An efficient aerobic oxidation for *p*-xylene to *p*-toluic acid by unsymmetrical Schiff base manganese(III) complexes with pendant benzo-10-aza-crown ether or morpholino-groups

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Unsymmetrical Schiff base Mn(III) complexes with pendant aza-crown or morpholino groups have been synthesised and studied as catalysts in aerobic oxidation of *p*-xylene to *p*-toluic acid (PTA). The oxidation of *p*-xylene to *p*-toluic acid with air at 120 °C under normal atmospheric pressure occurred efficiently in the presence of aza-crown ether substituted unsymmetrical Schiff base Mn(III) complexes. Significant selectivity (up to ~90%) and conversion levels (up to ~40%) were obtained. The effect of the pendant aza-crown ether group in Mn(III) Schiff base complexes on the oxidation of *p*-xylene was also investigated by comparison with the pendant morpholino-group analogues. The addition of Na^+ cation accelerated the rate of conversion of *p*-xylene to *p*-toluic acid.

Keywords: benzo-10-aza-15-crown-5, unsymmetrical salicylaldimine bis-Schiff base, aerobic oxidation, Schiff base manganese (III) complexes, oxidation of *p*-xylene

With the increasing environmental and economical concerns in recent years, much attention has been directed toward the development of environmentally benign catalytic reactions that use molecular oxygen as a primary oxidant, which is readily available and produces water as the sole byproduct.[1–3] The oxidation of *p*-xylene to *p*-toluic acid is an industrially important process since substituted benzoic acids are very important materials in the chemical and pharmaceutical industries. In recent years, many studies on the oxidation of *p*-xylene to *p*-toluic acid catalysed by $Co(OAc)_2/NaBr/AcOH$ or $Co(C_{18}H_{35}O_2)_2$(cobalt stearate)/NH_4Br have been reported, however, under these conditions, the selectivity (<25%) for *p*-toluic acid is low.[4,5] Eastman–Kodak Tory and Amoco/Mid-Century[6,7] processes are used for the manufacture of *p*-toluic using a $Co(OAc)_2$/ $Mn(OAc)_2$/NaBr catalyst in liquid phase with air as oxidant. Both of these processes operate at 200 °C and 30 atm air to give terephthalic acid (>97%) at a *p*-xylene conversion of 99%. However, because of the environmental issues associated with the production of large volume chemicals and the corrosive nature of the by-products in the above catalyst system, many researchers have been trying to develop highly efficient and selective catalysts for the oxidation of *p*-xylene to *p*-toluic acid and to achieve environmentally friendly and highly economic processes. The biomimetic catalytic oxidation of *p*-xylene to *p*-toluic acid using Co(II) hydroxamates complexes in liquid phase with air as oxidant has been reported.[8,9] To the best of our knowledge, previous studies on the Schiff base complexes with pendant aza-crown group as catalyst in aerobic oxidation of *p*-xylene to *p*-toluic acid are rare.[10,11] Crown ether rings endow interesting properties conferred by the hydrophobicity of the outer ethylene groups and orderly arrangement of inner oxygen atoms.[12,13] Crown ether-containing Schiff bases are known to bind cations in the crown ether cavity in addition to coordination of a transition metal center through the N_2O_2 donor atoms. Co-complexation of a hard cation close to the transition metal centre is believed to play an important role in improving its oxygen binding properties.[14,15] As part of a research program aimed at studying the effects of the aza-crown ether group pendant in Mn(III) Schiff base complexes and the addition of alkali metal cations into the reactive system on the catalytic oxidation performance of *p*-xylene, we have synthesised novel unsymmetrical Schiff base Mn(III) complexes with pendant aza-crown or morpholino-groups and report the homogeneous direct catalytic oxidation of *p*-xylene to *p*-toluic acid by air in the presence of the Schiff base Mn(III) complexes under mild conditions. The structures of unsymmetrical Schiff base Mn(III) complexes are shown in Fig. 1.

Experimental

Melting points were determined on a Yanaco MP-500 micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-1705X spectrometer. ^1H NMR spectra were recorded on a Bruker AC-200MHz spectrometer using Me_4Si as internal standard. Mass spectra were obtained on a Finnigan LCQ spectrometer. The metal ion content was measured using an IRIS-Advantage ICP emission spectrometer. The halogen analysis was measured using a mercury titration method,[16,17] and other elementary analyses were performed on a Carlo Erba 1106 elemental analyser. Molar conductances were obtained on a DDS-11A conductivity meter in DMF solutions (1.0×10^{-3} mol L^{-1}). The molar magnetic susceptibility was obtained on a magnetic balance T3-200 at 25 °C.

Salicylaldehyde, 1,2-phenylenediamine and *p*-xylene were purchased in China. Standard samples of *p*-toluic acid, *p*-tolualdehyde, terephthalic acid, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde and 5-methylsalicylaldehyde were obtained from Aldrich Co. *N*-(2-hydroxy-3-formyl-5-chlorobenzyl)morpholine and *N*-(2-hydroxy-3-formyl-5-bromo-benzyl)morpholine were prepared according to the literature;[13] unsymmetrical Schiff base ligand H_2L^2 was prepared according to the literature,[18] H_2L^1, H_2L^4 and their Mn(III) complexes (MnL^1Cl and MnL^4Cl) were prepared according to the literature.[19] *p*-Xylene was purified prior to use. Other reagents were of analytical grade and were used without further purification.

Synthesis of unsymmetrical Schiff base ligands

(For formulae and structure of ligands see Fig. 1)

Ligand H_2L^3 was prepared as described for *H_2L^1* except starting with *N*-(2-hydroxy-3-formyl-5-methylbenzyl)benzo-10-aza-15-crown-5 instead of *N*-(2-hydroxy-3-formyl-5- chlorobenzyl)benzo-10-aza-15-crown-5 to give a yellow solid, yield 74%, m.p. 84–86 °C. ^1H NMR δ (p.p.m.): 12.53 (s, 1H, OH, D_2O exchange), 9.98 (s, 1H, OH, D_2O exchange), 8.62 (s, 1H, N=CH), 8.40 (s, 1H, N=CH), 7.67–6.64 (m, 14H, ArH), 4.12–3.71 (m, 14H, OCH_2, NCH_2Ar), 2.82 (t, *J*=5.6Hz, 4H, NCH_2), 2.32 (s, 3H, CH_3); IR (KBr, cm^{-1}) ν_{max}: 3430, 3228, 2968, 2930, 2858, 1617, 1602, 1500, 1250, 1129, 1052, 930; ESI-MS *m/z*: 675 (M^++1). Found: C, 70.77; H, 6.52; N, 6.54. $C_{36}H_{39}N_3O_6$. Calcd: C, 70.94; H, 6.40; N, 6.70%.

Ligand H_2L^5 was prepared as described for *H_2L^4* except starting with *N*-(2-hydroxy-3-formyl-5-bromobenzyl)morpholine instead of N-(2-hydroxy-3-formyl-5-chlorobenzyl) morpholine to give a yellow solid, yield 73%, m.p. 77–79 °C. ^1H NMR δ (p.p.m.): 13.06 (s, 1H, OH, D_2O exchange), 10.15 (s, 1H, OH, D_2O exchange), 8.60 (s, 1H, N=CH), 8.46 (s, 1H, N=CH), 7.56–6.88 (m, 10H, ArH), 3.72–3.49 (m,

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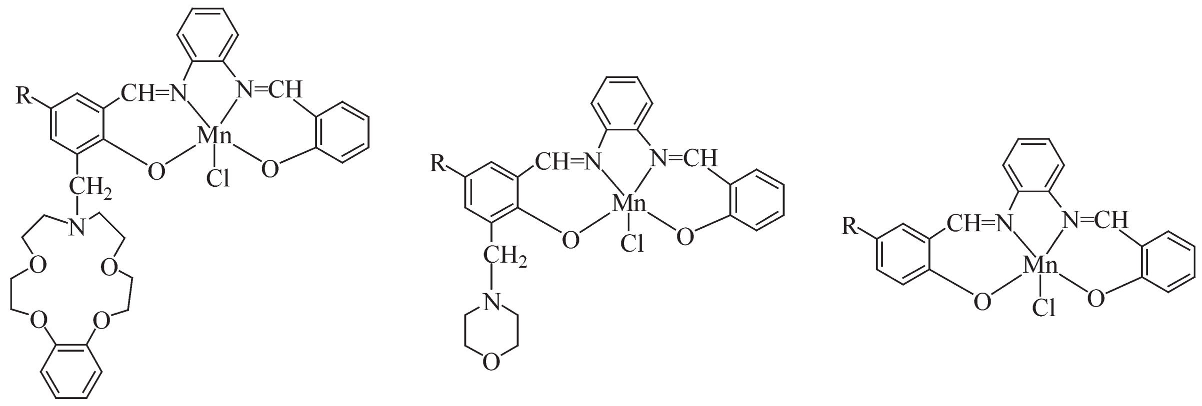


MnL^{1}Cl R = Cl
MnL^{2}Cl R = Br
MnL^{3}Cl R = CH$_3$

MnL^{4}Cl R = Cl
MnL^{5}Cl R = Br

MnL^{6}Cl R = Cl
MnL^{7}Cl R = Br

Fig. 1 The structures of unsymmetrical Schiff base Mn(III) complexes.

6H, OCH$_2$, NCH$_2$Ar), 2.62 (t, *J*=5.2Hz, 4H, NCH$_2$); IR (KBr, cm^{-1}) v_{max}: 3444, 3231, 2938, 2857, 1615, 1600, 1501, 1274, 1192, 1040; ESI-MS *m/z*: 495 (M$^+$+1). Found: C, 60.89; H, 4.72; N, 8.38; Br, 16.07. C$_{25}$H$_{24}$N$_3$O$_3$Br. Calcd: C, 60.73; H, 4.86; N, 8.50; Br, 16.19%.

Ligand H$_2$L^6 was prepared as described for *H$_2$L^4* except starting with 5-chlorosalicylaldehyde instead of N-(2-hydroxy-3-formyl-5-chlorobenzyl)morpholine to give a yellow solid, yield 71%, m.p. 167–169 °C. ^{1}H NMR δ (p.p.m.): 12.98 (s, 2H, OH, D$_2$O exchange), 8.54 (s, 1H, N=CH), 8.41 (s, 1H, N=CH), 7.55–6.80 (m, 11H, ArH), IR (KBr, cm^{-1}) v_{max}: 3241, 1612, 1599; ESI-MS *m/z*: 352 (M$^+$+1). Found: C, 68.62; H, 4.47; N, 7.81; Cl, 10.06. C$_{20}$H$_{15}$N$_2$O$_2$Cl. Calcd: C, 68.47; H, 4.28; N, 7.99; Cl, 10.11%.

*Ligand H$_2$L^7*was prepared as described for *H$_2$L^4* except staring with 5-bromosalicylaldehyde instead of N-(2-hydroxy-3-formyl-5-chlorobenzyl)morpholine to give a yellow solid, yield 78%, m.p. 173–175 °C. ^{1}H NMR δ (p.p.m.): 12.92 (s, 2H, OH, D$_2$O exchange), 8.50 (s, 1H, N=CH), 8.38 (s, 1H, N=CH), 7.60–6.86 (m, 11H, ArH), IR (KBr, cm^{-1}) v_{max}: 3245, 1614, 1601; ESI-MS *m/z*: 396 (M$^+$+1). Found: C, 60.58; H, 3.61; N, 7.26; Br, 20.06. C$_{20}$H$_{15}$N$_2$O$_2$Br. Calcd: C, 60.76; H, 3.80; N, 7.09; Br, 20.25%.

Preparation of manganese complexes; general procedure

A solution of ligand (1.0 mmol) and MnCl$_2$.4H$_2$O (1.1 mmol) in EtOH (15 cm^3) was stirred for 2 h under an N$_2$ atmosphere at 70 °C, and then the mixture was cooled, filtered, and washed with EtOH to give the complexes. The pure product was obtained after recrystallisation from EtOH.

MnL^{2}Cl: Brown, 81% yield, m.p. 252–253 °C; IR (KBr, cm^{-1}) v_{max}: 2929, 2858, 1607, 1601, 1502, 1252, 1130, 1051, 931; ESI-MS *m/z*: 764 (M+1). Found: C, 54.99; H, 4.37; N, 5.78; Cl, 4.51; Br, 10.68; Mn, 7.08 C$_{35}$H$_{34}$N$_3$ClBrO$_6$Mn. Calcd: C, 55.08; H, 4.46; N, 5.51; Cl, 4.66; Br, 10.49; Mn, 7.21%. Λ_m(S cm^2 mol^{-1}): 119.75. Molar magnetic susceptibility $\chi_M = 1.12 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.80 \times 10^{-23}$ J T^{-1}.

MnL^{3}Cl: Brown, 78% yield, m.p. 198–200 °C; IR (KBr, cm^{-1}) v_{max}: 3430, 2968, 2930, 2858, 1606, 1602, 1500, 1250, 1129, 1052, 930; ESI-MS *m/z*: 699 (M$^+$+1). Found: C, 61.80; H, 5.44; N, 6.21; Cl, 4.94; Mn, 8.78 C$_{36}$H$_{37}$N$_3$ClO$_6$Mn. Calcd: C, 61.94; H, 5.30; N, 6.02; Cl, 5.09; Mn, 8.89%. Λ_m(S cm^2 mol^{-1}): 106.58, $\chi_M = 1.06 \times 10^{-1}$ J mol^{-1} T^{-2}, $\mu_m = 4.67 \times 10^{-23}$ J T^{-1}.

*MnL^{5}Cl***:** Brown, 75% yield, m.p. 245–247 °C; IR (KBr, cm^{-1}) v_{max}: 2938, 2859, 1605, 1697, 1503, 1276, 1195, 1044; ESI-MS *m/z*: 583 (M$^+$). Found: C, 51.69; H, 3.66; N, 7.06; Cl, 6.27; Br, 13.61; Mn, 9.51 C$_{25}$H$_{22}$N$_3$ClBrO$_3$Mn. Calcd: C, 51.50; H, 3.78; N, 7.21; Cl, 6.09; Br, 13.73; Mn, 9.44%. Λ_m(S cm^2 mol^{-1}): 106.92, $\chi_M = 1.14 \times 10^{-1}$ J mol^{-1} T^{-2}, $\mu_m = 4.84 \times 10^{-23}$ J T^{-1}.

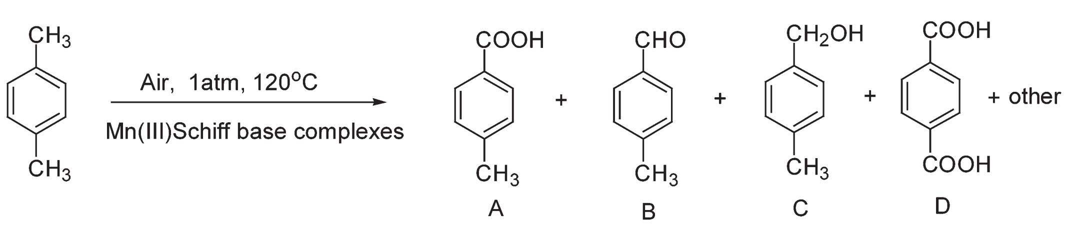
*MnL^{6}Cl***:** Brown, 75% yield, m.p. 238–239 °C; IR (KBr, cm^{-1}) v_{max}: 1605, 1596 1502; ESI-MS *m/z*: 440 (M$^+$). Found: C, 54.79; H, 2.78; N, 6.15; Cl, 16.27; Mn, 12.63 C$_{20}$H$_{13}$N$_2$O$_2$Cl$_2$Mn. Calcd: C, 54.67; H, 2.96; N, 6.38; Cl, 16.17; Mn, 12.53%). Λ_m(S cm^2 mol^{-1}): 106.92. $\chi_M = 1.08 \times 10^{-1}$ J mol^{-1} T^{-2}, $\mu_m = 4.71 \times 10^{-23}$ J T^{-1}.

MnL^{7}Cl: Brown, 79% yield, m.p. 259–261 °C; I.r (KBr, cm^{-1}) v_{max}: 1606, 1598 1499; ESI-MS *m/z*: 485 (M$^+$). Found: C, 49.79; H, 2.88; N, 5.65; Cl, 7.27; Br, 16.36; Mn, 11.43 C$_{20}$H$_{13}$N$_2$O$_2$ClBrMn. Calcd: C, 49.64; H, 2.69; N, 5.79; Cl, 7.34; Br, 16.55; Mn, 11.37%. Λ_m(S cm^2 mol^{-1}): 113.42, $\chi_M = 1.10 \times 10^{-1}$ J mol^{-1} T^{-2}, $\mu_m = 4.74 \times 10^{-23}$ J T^{-1}.

Oxidation of p-xylene to p-toluic acid(PTA) with air; general procedure

(For reaction pathway see Scheme 1)

The oxidation of *p*-xylene was carried out in a general gas-liquid reactor. Fresh air was bubbled at 120 °C with a flow rate of 0.05 L.h^{-1} into a mixture of *p*-xylene (1.21 × 10^{-1} mol, 15 cm^3) and Mn(III) Schiff base complex (1.5 × 10^{-5} mol). The oxidation products were analysed at regular intervals by HPLC (Afilent 1100LC, Hypersil ODS 100 mm × 4.6 mm, 5 μm). Authenticated standard samples were used to confirm the identity of products. The oxidation was stopped upon reaching the maximum value of accumulated content of PTA, and the total conversion and product distribution were evaluated by using calibration curves, which were obtained by injecting a known amount of authenticated standard samples. Conversions and selectivity were calculated based on the amount of *p*-xylene reacted and oxidation products formed by HPLC.



Scheme 1 The oxidation of p-xylene to PTA catalyzed by Mn(III) Schiff base complexes.

Results and discussion

Synthesis

Unsymmetrical bis-Schiff base ligands (H_2L^3, H_2L^5, H_2L^6 and H_2L^7) were prepared by the reaction of the Schiff base half units with substituted salicylaldehyde and their Mn(II) complexes were obtained and characterised (see Fig. 1). Compared with the IR spectra of the free Schiff bases, these complexes had almost identical spectra, except for the C=N stretching vibration which shifted slightly (7–11 cm^{-1}) to lower frequency and also showed greater intensity compared to the free imine. The absence of an OH stretching vibration (~3230 cm^{-1}) in the complexes indicated deprotonation of OH in the Schiff base upon complex formation, suggesting the formation of a Mn–O coordination bond. The C–O stretching vibrations in the crown ether ring for the complexes were at almost the same frequencies as for the free Schiff bases. These facts indicate manganese ion only interacts with the Ar–OH and CH=N groups.[20] The observed molar conductance of all complexes in DMF solution (1.0×10^{-3} mol L^{-1}) at 25 °C also showed that they were electrolytes.[21] The molar magnetic susceptibility χ_M and magnetic moment μ_m values indicated that manganese has four non-paired electrons in all of these complexes and therefore is trivalent. The ESI-MS mass spectra and elemental analysis of the complexes indicated that all unsymmetrical bis-Schiff bases formed 1:1(ligand/metal) complexes, respectively. The facts above showed that Schiff base ligand can coordinate with manganese atom as in Fig. 1.

Oxidation of p-xylene to PTA

The oxidation of *p*-xylene to PTA was carried out using Mn(III) Schiff base complexes as catalyst as in Scheme 1. The results of oxidation of *p*-xylene to PTA are shown in Table 1. The data in Table 1 indicated that the induction periods required for initiating the oxidation of *p*-xylene catalysed by Mn(III) Schiff base complexes are 5 h for MnL^3Cl, 5.3 h for MnL^2Cl, 5.5 h for MnL^1Cl, 8 h for MnL^5Cl, 8.3 h for MnL^4Cl, 9 h for MnL^7Cl, 9.2 h for MnL^6Cl, respectively. This fact shows that the induction periods of initiating the oxidation of *p*-xylene catalysed by the aza-crown Mn(III) Schiff base complexes are shorter than those for the oxidation of *p*-xylene catalysed by the morpholino-Mn(III) Schiff base complexes (MnL^4Cl, MnL^5Cl) or the other crown-free Mn(III) Schiff base complexes (MnL^6Cl, MnL^7Cl). The time taken for PTA to reach the maximum concentration during the oxidation of *p*-xylene catalysed by the aza-crown Mn(III) Schiff base complexes is also shorter than that for crown-free Mn(III) Schiff base complexes. This may be due to the presence of the aza-crown ring which can control efficiently the microenvironment of the active centre owing to the hydrophobicity of the outer ethylene groups and orderly arrangement of inner oxa atoms.

Compared with the electron-donating effect, the macrocycle effect of the aza crown ring may be factor for the catalytic oxidation performance of Schiff base Mn(III) complexes, allowing the oxygen molecule to approach the coordination centre of the aza-crown Schiff base Mn(III) complexes. The previous studies[22] on the X-ray crystal structure of Schiff base complexes with pendant aza-crown groups indicate the aza crown ether group closes near to the coordination group, and the aza-crown ether group controls the coordination environment more efficiently than does the morpholino-group. On the other hand, a very obvious relationship exists between of the induction periods of oxidation reaction and the electronic properties of substituent group on the aromatic rings of the Mn(III) Schiff base complexes. As illustrated in Table 1, the induction periods of oxidation reaction of MnL^3Cl containing electron-donating group ($–CH_3$) is shorter than that of MnL^2Cl containing electron–withdrawing group (–Br) or MnL^1Cl containing electron-withdrawing group (–Cl). The induction periods of oxidation reaction follow the order $–CH_3 < –Br < –Cl$ when the structures of the ligands are similar.

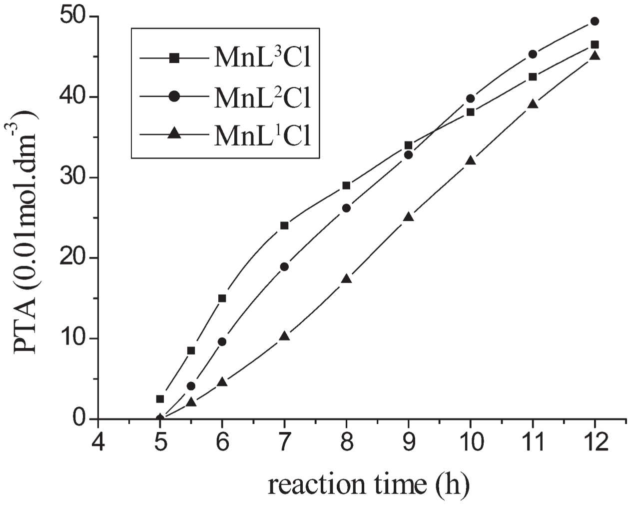


Fig. 2 The effect of substituent groups on the accumulated content of PTA.

The effect of substituent groups on the accumulated content of PTA is obvious. Figure 2 shows that during the initial stage of oxidation, the catalytic activity of MnL^3Cl containing electron-donating group ($–CH_3$) is higher compared with MnL^2Cl containing electron-withdrawing group (–Br). When the oxidation reaction was carried out up to 9.5 h, the accumulated content of PTA in mixture for MnL^3Cl increased slowly, and MnL^3Cl showed poorer catalytic activity compared with MnL^2Cl, this should be because the electron-donating group ($–CH_3$) of MnL^3Cl can increase the electron density of the aromatic rings and activate MnL^3Cl toward electron-seeking oxidation attack. In contrast, MnL^2Cl, containing a mild electron-withdrawing group (–Br) in its aromatic rings, possesses stronger resistance to oxidation degradation to some extent at higher temperature, and shows better catalytic oxidation performance after the oxidation reaction has proceeded for 9.5 h.

Moreover, as shown in Table 1, it can be seen that the selectivity for the oxidation product PTA, conversion and turnover frequency (TOF) for the oxidation of *p*-xylene catalysed by the Schiff base Mn(III) complexes with pendant aza-crown group are also excellent by comparison with those of the oxidation of *p*-xylene catalysed by the morpholino-Mn(III) Schiff base complex analogues. Although the conversion (~50%) for the oxidation of *p*-xylene catalysed by the Schiff base Mn (III) complexes with pendant aza-crown group is lower than that of $Co(OAc)_2/NaBr/AcOH$ or $Co(C_{18}H_{35}O_2)_2/NH_4Br$, the selectivity (up to ~90%) for the oxidation product PTA is higher than that of $Co(OAc)_2/NaBr/AcOH$, and the reaction conditions for

Table 1 Mn(III) Schiff base complex catalysed oxidation of *p*-xylene to PTA[a]

Entry	Catalyst	Induction period /h	Convn. /wt %	TOF	Selectivity for products[b]				
					A	B	C	D	Others
1	MnL^1Cl	5.5	45	302	91.2	2.3	1.9	1.8	2.8
2	MnL^2Cl	5.3	49	329	91.8	2.0	2.1	1.3	2.8
3	MnL^3Cl	5	47	316	90.4	1.2	2.6	2.1	3.7
4	MnL^4Cl	8.3	17	114	82.4	3.7	5.8	2.1	6.0
5	MnL^5Cl	8	18	121	81.1	6.9	3.3	2.1	6.6
6	MnL^6Cl	9.2	11	74	84.5	4.1	5.4	1.1	4.9
7	MnL^7Cl	9	12	81	82.2	5.9	4.1	2.0	5.8

[a] Conditions: p-xylene: 15 cm^{-3} (1.21×10^{-1}mol); Mn(III) Schiff base complexes: 1.0×10^{-3} mol dm^{-3}; flow rate for air: 2.4L. L^{-1} h^{-1}; Reaction temp.: 120 °C; Reaction time: 12 h.

[b] Legend: A = *p*-toluic acid; B = *p*-tolyl alchol; C = *p*-tolualdehyde; D = terephalic acid; TOF = Turnover frequency (mol *p*-xylene converted per mol catalyst per h).

Table 2 Effect of addition of alkali metal nitrate on Mn(III) Schiff base complex catalysed oxidation of *p*-xylene to PTA[a]

Entry	Catalyst	Convn. / wt %	TOF	Selectivity for products[b]				
				A	B	C	D	Others
1	$NaNO_3$	0	0	0	0	0	0	0
2	$MnL^1Cl + LiNO_3$	49	329	91.4	2.4	2.9	1.8	1.5
3	$MnL^1Cl+ NaNO_3$	63	424	93.0	1.8	2.4	1.6	1.2
4	$MnL^1Cl + KNO_3$	51	343	92.1	2.1	2.3	2.2	1.3
5	$MnL^2Cl + LiNO_3$	54	363	92.4	1.8	1.8	2.1	1.9
6	$MnL^2Cl + NaNO_3$	69	464	93.4	1.4	1.9	1.6	1.7
7	$MnL^2Cl + KNO_3$	55	370	92.3	2.2	1.5	2.0	2.0
8	$MnL^3Cl + LiNO_3$	51	343	91.8	2.3	2.4	2.1	1.4
9	$MnL^3Cl + NaNO_3$	65	437	93.5	1.6	1.8	1.5	1.6
10	$MnL^3Cl + KNO_3$	53	356	91.3	2.2	1.6	2.5	2.4
11	$MnL^4Cl + LiNO_3$	22	148	83.6	3.3	5.4	1.3	6.4
12	$MnL^4Cl + NaNO_3$	26	174	84.5	3.3	4.8	2.1	5.3
13	$MnL^4Cl + KNO_3$	24	161	84.4	2.6	4.7	2.6	5.7
14	$MnL^5Cl + LiNO_3$	24	161	83.7	4.7	2.4	2.4	6.8
15	$MnL^5Cl + NaNO_3$	27	182	83.2	3.5	4.4	3.5	5.4
16	$MnL^5Cl + KNO_3$	25	168	83.6	4.1	3.4	3.2	5.7
17	$MnL^6Cl + LiNO_3$	15	101	82.8	4.4	5.1	2.3	5.4
18	$MnL^6Cl + NaNO_3$	16	108	83.5	3.9	4.6	2.7	5.3
19	$MnL^6Cl + KNO_3$	16	108	84.3	3.2	4.2	3.2	5.1
20	$MnL^7Cl + LiNO_3$	16	108	83.9	3.4	4.1	3.3	5.3
21	$MnL^7Cl + NaNO_3$	17	114	84.1	3.1	4.5	3.1	5.2
22	$MnL^7Cl + KNO_3$	18	121	83.7	3.5	4.8	3.6	4.4

[a] Reaction conditions are the same as those in Table 1.

[b] Legend: A = *p*-toluic acid; B = *p*-tolyl alchol; C = *p*-tolualdehyde; D = terephalic acid; TOF = Turnover frequency (mol *p*-xylene converted per mol catalyst per h).

the oxidation of *p*-xylene catalysed by the aza-crown Mn(III) Schiff base complexes is milder than that of other inorganic catalysts.[4,5] Comparing the catalytic oxidation activities of Schiff base Mn(III) complexes with pendant aza-crown groups, the effect of substituent group of the aromatic ring on the oxidation of *p*-xylene seems to be small, and the same phenomenon was also observed for the Schiff base Mn(III) complexes with pendant morpholino-groups.

Table 2 also shows that the addition of alkali metal nitrate (nitrate / MnL^nCl = 2:1) can enhance the catalytic activity of Schiff base Mn(III) complexes with pendant aza-crown group (MnL^1Cl~MnL^3Cl), where the TOF values were significantly improved. In contrast, for MnL^4Cl~MnL^6Cl, there was almost no influence. This suggests that the alkali metal cations improve the catalytic activity only when they are coordinated within the crown ring of the complexes. Table 2 indicates that the catalytic activity of complexes containing aza-crown pendants is significantly enhanced by adding excess $NaNO_3$. However, the enhancement obtained by adding an equal quantity of $LiNO_3$ or KNO_3 is very limited. This may be because the Li^+ ion (d = 1.36 Å) is too small to match the cavity size of aza-15-crown-5 (d = 1.7–2.2 Å), whereas the K^+ ion (d = 2.66 Å) is too large. The Na^+ ion (d = 1.90 Å) matches well with the cavity size of aza-15-crown-5[23] and would be located near to the coordination centre. Moreover, the positive charge of Na^+ may enable molecular oxygen to be activated more easily.

Conclusion

Unsymmetrical Schiff base Mn(III) complexes with pendant aza-crown or morpholino-groups have been synthesised and studied as catalysts for aerobic oxidation of *p*-xylene to *p*-toluic acid. Significant selectivity (up to ~90%) and conversion levels (up to ~40%) were obtained. The study demonstrates that selective oxidation of *p*-xylene to *p*-toluic acid can successfully occur in the presence of Schiff base Mn(III) complexes with pendant aza-crown groups, which display a much better catalytic activity than the Schiff base Mn(III) complexes with pendant morpholino-groups. The crown ether-alkali metal complementarity can improve the conversion and TOF of the oxidation of *p*-xylene to *p*-toluic acid.

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