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Synthesis and study of mono-Schiff base Mn^{III} complexes with aza-crown or morpholino pendant as catalyst in aerobic oxidation of *p*-xylene to *p*-toluic acid

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Abstract

Novel mono-Schiff base Mn^{III} complexes with pendant aza-crown or morpholino groups have been synthesized and studied as catalysts in aerobic oxidation of *p*-xylene to *p*-toluic acid. The oxidation of *p*-xylene to *p*-toluic acid with air at 120 °C under normal atmospheric pressure occured efficiently in the presence of aza-crown ether substituted mono-Schiff base Mn^{III} complexes. Significant selectivity (up to $\sim$90%) and conversion levels (up to $\sim$38%) were obtained. The effect of the aza-crown ether pendant in Mn^{III} Schiff base complexes on the oxidation of *p*-xylene was also investigated by comparison with the morpholino pendant analogues. The addition of alkali metal ions accelerated the rate of conversion of *p*-xylene to *p*-toluic acid.

Introduction

Substituted benzoic acids are very important materials in the chemical and pharmaceutical industries [1, 2]. The oxidation of *p*-xylene to *p*-toluic acid is an industrially important process. In recent years, many studies on the oxidation of *p*-xylene to *p*-toluic acid catalyzed by $Co(OAc)_2/NaBr/AcOH$ or $Co(C_{18}H_{35}O_2)_2/NH_4Br$ have been reported. However, under these conditions, the selectivity (<25%) for *p*-toluic acid is low [3, 4]. Eastman-Kodak Tory and Amoco/Mid-Century[5, 6] processes are used for the manufacture of *p*-toluic using $Co(OAc)_2/Mn(OAc)_2/NaBr$ catalyst in the 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 above the catalyst system, many researchers have been working hard to develop high efficiency and selectivity catalysts for the oxidation of *p*-xylene to *p*-toluic acid and to achieve environmentally friendly and high-economy processes. To the best of our knowledge, previous studies on Schiff base complexes, especially the one substituted with aza-crown ether Schiff base complexes as catalyst in the aerobic oxidation of *p*-xylene to *p*-toluic acid, are infrequent [7, 8]. Crown ether rings endow special performance and characteristics due to the hydrophobicity of the outer ethylene groups and orderly arrangement of the inner oxygen atoms [9, 10]. 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 center is believed to play an important role in improving its oxygen binding properties [11–13]. Herein, as part of a research program aimed at studying the effects of the bonded aza-crown ether ring appended in the ligand and the addition of alkali metal ions into the reactive system on the catalytic oxidation performance of Schiff base Mn^{III} complexes, we have synthesized novel mono-Schiff base Mn^{III} complexes with aza-crown or morpholino pendant and reported 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 route for the synthesis of Schiff base Mn^{III} complexes is shown in Scheme 1.

Experimental

General methods and materials

Melting points were determined on a Yanaco MP-500 micro-melting point apparatus and are

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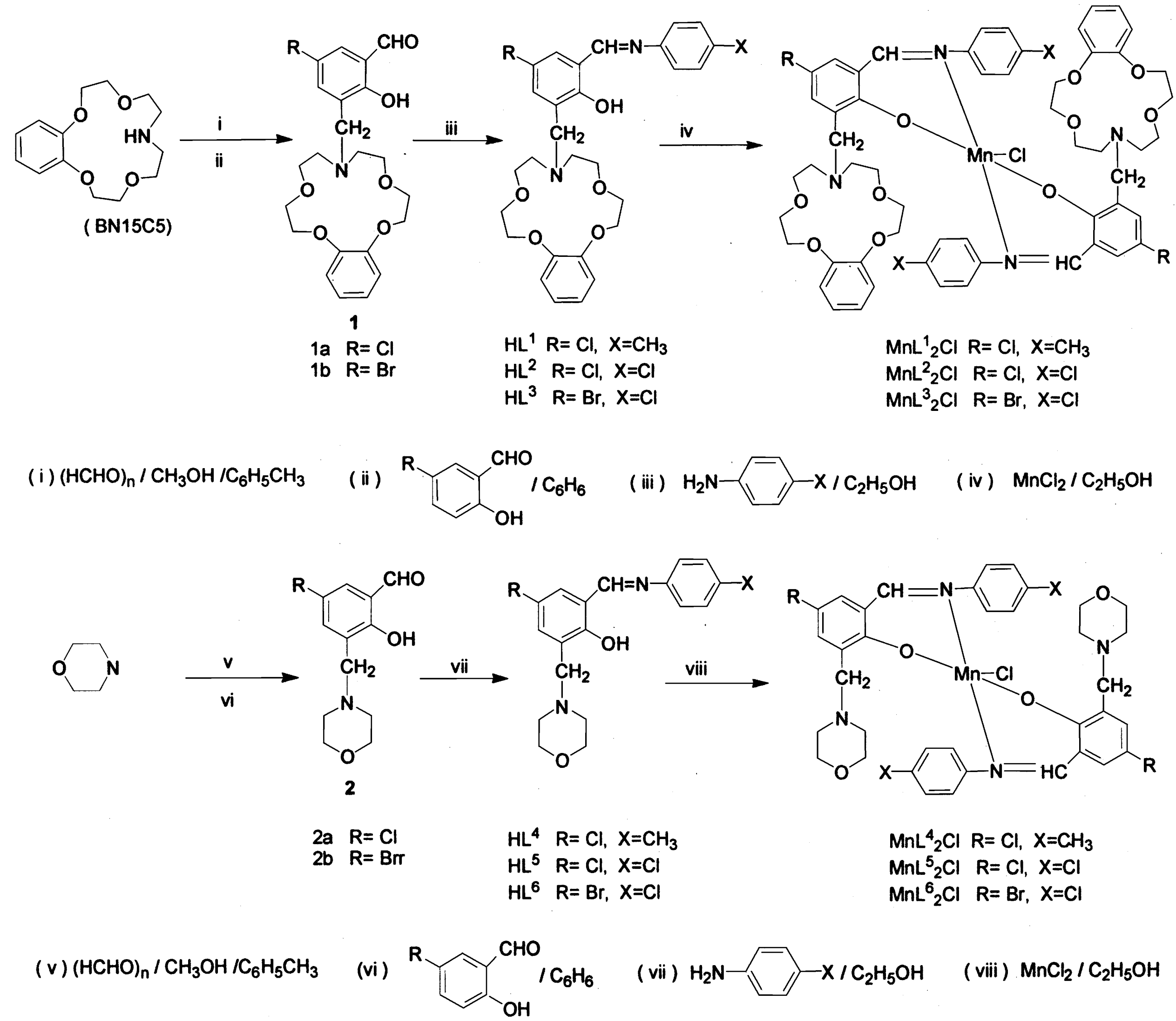


Scheme 1.

uncorrected. I.r. spectra were recorded on a Nicolet-1705X spectrometer. ^{1}H-n.m.r. spectra were recorded on a Bruker AC-200 MHz spectrometer using Me$_4$Si as internal standard. Mass spectra were obtained on a Finnigan LCQ^{-DECA} spectrometer. The metal ion content was measured using an IRIS-Advantage ICP emission spectrometer. Other elementary analyses were performed on a Carlo Erba 1106 elemental analyzer. Molar conductances were obtained on a DDS-11A conductivitimeter. Molar Magnetic Susceptibility was obtained on a magnetic balance T3–200.

Fresh air, paraformaldehyde, morpholino, *p*-xylene and silica gel (60H for TLC, Qingdao, China) were purchased from China. Standard samples of *p*-toluic acid, *p*-tolualdehyde, terephthalic acid and 5-chlorosalicylaldehyde were obtained from Aldrich Co. The following compounds were prepared according to the literature: 5-bromosalicylaldehyde [14] and benzo-10-aza-15-crown-5(BN15C5) [15]. *p*-Xylene was purified prior to use. Other reagents were of analytical grade and were used without further purification.

Synthesis of mono-Schiff base with aza-crown or morpholino pendant and their Mn^{III} complexes

Synthesis of intermediate N-(2-hydroxy-3-formyl-5-chlorobenzyl) benzo-10-aza-15-crown-5 (1a)

A solution of benzo-10-aza-15-crown-5 (5.32 g, 20 mmol), paraformaldehyde (2.0 g) in MeOH (25 cm^3) and PhMe (80 cm^3) was stirred under a N$_2$ atmosphere at 25 °C for 12 h. After the solvent was removed by evaporation, 5-chlorosalicylaldehyde (3.03 g, 0.02 mol) and benzene (80 cm^3) were added. The mixture was refluxed for 12 h in a N$_2$ atmosphere, cooled, and then filtered. The solvent was removed by evaporation and the residual mass was chromatographed on a silica gel column using CH$_2$C1$_2$ as an eluent to give the pure product as a white solid, 7.4 g, yield: 85%, m.p.139–140 °C. ^{1}H-n.m.r (CDCl$_3$) δ: 10.41 (s, 1H, OH, D$_2$O exchangeable), 9.89 (s, 1H, CHO), 7.57–6.89(m, 6H, ArH), 4.16–3.79(m, 14H, OCH$_2$, NCH$_2$Ar), 2.84 (t, $J = 5.3$ Hz, 4H, NCH$_2$). I.r. (KBr, cm^{-1}) ν_{max}: 3455, 2944, 2851, 1658, 1601, 1500, 1256, 1128, 1051; ESI-MS *m/z*: 437 ($M^+ + 1$). (Found C 60.5, H 6.2, N 3.4, Cl 8.0, $C_{22}H_{26}NClO_6$ calcd.: C 60.6, H 6.0, N 3.2, Cl 8.2%).

N-(2-hydroxy-3-formyl-5-bromobenzyl) benzo-10-aza-15-crown-5(1b)

(1b) was prepared as described for (*1a*) to give white crystals, yield: 82%, m.p. 166–168 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 10.44 (s, 1H, OH, D_2O exchangeable), 9.86 (s,1H, CHO), 7.71–6.88 (m, 6H, ArH), 4.16–3.75 (m, 14H, OCH_2 NCH_2Ar), 2.84 (t, $J = 5.2$ Hz 4H, NCH_2); I.r. (KBr, cm^{-1}) ν_{max}: 3448, 2949, 2856, 1656, 1600, 1501, 1255, 1130, 1050; ESI-MS *m/z*: 480 ($M^+ + 1$). (Found C 55.2, H 5.3, N 2.7, Br 16.8. $C_{22}H_{26}NBrO_6$ calcd.: C 55.0, H 5.4, N 2.9, Br 16.7%).

N-(2-hydroxy-3-formyl-5-chlorobenzyl)morpholine (2a)

(2a) was prepared as described for *(1a)* except starting with morpholine instead of BN15C5 to give a buff solid, yield: 75%, m.p. 89–91 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 10.21 (s, 1H, OH, D_2O exchangeable), 9.84 (s, 1H, CHO), 7.75–7.26 (m, 2H, ArH), 3.78–3.69 (m, 6H, OCH_2, NCH_2Ar), 2.59 (t, $J = 5.2$ Hz, 4H, NCH_2); I.r. (KBr, cm^{-1}) ν_{max}: 3439, 2931, 2864, 1654, 1599, 1501, 1290, 1125, 1040; ESI-MS *m/z*: 257 ($M^+ + 1$). (Found C 56.2, H 5.6, N 5.3, Cl 14.0. $C_{12}H_{14}NClO_3$ calcd.: C 56.4, H 5.5, N 5.5, Cl 13.9%).

N-(2-hydroxy-3-formyl-5-bromobenzyl) morpholine (2b)

(2b) was prepared as described for (*1b*) except starting with morpholine instead of BN15C5 to give a buff solid, yield: 71%, m.p. 72–73 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 10.25 (s, 1H, OH, D_2O exchangeable), 9.85 (s, 1H, CHO), 7.73–7.24 (m, 2H, ArH), 3.76–3.68 (m, 6H, OCH_2, NCH_2Ar), 2.57 (t, $J = 5.5$ Hz, 4H, NCH_2); I.r. (KBr, cm^{-1}) ν_{max}: 3440, 2933, 2866, 1657, 1601, 1500, 1288, 1126, 1042; ESI-MS *m/z*: 257 ($M^+ + 1$). (Found C 48.2, H 4.5, N 4.8, Br 26.6. $C_{12}H_{14}NBrO_3$ calcd.: C 48.0, H 4.7, N 4.7, Br 26.7%).

Synthesis of mono-Schiff base ligands HL^1–HL^6

Ligand HL^1

A solution of compound *(1a)* (1.74 g, 4 mmol) and *p*-toluidine (0.43 g, 4 mmol) in EtOH (20 cm^3) was stirred for 4 h under a N_2 atmosphere at 80 °C, and then the mixture was cooled. The resulting yellow precipitate was filtered and washed with EtOH. Upon recrystallization from EtOH, a yellow crystal (1.72 g, yield: 82%) was obtained. M.p. 88–90 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 9.95 (s, 1H, OH, D_2O exchangeable), 8.22 (s, 1H, N=CH 7.57–6.42 (m, 10H, ArH), 4.21–3.71 (m, 14H, OCH_2, NCH_2Ar), 2.84 (t, $J = 5.3$ Hz, 4H, NCH_2), 2.27(s, 3H, CH_3); I.r. (KBr, cm^{-1}) ν_{max}: 3428, 2968, 2862, 1624, 1596, 1503, 1257, 1130, 1050; ESI-MS *m/z*: 526 ($M^+ + 1$). (Found C 66.2, H 6.5, N 5.2, Cl 6.9. $C_{29}H_{33}N_2O_5Cl$ calcd.: C 66.4, H 6.3, N 5.3, Cl 6.8%).

Ligand HL^2

HL^2 was prepared as described for (*HL^1*) except starting with 4-chloroaniline instead of *p*-toluidine to give a yellow solid, yield: 72%, m.p. 95–97 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 9.98 (s, 1H, OH, D_2O exchangeable), 8.19 (s, 1H, N=CH), 7.54–6.42 (m, 10H, ArH), 4.19–3.67 (m, 14H, OCH_2, NCH_2Ar), 2.82 (t, $J = 5.1$ Hz, 4H, NCH_2); I.r. (KBr, cm^{-1}) ν_{max}: 3442, 2933, 2858, 1623, 1600, 1500, 1252, 1131, 1050; ESI-MS *m/z*: 546 ($M^+ + 1$). (Found C 61.8, H 5.3, N 5.3, Cl 13.2. $C_{28}H_{30}N_2O_5Cl_2$ calcd.: C 61.7, H 5.5, N 5.1, Cl 13.0%).

Ligand HL^3

HL^3 was prepared as described for (*HL^2*), except starting with (*1b*) instead of (*1a*), to give a yellow solid, yield: 76%, m.p. 99–101°C. ^{1}H-n.m.r. ($CDC1_3$) δ: 9.96 (s, 1H, OH, D_2O exchangeable), 8.24 (s, 1H, N=CH), 7.60–6.46 (m, 10H, ArH), 4.19–3.67 (m, 14H, OCH_2, NCH_2Ar), 2.82 (t, $J = 5.1$ Hz, 4H, NCH_2); I.r.(KBr, cm^{-1}) ν_{max}: 3444, 2932, 2860, 1623, 1600, 1500, 1252, 1132, 1052; ES-IMS *m/z*: 501($M^+ + 1$). (Found C 57.2, H 5.2, N 5.5, Cl 6.2, Br 13.4. $C_{28}H_{30}N_2O_5ClBr$ calcd.: C 57.0, H 5.1, N 5.6, Cl 6.0, Br 13.6%).

Ligand HL^4

HL^4 was prepared as described for (*HL^1*), except starting with (*2a*) instead of *(1a)*, to give a yellow solid, yield: 80%, m.p. 106–108 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 9.94 (s, 1H, OH, D_2O exchangeable), 8.32 (s, 1H, N=CH), 7.50–6.88 (m, 6H, ArH), 3.73–3.50 (m, 6H, OCH_2, NCH_2Ar), 2.82 (t, $J = 5.5$ Hz, 4H, NCH_2), 2.26 (s, 3H, CH_3); I.r. (KBr, cm^{-l}) ν_{max}: 3439, 2961, 2857, 1621, 1601, 1500, 1252, 1191, 1119; ESI-MS *m/z*: 346 ($M^+ + 1$). (Found C 66.4, H 6.1, N 8.3, Cl 10.1. $C_{19}H_{21}N_2O_2Cl$ calcd.: C 66.2, H 6.1, N 8.1, Cl 10.3%).

Ligand HL^5

HL^5 was prepared as described for (*HL^2*) except starting with *(2a)* instead of *(1a)* to give a yellow solid, yield: 71%, m.p. 101–103 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 9.97(s, 1H, OH, D_2O exchangeable), 8.39 (s, 1H, N=CH), 7.56–6.81 (m, 6H, ArH), 3.70–3.54 (m, 6H, OCH_2, NCH_2Ar), 2.82 (t, $J = 5.3$ Hz, 4H, NCH_2). I.r. (KBr, cm^{-1}) ν_{max}: 3442, 2936, 2854, 1624, 1601, 1502, 1252, 1198, 1119; ESI-MS *m/z*: 366 ($M^+ + 1$). (Found C 59.1, H 4.8, N 7.6, Cl 19.6. $C_{18}H_{18}N_2O_2Cl_2$ calcd.: C 59.2, H 4.9, N 7.7, Cl 19.5%).

Ligand HL^6

HL^6 was prepared as described for (*HL^3*) except starting with *(2b)* instead of *(1b)* to give a yellow solid, yield: 71%, m.p. 112–114 °C. ^{1}H-n.m.r. ($CDC1_3$) δ: 9.99(s, 1H, OH, D_2O exchangeable), 8.35 (s, 1H, N=CH), 7.56–6.86 (m, 6H, ArH), 3.72–3.50 (m, 6H, OCH_2, NCH_2Ar), 2.82 (t, $J = 5.3$ Hz, 4H, NCH_2). I.r.

(KBr, cm^{-1}) ν_{max}: 3444, 2939, 2852, 1622, 1600, 1501, 1253, 1194, 1117; ESI-MS *m*/*z*: 411 (M$^+$ + 1). (Found C 52.9, H 4.2, N 6.7, Cl 8.6, Br 19.4. $C_{18}H_{18}N_2O_2C1Br$ calcd.: C 52.7, H 4.4, N 6.8, Cl 8.7, Br 19.5%).

General method for preparation of manganese complexes

A solution of ligand (2.0 mmol) and $MnC1_2 \cdot 4H_2O$ (1.1 mmol) in EtOH (15 cm^3) was stirred for 2 h under a 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 recrystallization from EtOH.

$\mathrm{MnL^1_2Cl}$: brown, yield: 78%, m.p. 235–237 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2965, 2860, 1610, 1598, 1500, 1253, 1130, 1051; ESI-MS *m*/*z*: 1139 (M$^+$ + 1). (Found C 61.4, H 5.5, N 5.1, Cl 9.6, Mn 4.7. $C_{58}H_{64}N_4O_{10}Cl_3Mn$ calcd.: C 61.2, H 5.6, N 4.9, Cl 9.4, Mn 4.8%). Λ_m (S cm^2 mol^{-1}): 102.76. Molar magnetic susceptibility $\chi_M = 1.06 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.67 \times 10^{-23}$ J T^{-1}.

$\mathrm{MnL^2_2Cl}$: brown, yield: 80%, m.p. 251–253 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2932, 2856, 1612, 1600, 1502, 1250, 1133, 1049; ESI-MS *m*/*z*: 1180 (M$^+$ + 1). (Found C 57.2, H 4.8, N 5.0, Cl 15.2, Mn 4.8. $C_{56}H_{58}N_4O_{10}Cl_5Mn$ calcd.: C 57.0, H 4.9,.N 4.8, Cl 15.1, Mn 4.7%). Λ_m(S cm^2 mol^{-1}): 113.57. Molar magnetic susceptibility. $\chi_M = 1.05 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.64 \times 10^{-23}$ JT^{-1}.

$\mathrm{MnL^3_2Cl}$: brown, yield: 83%, m.p. 179–180 °C; (KBr, cm^{-1}) ν_{max}: 3441, 2930, 2859, 1611, 1601, 1500, 1250, 1131, 1053; ESI-MS *m*/*z*: 1269 (M$^+$ + 1). (Found C 53.2, H 4.7, N 4.6, Cl 8.2, Br 12.5, Mn 4.2. $C_{56}H_{58}N_4O_{10}Cl_3Br_2Mn$ calcd.: C 53.0, H 4.6, N 4.4, Cl 8.4, Br 12.6, Mn 4.3%). Λ_m(S cm^2 mol^{-1}) 117.58. Molar magnetic susceptibility $\chi_M = 1.02 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.62 \times 10^{-23}$ J T^{-1}.

$\mathrm{MnL^4_2Cl}$: brown, yield: 71%, m.p. 193–195 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2961, 2856, 1610, 1601, 1501, 1251, 1189, 1117; ESI-MS *m*/*z*: 779 (M$^+$ + 1). (Found C 58.5, H 5.3, N 7.4, Cl 13.6, Mn 7.2. $C_{38}H_{40}N_4O_4Cl_3Mn$ calcd.: C 58.7, H 5.1, N 7.2, Cl 13.7, Mn 7.1%). Λ_m(S cm^2 mol^{-1}): 115.47. Molar magnetic susceptibility $\chi_M = 1.02 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.58 \times 10^{-23}$ J T^{-1}.

$\mathrm{MnL^5_2Cl}$: brown, yield: 76%, m.p. 218–220 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2935, 2853, 1612, 1601, 1500, 1251, 1196, 1115; ESI-MS *m*/*z*: 820 (M$^+$ + 1). (Found C 52.6, H 4.4, N 6.7, Cl 21.5, Mn 6.9. $C_{36}H_{34}N_4O_4Cl_5Mn$ calcd.: C 52.8, H 4.2; N 6.8, Cl 21.7, Mn 6.7%). Λ_m(S cm^2 mol^{-1}): 118.82. Molar magnetic susceptibility $\chi_M = 9.97 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.52 \times 10^{-23}$ J T^{-1}.

$\mathrm{MnL^6_2Cl}$: brown, yield: 73%, m.p. 221–223 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2938, 2852, 1610, 1600, 1500, 1251, 1195, 1115; ESI-MS *m*/*z*: 909 (M$^+$ + 1). (Found C 47.5, H 3.9, N 6.0, Cl 11.6, Br 17.8, Mn 6.2. $C_{36}H_{34}N_4O_4C1_3Br_2$ Mn calcd.: C 47.6, H 3.8, N 6.2, Cl 11.7, Br 17.6, Mn 6.1%). Λ_m(S cm^2 mol^{-1}): 112.76. Molar magnetic susceptibility $\chi_M = 9.75 \times 10^{-2}$ J mol^{-1} T^{-2} magnetic moment $\mu_m = 4.47 \times 10^{-23}$ J T^{-1}.

General procedure for the oxidation of p-xylene *to p-toluic acid(PTA) with air*

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 analyzed at regular intervals by HPLC (high performance liquid chromatography) (Afilent 1100LC, Hypersil ODS 100 × 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.

Results and discussion

Synthesis

Compared with the i.r. spectra of the ligand, those of complexes were almost at the same frequency, except for the C=N stretching vibration shifted 10–12 cm^{-1} to lower frequency and its intensity was greater than that of free ligand. Moreover the absence of OH stretching vibration (~3440 cm^{-1}) in the complexes indicated deprotonation of OH in the ligand after complexes formation. This indicated the formation of a N–O···Mn coordination bond; while the C–O–C stretching vibrations in the crown ether ring for the complexes were almost at the same frequency. These facts indicate that manganese ion only interacts with the Ar–OH and CH=N groups [16]. 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 [17]. The molar magnetic susceptibility χ_M and magnetic moment μ_m of all complexes indicated that manganese has four non-paired electrons. Combining this phenomenon with the results of the molar conductances and magnetic moments of the complexes indicates that manganese in the complexes is trivalent. The ESI-MS Mass spectra and elemental analysis of the complexes indicated that HL^1–HL^6 formed 2:1(ligand/metal) complexes (ML_2), respectively. The facts above showed that Schiff base ligands can coordinate with manganese ion as in Scheme 1.

Oxidation of p-xylene

The oxidation of *p*-xylene to PTA was carried out by using $\mathrm{Mn^{III}}$ Schiff base complexes as catalyst (Scheme 2).

The plot of the accumulated content of PTA *vs.* reaction time (Figure 1) indicated that the induction periods required for initiating the oxidation of *p*-xylene catalyzed by the aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes (~6.0 h for $\mathrm{MnL^1_2Cl}$, $\mathrm{MnL^2_2Cl}$ and $\mathrm{MnL^3_2Cl}$) are shorter than those for the oxidation of *p*-xylene catalyzed by the morpholino $\mathrm{Mn^{III}}$ Schiff base complexes (~8.0 h for $\mathrm{MnL^4_2Cl}$, $\mathrm{MnL^5_2Cl}$ and $\mathrm{MnL^6_2Cl}$). The time taken for PTA to reach the maximum concentration during the oxidation of *p*-xylene catalyzed by the aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes is also shorter than that for morpholino $\mathrm{Mn^{III}}$ Schiff base complexes. This observation could be due to macrocycle effect of the crown ether ring that probably facilitates the oxygen molecule to approach the coordination center of the aza-crown Schiff base $\mathrm{Mn^{III}}$ complexes. This may be due to the presence of the aza-crown ring which can control efficiently the microenvironment of the active center owing to its hydrophobicity of the outer ethylene groups and orderly arrangement of inner oxa atoms. The previous studied results [18] show that the X-ray crystal structure of aza crown substituted salicylaldimine Schiff base ligand suggest the aza crown ether ring does close nearer to the coordination group compared to the benzo-crown ring, and the molecular structure of its complexes can be compared to that of a flying bird where the two aza-crown ether rings resemble the wings that extend from the coordination center. This indicated that the aza crown ether ring does control more efficiently the coordination environment.

Moreover, as shown in Table 1, it can be seen that the selectivities for the oxidation product PTA, conversion and turnover frequency (TOF) for the oxidation of *p*-xylene catalyzed by the aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes are also excellent by comparison with those of the oxidation of *p*-xylene catalyzed by the morpholino $\mathrm{Mn^{III}}$ Schiff base complexes. Although the conversion for the oxidation of *p*-xylene catalyzed by the aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes is lower than that of other inorganic catalysts, the selectivity (up to ~90%) for the oxidation product PTA is higher than that of other inorganic catalysts, and the reaction condition for the oxidation of *p*-xylene catalyzed by the aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes is milder than that of other inorganic catalysts [3, 4]. Comparing the catalytic oxidation activities of aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes, the effect of substituents group of aromatic ring on the oxidation seems to be small, and the same phenomenon was also observed for the morpholino $\mathrm{Mn^{III}}$ Schiff base complexes.

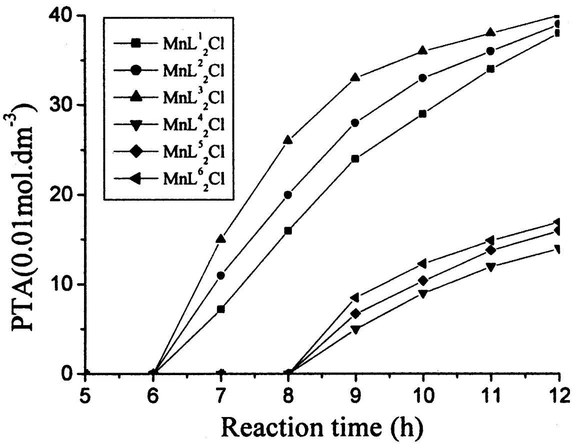
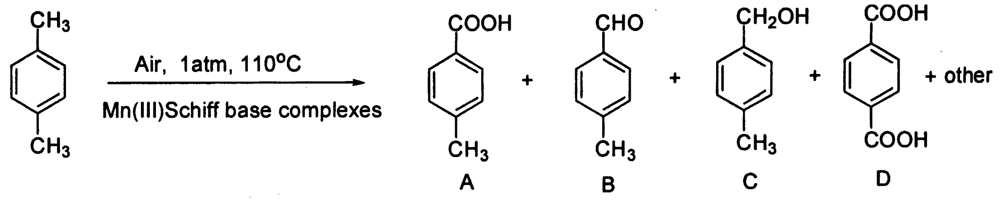


Fig. 1. Accumulated content of PTA plotted against reaction time.

It is interesting that the addition of alkali metal nitrate (nitrate/ $\mathrm{MnL_2Cl}$ = 2:1 mol/mol) can enhance the catalytic activity of aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes (see Table 2), where the TOF values were significantly improved. On the contrary, the above phenomenon was not observed when $\mathrm{NaNO_3}$ was added to the morpholino $\mathrm{Mn^{III}}$ Schiff base complexes. This may be because the dimension of the alkali metal $\mathrm{Na^+}$ (d = 0.19 nm) matched well with that of crown ring (N–15–C–5) cavity (d = 0.17 ~0.22 nm) [19] and was located near to the coordination center. Moreover, the positive charge of $\mathrm{Na^+}$ may enable the molecular oxygen to be activated more easily.

Conclusion

In this paper, novel mono-Schiff base $\mathrm{Mn^{III}}$ complexes with penadant aza-crown or morpholino have been synthesized and studied as catalysts in aerobic oxidation of *p*-xylene to *p*-toluic acid. Significant selectivity



Scheme 2.

Table 1. $\mathrm{Mn^{III}}$ Schiff base complexes catalytic oxidation of *p*-xylene to PTA[a]

Catalyst	Induction Period (h)	Convn. (wt%)	TOF	Selectives for products[b] A	B	C	D	Others
$\mathrm{MnL^1_2Cl}$	7.1 h	38	253	90.4	2.1	2.7	1.1	3.7
$\mathrm{MnL^2_2Cl}$	6.5 h	39	260	88.9	3.4	3.2	1.7	2.8
$\mathrm{MnL^3_2Cl}$	6.0 h	40	269	89.3	2.8	2.2	1.1	4.6
$\mathrm{MnL^4_2Cl}$	8.7 h	14	93	82.6	3.7	5.6	1.1	7.0
$\mathrm{MnL^5_2Cl}$	8.5 h	16	107	80.8	5.7	3.2	1.8	7.5
$\mathrm{MnL^6_2Cl}$	8.2 h	17	11.4	80.7	5.6	5.2	1.3	7.2

[a] Condition: *p*-xylene: 15 $\mathrm{cm^{-3}}$ (1.21×10^{-1} mol); $\mathrm{Mn^{III}}$-Schiff base complexes: 1.0×10^{-3} mol $\mathrm{dm^{-3}}$; flow rate for air: 2.4 l $\mathrm{h^{-1}}$; Reaction temp.: 120 °C; Reaction time: 12 h. [b] Ligand: A = *p*-toluic acid; B = *p*-tolyl alchol; C = *p*-tolualdehyde; D = terepthalic acid; TOF = Turnover frequency (mol *p*-xylene converted per mol catalyst per h).

Table 2. Effect of addition of alkali metal nitrate on $\mathrm{Mn^{III}}$ Schiff base complexes catalytic oxidation for *p*-xylene to PTA[a]

Catalyst	Convn. (wt%)	TOF	Selectives for Products[b] A	B	C	D	Others
$\mathrm{NaNO_3}$	0	0	0	0	0	0	0
$\mathrm{MnL^1_2Cl + LiNO_3}$	47	316	91.6	2.5	2.7	1.6	1.6
$\mathrm{MnL^1_2Cl + NaNO_3}$	55	370	92.1	2.2	2.4	1.4	1.9
$\mathrm{MnL^1_2Cl + KNO_3}$	49	329	91.3	2.3	2.8	2.1	1.5
$\mathrm{MnL^2_2Cl + LiNO_3}$	47	316	90.5	2.6	2.9	2.1	1.9
$\mathrm{MnL^2_2Cl + NaNO_3}$	56	376	92.5	1.9	2.0	1.8	1.8
$\mathrm{MnL^2_2Cl + KNO_3}$	51	343	91.9	2.4	1.2	2.3	2.2
$\mathrm{MnL^3_2Cl + LiNO_3}$	48	323	91.5	2.3	2.1	2.3	1.8
$\mathrm{MnL^3_2Cl + NaNO_3}$	58	390	93.6	1.4	1.9	1.5	1.6
$\mathrm{MnL^3_2Cl + KNO_3}$	50	336	91.4	2.1	1.8	2.5	2.2
$\mathrm{MnL^4_2Cl + LiNO_3}$	15	101	83.8	3.2	5.3	1.1	6.6
$\mathrm{MnL^4_2Cl + NaNO_3}$	16	108	84.1	3.5	4.9	1.9	5.6
$\mathrm{MnL^4_2Cl + KNO_3}$	16	108	84.4	2.9	4.6	2.3	5.8
$\mathrm{MnL^5_2Cl + LiNO_3}$	17	114	83.8	4.7	2.6	2.4	6.5
$\mathrm{MnL^5_2Cl + NaNO_3}$	18	121	82.9	3.7	4.4	3.6	5.4
$\mathrm{MnL^5_2Cl + KNO_3}$	19	128	83.1	4.1	3.8	3.2	5.8
$\mathrm{MnL^6_2Cl + LiNO_3}$	17	107	82.6	4.6	5.1	2.2	5.5
$\mathrm{MnL^6_2Cl + NaNO_3}$	19	128	83.5	3.6	4.9	2.9	5.1
$\mathrm{MnL^6_2Cl + KNO_3}$	19	128	84.1	3.1	4.3	3.1	5.4

[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 = terephthalic acid; TOF = Turnover frequency (mol *p*-xylene converted per mol catalyst per h).

(up to ~90%) and conversion levels (up to ~38%) were obtained. The study demonstrates that selective oxidation of *p*-xylene to *p*-toluic acid can successfully occur in the presence of aza-crown $\mathrm{Mn^{III}}$ Schiff base complexes, which display a much better catalytic activity than the morpholino $\mathrm{Mn^{III}}$ Schiff base complexes do. The crown ether–alkali metal complementarity can improve the conversion and TOF of the oxidation of *p*-xylene. Further studies into the mechanism and scope of this catalytic oxidation are now underway in our laboratory.

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