 (M^+).

2.4. Preparation of iron(III) and manganese(III) pyridine-2-carboxamido complexes

General procedure for the preparation of the mononuclear iron(III) complexes [20]: ligand (0.50 mmol) was added to a solution of $[Et_4N][FeCl_4]$ (164 mg, 0.50 mmol) in 10 mL DMF under argon. The mixture was added 0.3 mL triethylamine and the suspension quickly changed to a clear green solution. The solution was heated to 90 °C for 10 min. After concentration, the green solid product was obtained after recrystallization from chloroform/diethyl ether.

[NEt_4][Fe(bpb)Cl_2]. Yield: 200 mg (70%). Selected IR data (KBr, cm^{-1}): 2977 (m), 1618 (amide I band, s), 1590 (amide II band, s), 1173 (m), 1096 (s), 750 (m), 695 (m). Anal. calculated for $C_{26}H_{32}Cl_2N_5O_2Fe$: C, 54.47; H, 5.63; N, 12.37. Found: C, 54.82; H, 5.43; N, 12.19. MS (FAB): 442 ([Fe(bpb)Cl_2]$^+$).

[NEt_4][Fe(bpc)Cl_2]. Yield: 199 mg (62%). Selected IR data (KBr, cm^{-1}): 2976 (m), 1606 (amide I band, s), 1570 (amide II band, s), 1492.22 (s), 1386.89 (s), 1247 (m), 996 (m), 769 (m), 674 (m). Anal. calculated for $C_{26}H_{30}Cl_4N_5O_2Fe$: C, 48.63; H, 4.71; N, 10.91. Found: C, 48.97; H, 4.51; N, 10.68. MS (FAB): 512 ([Fe(bpc)Cl_2]$^+$).

[NEt_4][Fe(bbpc)Cl_2]. Yield: 213 mg (57%). Selected IR data (KBr, cm^{-1}): 2968 (m), 1626 (amide I band, s), 1596 (amide II band, s), 1375 (s), 1171 (m), 957 (m), 853 (m). Anal. calculated for $C_{34}H_{46}Cl_4N_5O_2Fe$: C, 54.13; H, 6.15; N, 9.28. Found: C, 53.87; H, 6.36; N, 9.05. MS (FAB): 624 ([Fe(bbpc)Cl_2]$^+$).

[NEt_4][Fe(bmpb)Cl_2]. Yield: 195 mg (65%). Selected IR data (KBr, cm^{-1}): 2978 (m), 1624 (amide I band, s), 1594 (amide II band, s), 1470 (s), 1348 (s), 1173 (s), 1038 (m), 840 (m). Anal. calculated for $C_{28}H_{36}Cl_2N_5O_2Fe$: C, 55.92; H, 6.03; N, 11.65. Found: C, 55.42; H, 6.24; N, 11.38. MS (FAB): 470 ([Fe(bmpb)Cl_2]$^+$).

[NEt_4][Fe(bcpb)Cl_2]. Yield: 186 mg (58%). Selected IR data (KBr, cm^{-1}): 2976 (m), 1617 (amide I band, s), 1607 (amide II

band, s), 1582 (s), 1448 (m), 1345 (m), 1171 (m), 1037 (m), 841 (m). Anal. calculated for $C_{26}H_{30}Cl_4N_5O_2Fe$: C, 48.63; H, 4.71; N, 10.91. Found: C, 48.26; H, 5.08; N, 10.82. MS (FAB): 512 ([Fe(bcpb)Cl_2]$^+$).

[NEt4][Fe(bmpc)Cl2]. Yield: 201 mg (60%). Selected IR data (KBr, cm^{-1}): 2977 (m), 1626 (amide I band, s), 1600 (amide II band, s), 1557 (s), 1457 (s), 1337 (s), 1228 (m), 961 (m), 849 (m). Anal. calculated for $C_{28}H_{34}Cl_4N_5O_2Fe$: C, 50.17; H, 5.11; N, 10.45. Found: C, 49.85; H, 5.31; N, 10.17. MS (FAB): 540 ([Fe(bmpc)Cl_2]$^+$).

[NEt4][Fe(bcpc)Cl2]. Yield: 160 mg (45%). Selected IR data (KBr, cm^{-1}): 2977 (m), 1618 (amide I band, s), 1584 (amide II band, s), 1485 (s), 1458 (m), 1172 (m), 1036 (m), 847 (m). Anal. calculated for $C_{26}H_{28}Cl_6N_5O_2Fe$: C, 43.92; H, 3.97; N, 9.85. Found: C, 43.85; H, 4.21; N, 9.65. MS (FAB): 580 ([Fe(bcpc)Cl_2]$^+$).

Preparation of dinuclear iron(III) complex [Fe(III)(Hbbpc)Cl_2]$_2$: H_2bbpc (250 mg, 0.50 mmol) was added to a solution of [Et_4N][$FeCl_4$] (164 mg, 0.50 mmol) in 10 mL DMF. The reaction mixture was stirred for 10 min and 0.3 mL of triethylamine was then added. The mixture was stirred at 90 °C for 30 min to obtain green solution of [NEt_4][Fe(bbpc)Cl_2] and then cooled to room temperature. After 1 day, the color of the solution changed from green to brown. After filtration and concentration, orange solid was obtained. Pure orange product was obtained by recrystallization from acetonitrile/ether. Yield: 40 mg (13%). Anal. calculated for $C_{52}H_{54}N_8Cl_8Fe_2O_4$: C, 50.00; H, 4.32; N, 8.96. Found: C, 49.75; H, 4.15; N, 8.68. Selected IR data (KBr pellet, cm^{-1}): 2968 (m), 1642 (s), 1606 (s), 1541 (s), 1517 (s), 1388 (s), 1364 (s), 1247 (m), 936 (m), 869 (m).

General procedure for the preparation of Mn(III) complexes: after refluxing $Mn(OAc)_3$ (0.5 mmol) with ligand (0.5 mmol) and LiCl (1 mmol) in 20 mL DMF for 1 h, brownish solid could be obtained after removal of solvent under vacuum. The solid was washed with methanol, and purified by crystallization from DMF/ether to give brown solid product.

[Mn(bpb)Cl(DMF)]. Yield: 172 mg (72%). Selected IR data (KBr, cm^{-1}): 1646 (amide I band, s), 1601 (amide II band, s), 1590 (s), 1474 (s), 1350 (s), 1139 (m), 757 (m), 686 (m), 512 (m). Anal. calculated for $C_{21}H_{19}ClN_5O_3Mn$: C, 52.57; H, 3.99; N, 14.60. Found: C, 52.06; H, 4.21; N, 14.27. MS (FAB): 371 ([Mn(bpb)]$^+$).

[Mn(bpc)Cl(DMF)]. Yield: 186 mg (68%). Selected IR data (KBr, cm^{-1}): 1652 (s), 1602 (amide I band, s), 1566 (amide II band, s), 1373 (s), 1347 (s), 972 (m), 757 (m), 686 (m). Anal. calculated for $C_{21}H_{17}Cl_3N_5O_3Mn$: C, 45.97; H, 3.12; N, 12.76. Found: C, 45.87; H, 3.42; N, 12.58. MS (FAB): 439 ([Mn(bpc)]$^+$).

[Mn(bmpb)Cl(DMF)]. Yield: 142 mg (56%). Selected IR data (KBr, cm^{-1}): 1645 (s), 1606 (amide I band, s), 1570 (amide II band, s), 1357 (s), 1340 (s), 1031 (s), 960 (m), 769 (m), 590 (m), 507 (m). Anal. calculated for $C_{23}H_{23}ClN_5O_3Mn$: C, 54.40; H, 4.56; N, 13.79. Found: C, 54.64; H, 4.42; N, 13.81. MS (FAB): 399 ([Mn(bmpb)]$^+$).

[Mn(bmpc)Cl(DMF)]. Yield: 182 mg (63%). Selected IR data (KBr, cm^{-1}): 1655 (s), 1610 (amide I band, s), 1580 (amide II band, s), 1375 (s), 1350 (s), 965 (m), 760 (m), 650 (m), 521 (m). Anal. calculated for $C_{23}H_{21}Cl_3N_5O_3Mn$: C, 47.90; H, 3.67; N, 12.14. Found: C, 47.56; H, 3.31; N, 12.23. MS (FAB): 467 ([Mn(bmpc)]$^+$).

[Mn(bcpc)Cl(DMF)]. Yield: 210 mg (68%). Selected IR data (KBr, cm^{-1}): 1711 (s), 1654 (amide I band, s), 1590 (amide II band, s), 1515 (s), 1463 (s), 1371 (s), 1330 (m), 972 (m), 799 (m), 537 (m). Anal. calculated for $C_{21}H_{15}Cl_5N_5O_3Mn$: C, 40.84; H, 2.45; N, 11.34. Found: C, 40.68; H, 2.46; N, 11.65. MS (FAB): 507 ([Mn(bcpc)]$^+$).

[Mn(bbpc)Cl(DMF)]. Yield: 149 mg (45%). Selected IR data (KBr, cm^{-1}): 2965 (m), 1655 (amide I band, s), 1612 (amide II band, s), 1468 (s), 1372 (s), 1340 (s), 1288 (m), 1228 (m), 847 (m), 590 (m). Anal. calculated for $C_{29}H_{33}Cl_3N_5O_3Mn$: C, 52.69; H, 5.03; N, 10.60. Found: C, 53.01; H, 5.03; N, 10.45. MS (FAB): 551 ([Mn(bbpc)]$^+$).

2.5. X-ray structure determination

Suitable crystals of [Et_4N][Fe(bbpc)Cl_2], [Fe(Hbbpc)Cl_2]$_2$ and [Mn(bpc)(DMF)Cl] for X-ray structural analysis were obtained by slow diffusion of ether into chloroform solution, ether into acetonitrile and ether into DMF solution, respectively. Diffraction data for [NEt_4][Fe(bbpc)Cl_2]·$CHCl_3$, [Fe(Hbbpc)Cl_2]$_2$, and [Mn(bpc)Cl(DMF)] were collected at 294 K on a Bruker SMART 1000 system. Mo Kα (0.71073 Å) radiation was used, and the data were corrected for absorption. A solution was provided by direct method with SHELXS-97, refined by full-matrix least-squares on F^2 using SHELXL-97 and analyzed with PLATON [21].

2.6. General procedure for catalytic epoxidation of olefins

Iron(III) or manganese(III) complexes (5 μmol), PhIO (0.1 mmol) and organic substrate (0.5 mmol) in solvent (5 mL) were stirred at room temperature for 6 h. After filtration, residue was determined by GC with 1,4-dichlorobenzene as internal standard and the yields were calculated based on PhIO used.

3. Results and discussion

3.1. Preparation of ligands and complexes

Seven tetradentate pyridine-2-carboxamido ligands and 14 complexes derived from them were synthesized. Among them, 4 ligands including H_2bmpb, H_2bcpb, H_2bmpc, and H_2bcpc along with 10 complexes have never been reported.

The ligands were prepared by condensation of 1,2-diaminobenzene with pyridinecarboxylic acids. And the complexes were prepared according to the method described in literature except that NaH was replaced by triethylamine in our studies [22].

The mononuclear iron(III) complexes were prepared from [Et_4N][$FeCl_4$] and corresponding substituted pyridine-2-carboxamido ligands as dark-green solid. This complex was not stable in solvent in the air, for example, green solution of [Et_4N][Fe(bbpc)Cl_2] could changed to be brown solution of stable dimeric complex [Fe(Hbbpc)Cl_2]$_2$. Manganese analogs

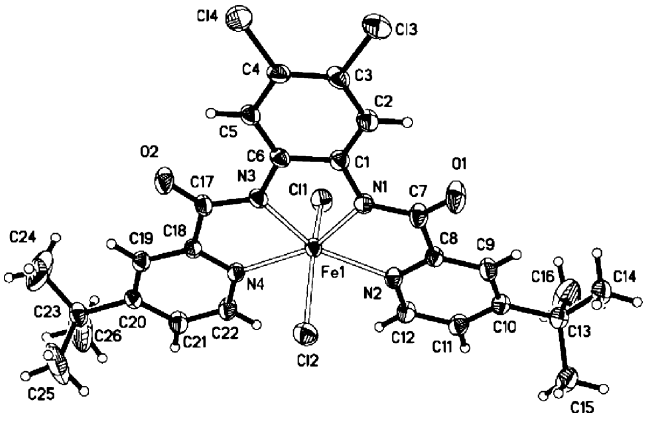


Fig. 1. A perspective drawing of anion of complex $[Fe(bbpc)Cl_2]^-$.

were prepared from manganese(III) acetate and corresponding ligands in the presence of LiCl.

3.2. Characterization of complexes

All the new complexes were characterized by MS, IR, UV–vis, and elemental analysis; suitable single crystals of these three kinds of complexes have also been determined. Owing to the paramagnetic nature of the complexes, NMR spectra of good quality were not obtained.

The perspective drawings of $[Et_4N][Fe(bbpc)Cl_2]$, $[Fe(Hbbpc)Cl_2]_2$ and [Mn(bpc)(DMF)Cl] structures were shown in Figs. 1–3, respectively. As shown in Figs. 1 and 3 for the structures of mononuclear complexes of Fe(III) and Mn(III), the central metal ions are both six-coordinated in a form of distorted octahedron. The four coordination nitrogen atoms are in the equatorial plane and two axial sites are occupied by chloride or solvent molecules. In the case of dimeric

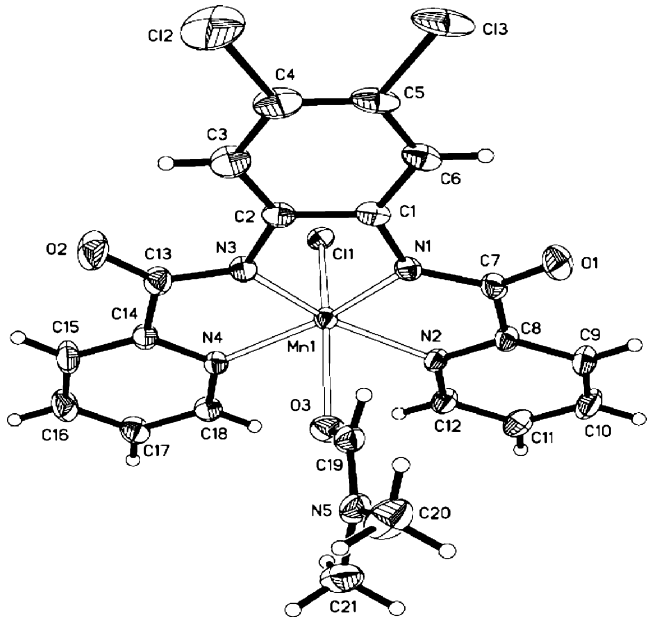


Fig. 3. A perspective drawing of complex [Mn(bpc)(DMF)Cl].

$[Fe(Hbbpc)Cl_2]_2$ complex, the two central ions are as usual to be six-coordinated to form distorted octahedron configuration as shown in Fig. 2. However, each of the two central metal ions coordinates with nitrogen atom of pyridine and neighboring carbonyl group as well as two nitrogen atoms of another ligand. The left two non-coordinated N(amide) and O(carboxyl) atoms in the same ligand form a hydrogen bond.

UV–vis spectra show the differences between free ligand and its metal complexes. After coordination, the peaks of ligands almost disappeared or were much weakened; there appeared a new peak around 347, 360, or 380 nm for the complexes

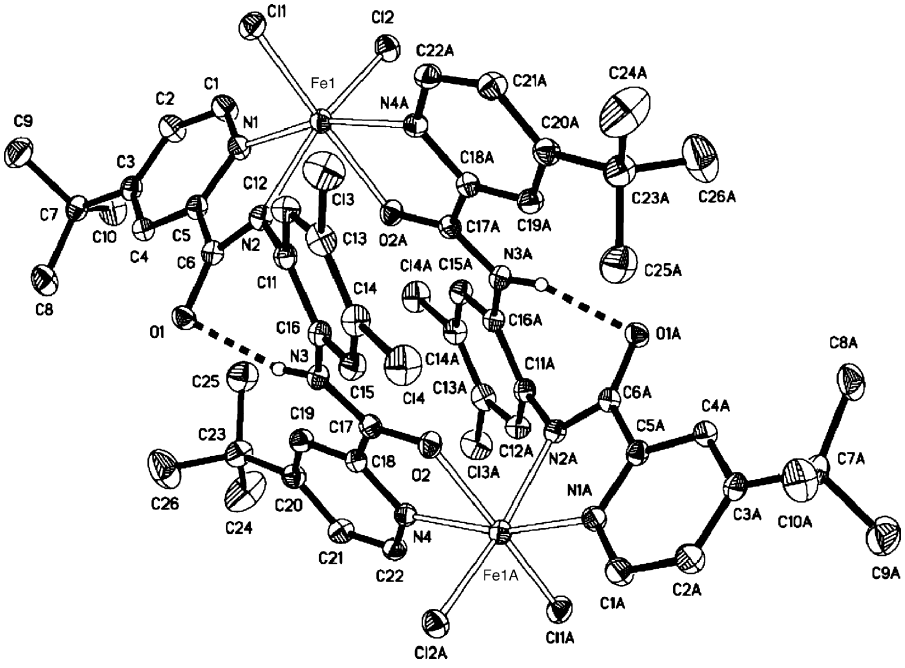
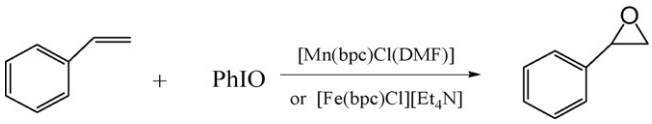


Fig. 2. A perspective drawing of complex $[Fe(Hbbpc)Cl_2]_2$.



Scheme 2.

$[Fe(Hbbpc)Cl_2]_2$, mononuclear iron(III) complexes, and manganese(III) complexes respectively, indicating the formation of complexes.

3.3. Epoxidation of alkenes

3.3.1. Optimization of reaction conditions

For the catalytic activities, the low solubility of bpb complexes in normal organic solvents retarded their applications in catalysis as mentioned before [13]. Actually, in this work, substituents in pyridine ring improved the solubilities of the complexes as well as catalytic activities.

In general, during the process of reaction, the yield increased considerably in the first 2–3 h according to the reaction temperature. Besides epoxide and oxidative-cleavage product, namely benzaldehyde was also generally formed in the epoxidation of styrene.

As shown in Scheme 2, the influences of reaction conditions such as temperature, solvents and amount of catalyst are optimized by using [Mn(bpc)Cl(DMF)] and $[Fe(bpc)Cl_2][Et_4N]$ as catalyst, the results were listed in Table 1.

In general, as observed in Table 1, lower temperature than 25 °C seemed to have few effect on the chemical yield although it diminished the activity of the catalyst, which resulted in longer time for the completion of reaction (Table 1, entries 1–3). However, when the temperature increased from 25 to 40 °C, the yield decreased significantly from 73% to 46% (Table 1, entries 3 and 4). The acceleration of decomposition of PhIO with higher temperature may account for this phenomenon. Thus the reaction temperature of 25 °C was selected for the further studies.

Table 1
Influences of temperature and solvents[a]

Entry	Catalyst	Temperature (°C)	Solvent	Yield (%)[b]
1	[Mn(bpc)Cl(DMF)]	−25	CH_2Cl_2	75[c]
2		0	CH_2Cl_2	72[d]
3		25	CH_2Cl_2	73
4		40	CH_2Cl_2	46
5		25	DMF	65
6		25	MeCN	69
7		25	Benzene	35
8		25	Ethanol	Trace
9	$[Fe(bpc)Cl_2][Et_4N]$	25	CH_2Cl_2	20
10		25	DMF	38
11		25	MeCN	18
12		25	Benzene	10
13		25	Ethanol	Trace

[a] Reactions were performed by using catalyst (5 μmol), styrene (0.5 mmol) and PhIO (0.1 mmol) in 5 mL solvent with reaction time of 6 h.
[b] Determined by GC based on PhIO used.
[c] Twenty-four hours was needed for the completion of reaction.
[d] Ten hours was needed for the completion of reaction.

Table 2
Epoxidation of olefins with PhIO catalyzed by Fe(III) and Mn(III) complexes[a]

Entry	Catalyst	Substrate	Solvent	Yield (%)[b]
1	$[NEt_4][Fe(bpb)Cl_2]$	Styrene	DMF	28
2	$[NEt_4][Fe(bmpb)Cl_2]$	Styrene	DMF	30
3	$[NEt_4][Fe(bcpb)Cl_2]$	Styrene	DMF	30
4	$[NEt_4][Fe(bpc)Cl_2]$	Styrene	DMF	38
5	$[NEt_4][Fe(bmpc)Cl_2]$	Styrene	DMF	42
6	$[NEt_4][Fe(bcpc)Cl_2]$	Styrene	DMF	42
7	$[NEt_4][Fe(bbpc)Cl_2]$	Styrene	DMF	45
8	$[Fe(Hbbpc)Cl_2]_2$	Styrene	DMF	10
9	[Mn(bpb)Cl(DMF)]	Styrene	CH_2Cl_2	65
10	[Mn(bmpb)Cl(DMF)]	Styrene	CH_2Cl_2	75
11	[Mn(bpc)Cl(DMF)]	Styrene	CH_2Cl_2	73
12	[Mn(bmpc)Cl(DMF)]	Styrene	CH_2Cl_2	79
13	[Mn(bcpc)Cl(DMF)]	Styrene	CH_2Cl_2	70
14	[Mn(bbpc)Cl(DMF)]	Styrene	CH_2Cl_2	82
15		4-Methoxystyrene	CH_2Cl_2	92
16		4-Methylstyrene	CH_2Cl_2	90
17		4-Chlorostyrene	CH_2Cl_2	70
18		4-Fluorostyrene	CH_2Cl_2	55
19		Cyclohexene	CH_2Cl_2	88

[a] Reactions were performed by using catalyst (5 μmol), substrate (0.5 mmol) and PhIO (0.1 mmol) in 5 mL solvent at rt for 6 h.
[b] Determined by GC based on PhIO used.

Reaction solvents, on the other hand, exhibited great influence on the results. Polar aprotic solvent seemed to be beneficial for the catalysis. While CH_2Cl_2 was good for Mn(III) complexes and DMF for Fe(III) complexes (Table 1, entries 3 and 10), and there was only trace of product found in ethanol (Table 1, entries 8 and 13).

On the other hand, the effect of the amount of catalyst was also studied for styrene epoxidation catalyzed by [Mn(bpc)Cl(DMF)]. For example, when 1%, 5%, 10% or 15% catalyst was used, styrene oxide was obtained in the yields of 50%, 73%, 73% or 75%, respectively. It suggested that more catalyst than 5% was not necessary. At last, the optimal reaction conditions for the catalysis by Mn or Fe complex were: 5% catalyst, 25 °C, while reaction solvents were CH_2Cl_2 and DMF, respectively.

3.3.2. Using different iron(III) and manganese(III) pyridine-2-carboxamido complexes as catalysts

As usual, the catalytic activity of complexes is strongly dependent upon both central metal and ligands. In our research, the stable dinuclear complex $[Fe(Hbbpc)Cl_2]_2$, as expected, exhibited much less catalytic ability than its mononuclear analogue $[Et_4N][Fe(bbpc)Cl_2]$ with 10% and 45% yield, respectively (Table 2, entries 7 and 8). Therefore, the further studies were focused on using mononuclear complexes.

As shown in Table 2, the catalytic abilities of Mn(III) complexes are in general much higher than those of Fe(III) analogs. For instance, with the same ligand bbpc, 82% yield could be obtained for Mn complex, while only 45% for Fe analogue (Table 2, entries 7 and 14). Similar phenomenon could also be observed in the catalytic epoxidation with salen or porphrin

complexes [23–25]. It is presumed that an intermediate metal-oxo complex is first formed in some way similar to the oxidation chemistry found for high-valent oxo metalloporphyrin complex. Since Mn(IV) oxo complex is more easily formed [26], Mn complexes are thus more effective than Fe analogs.

More importantly, the structure of ligand affected the results significantly. When the hydrogen atom of benzene ring was replaced by chloride, the yields increased from 28% to 38% (Table 2, entries 1 and 4) or from 65% to 73% by using Fe or Mn catalysts, respectively (Table 2, entries 9 and 11). Meanwhile, substituents especially electron-donating alkyl groups in the pyridine ring benefited the reaction. Thus, the best result as 45% and 82% yields were gained for Fe and Mn complexes with bbpc as ligand in the epoxidation of styrene (Table 2, entries 7 and 14).

Epoxidation of other olefins was then carried out by using the most effective [Mn(bbpc)Cl(DMF)] as catalyst. As shown in Table 2, good to excellent results could be obtained for styrenes with electron-rich substituents, leading to the best yield as 92% for 4-methoxystyrene (Table 2, entry 15), which is higher than the reported results of 65–85% with salen as ligands [4,27]. The result is considered partially caused by the stability of pyridine-2-carboxamido complex to resist oxidation compared with the reactive C=N bond of Schiff base analogue [28]. It indicated the higher catalytic activities of this kind catalysts.

4. Conclusions

A series of substituted pyridine-2-carboxamido ligands have been designed and synthesized to coordinate with Fe(III) and Mn(III) ions, forming new catalysts for epoxidation reaction. Among them, the complex [Mn(bbpc)Cl(DMF)], which bears proper substituents both in benzene and pyridine rings, has been found to be an efficient catalyst for expoxidation. The further studies on the ligand modification and applications in asymmetric catalysis are in progress in this laboratory.

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Appendix A

Supplementary data for $[NEt_4][Fe(bbpc)Cl_2]$, $[Fe(Hbbpc)Cl_2]_2$ and [Mn(bpc)Cl(DMF)] are available free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk), quoting the deposition number: CCDC 288283, 288282 and 603300.

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