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Synthesis and Study of Unsymmetrical Schiff Base Mn(III) Complexes with Pendant Aza-crown or Morpholino Groups as Catalyst in Aerobic Oxidation for *p*-Xylene to *p*-Toluic Acid

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A series of novel unsymmetrical 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 (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 aza-crown ring appended in Mn(III) Schiff base complexes on the oxidation of *p*-xylene were also investigated by comparison with the morpholino group pendant analogues. The addition of alkali metal ions accelerates the rate of conversion of *p*-xylene to *p*-toluic acid.

Keywords: Synthesis; Benzo-10-aza-15-crown-5; Unsymmetrical salicylaldimine bis-Schiff base; Aerobic oxidation; *p*-Xylene

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 $Co(C_{18}H_{35}O_2)_2$(cobalt stearate)/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 acid using $Co(OAc)_2$/$Mn(OAc)_2$/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 corrosive nature of the by-products using above the catalyst system, many researchers have been working hard to develop highly efficient and selective catalysts for the oxidation of *p*-xylene to *p*-toluic acid for achieving environmentally friendly and high-economy processes. 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 infrequent [7,8]. Many studies already identified that 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 [11,12]. Herein, as part of a research program aimed at studying the effects of the aza-crown ether group appended in Mn(III) Schiff base complexes and the addition of alkali metal ions into the reactive system on the catalytic oxidation performance of *p*-xylene, we have synthesized a series of novel unsymmetrical Schiff base Mn(III) complexes with pendent aza-crown or morpholino groups and reported the homogeneous direct catalytic oxidation of *p*-xylene to *p*-toluic acid

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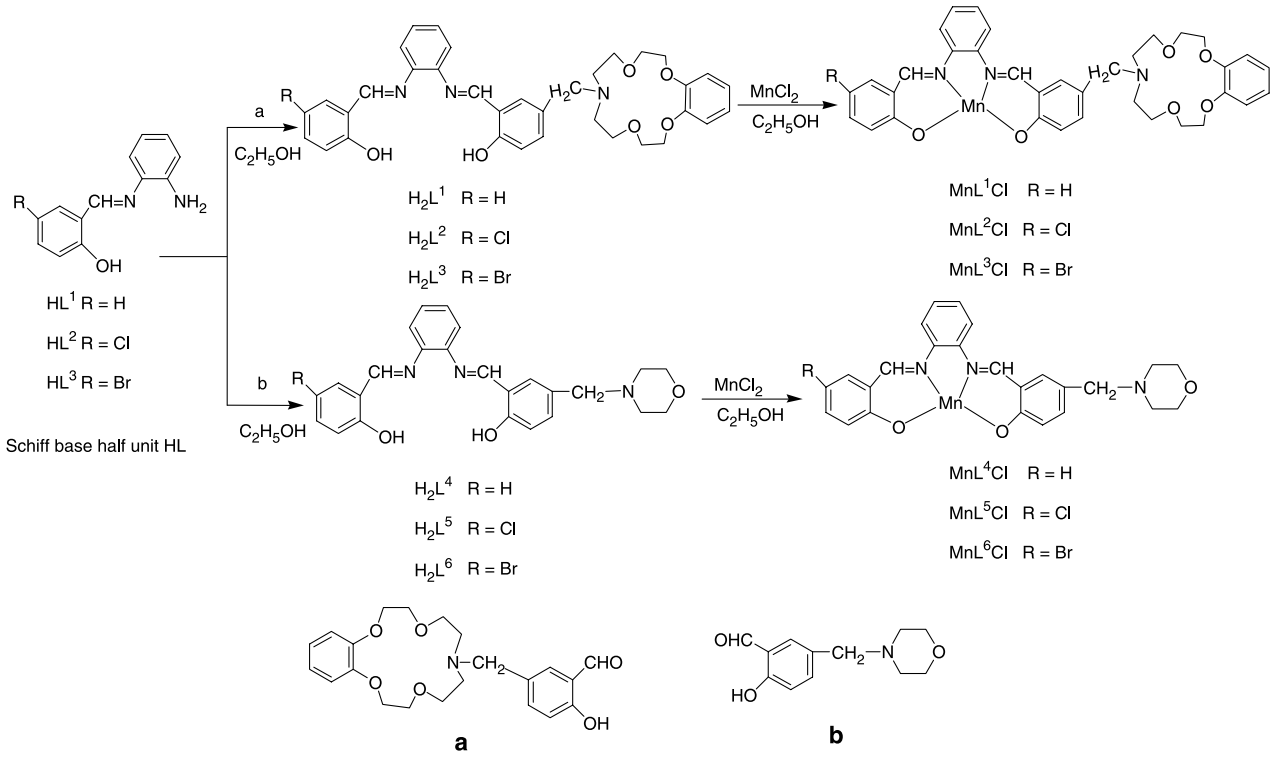


SCHEME 1 The route for the synthesis and structure of unsymmetrical Schiff base complexes.

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 uncorrected. IR spectra were recorded on a Nicolet-1705X spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-200 MHz spectrometer using Me_4Si 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. The halogen analysis was measured using mercury titration method [13,14], 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.

Salicylaldehyde, 1,2-phenylenediamine, fresh air and *p*-xylene were purchased from China. Standard samples of *p*-toluic acid, *p*-tolualdehyde, terephthalic acid, 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde were obtained from Aldrich Co. The following compounds were prepared according to the literature [15]: N-(3-firmyl-4-hydroxylbenzyl)-benzo-10-aza-15 -crown-5(*a*), N-(3-firmyl-4-hydroxylbenzyl)morpholine(*b*). *p*-Xylene was purified prior to use. Other reagents were of analytical grade and were used without further purification.

Synthesis of Unsymmetrical Schiff Base with Pendant Aza-crown or Morpholino Groups and their Mn(III) Complexes

Synthesis of Schiff Base Half Unit HL^1

To the vigorously stirred and cool dilute solution of 1,2-phenylenediamine (5.40 g, 50 mmol) in anhydrous CH_2Cl_2 (100 mL), was added dropwise a cooled solution of salicylaldehyde (5.0 mL, 50 mmol) in anhydrous CH_2Cl_2 (50 mL) for 2 h at 0°C, then the mixture was stirred for 6 h. The resulting solution was evaporated in vacuum to remove the solvent until a solid precipitated. The product was filtered and washed with ethanol, dried in vacuum to give yellow solid, 8.5 g, yield 80%, m.p. 69–70.5°C. ^{1}H NMR($CDCl_3$) δ: 12.83 (s, 1H, OH, D_2O exchange), 8.43 (s,1H, CH═N), 7.47–6.74 (m, 8H, ArH), 3.15 (br, 2H, NH_2); IR (KBr, film) ν_{max}: 3291, 3191, 1634, 1598, 1502; ESI-MS (m/z): 213 ($M^+ + 1$); Anal. calcd for $C_{13}H_{12}N_2O$: C, 73.58; H, 5.66; N, 13.21; found: C, 73.39; H, 5.75; N, 13.04%.

Half Unit HL^2

HL ^{2} was prepared as described for *HL* ^{1} except staring with 5-Chlorosalicylaldehyde instead of

salicylaldehyde to give yellow solid, yield 85%, m.p. 113–115°C. ^{1}H NMR($CDCl_3$) δ: 12.95 (s, 1H, OH, D_2O exchange), 8.49 (s,1H, CH═N), 7.55–6.87 (m, 7H, ArH), 3.10 (br, 2H, NH_2); IR (KBr, film) ν_{max}: 3341, 3208, 1630, 1603, 1500; ESI-MS (m/z): 248 ($M^+ + 1$); Anal. calcd for $C_{13}H_{11}N_2ClO$: C, 63.29; H, 4.46; N, 11.36; Cl, 14.40; found: C, 63.41; H, 4.28; N, 11.54; Cl, 14.22%.

Half Unit HL[3]

HL [3] was prepared as described for *HL* [1] except staring with 5-bromosalicylaldehyde instead of salicylaldehyde to give yellow solid, yield 83%, m.p. 124–126°C. ^{1}H NMR($CDCl_3$) δ: 13.14 (s, 1H, OH, D_2O exchange), 8.56 (s, 1H, CH═N), 7.59–6.74 (m, 7H, ArH), 3.15 (br, 2H, NH_2); IR (KBr, film) ν_{max}: 3365, 3213, 1631, 1604, 1500; ESI-MS (m/z): 292 ($M^+ + 1$); Anal. calcd for $C_{13}H_{11}N_2BrO$: C, 53.61; H, 3.78; N, 9.62; Br, 27.49; found: C, 53.46; H, 3.91; N, 9.53; Br, 27.33%.

Synthesis of Unsymmetrical Schiff Base Ligands H_2L^1-H_2L^6

Ligand H_2L^1

A solution of the precursor half unit (*HL* [1]) (2.12 g, 10 mmol) and N-(3-firmyl-4-hydroxylbenzyl)- benzo-10-aza-15-crown-5(*a*) (4.01 g, 10 mmol) in anhydrous EtOH(40 mL) was stirred for 4 h under N_2 atmosphere at 80°C, and then the mixture was cooled. The yellow precipitate was filtered and washed with EtOH. After recrystallization from EtOH, yellow crystal (4.46 g, yield 75%) was obtained. m.p. 90–92°C. ^{1}H NMR($CDCl_3$) δ: 12.92 (s, 2H, OH, D_2O exchange), 8.58 (s, 1H, N═CH), 8.46 (s, 1H, N═CH), 7.57–6.82 (m, 15H, ArH), 4.16–3.72 (m, 14H, OCH_2, NCH_2Ar), 2.83 (t, $J = 5.6$ Hz, 4H, NCH_2); IR (KBr, film) ν_{max}: 3224, 2938, 2864,1616,1600,1500, 1256, 1126, 1050, 930 cm^{-1}; ESI-MS m/z: 596 ($M^+ + 1$); Anal. calcd. for $C_{35}H_{37}N_3O_6$: C, 70.59; H, 6.22; N, 7.06; found: C, 70.45; H, 6.35; N, 6.91%.

Ligand H_2L^2

H_2L^2 was prepared as described for H_2L^1 except staring with half unit (*HL* [2]) instead of *HL* [1] to give yellow solid, yield 72%, m.p.106–108°C. ^{1}H NMR($CDCl_3$) δ: 12.95 (s, 2H, OH, D_2O exchange), 8.60 (s, 1H, N═CH), 8.49 (s, 1H, N═CH), 7.66–6.89 (m, 14H, ArH), 4.13–3.71 (m, 14H, OCH_2, NCH_2Ar), 2.81 (t, $J = 5.3$ Hz, 4H, NCH_2); IR (KBr, film) ν_{max}: 3226, 2927, 2861, 1617, 1600, 1502, 1256, 1128, 1052, 926 cm^{-1}; ESI-MS m/z: 631 ($M^+ + 1$); Anal. calcd. for $C_{35}H_{36}N_3O_6Cl$: C, 66.72; H, 5.72; N, 6.67; Cl, 5.64; found: C, 66.58; H, 5.85; N, 6.81; Cl, 5.45%.

Ligand H_2L^3

H_2L^3 was prepared as described for H_2L^1 except staring with half unit (*HL* [3]) instead of *HL* [1] to give yellow solid, yield 77%, m.p. 99–101°C. ^{1}H NMR($CDCl_3$) δ: 13.05 (s, 2H, OH, D_2O exchange), 8.62 (s, 1H, N═CH), 8.44 (s, 1H, N═CH), 7.68–6.81 (m, 14H, ArH), 4.10–3.74 (m, 14H, OCH_2, NCH_2Ar), 2.84 (t, $J = 5.5$ Hz, 4H, NCH_2); IR (KBr, film) ν_{max}: 3230, 2929, 2866, 1615, 1601, 1501, 1254, 1130, 1051, 929 cm^{-1}; ESI-MS m/z: 675 ($M^+ + 1$); Anal. calcd. for $C_{35}H_{36}N_3O_6Br$: C, 62.31; H, 5.34; N, 6.23; Br, 11.87; found: C, 62.48; H, 5.16; N, 6.09; Br, 11.98%.

Ligand H_2L^4

H_2L^4 was prepared as described for (H_2L^1) except staring with N-(3-firmyl-4-hydroxylbenzyl)morpholine(*b*) instead of N-(3-firmyl-4-hydroxylbenzyl)-benzo -10-aza-15-crown-5(*a*) to give a yellow solid, yield 75%, m.p.140–142°C. ^{1}H NMR ($CDCl_3$) δ: 12.97 (s, 2H, OH, D_2O exchange), 8.61 (s, 1H, N═CH), 8.48 (s, 1H, N═CH), 7.50–6.97 (m, 11H, ArH), 3.71–3.49 (m, 6H, OCH_2, NCH_2Ar), 2.68 (t, $J = 5.2$ Hz, 4H, NCH_2); IR (KBr, film) ν_{max}: 3249, 2932, 2854, 1614, 1600, 1502, 1275, 1192, 1042 cm^{-1}; ESI-MS m/z: 416 ($M^+ + 1$); Anal. calcd. for $C_{25}H_{25}N_3O_3$: C, 72.30; H, 6.02; N, 10.12; found: C, 72.46; H, 5.85; N, 10.93%.

Ligand H_2L^5

H_2L^5 was prepared as described for (H_2L^4) except staring with half unit (*HL* [2]) instead of *HL* [1] to give yellow solid, yield 71%, m.p. 188–190°C. ^{1}H NMR ($CDCl_3$) δ: 12.96 (s, 2H, OH, D_2O exchange), 8.58 (s, 1H, N═CH), 8.44 (s, 1H, N═CH), 7.50–6.86 (m, 10H, ArH), 3.73–3.46 (m, 6H, OCH_2, NCH_2Ar), 2.66 (t, $J = 5.3$ Hz, 4H, NCH_2); IR (KBr, film) ν_{max}: 3245, 2927, 2851, 1615, 1598, 1502, 1274, 1188, 1040 cm^{-1}; ESI-MS m/z: 451 ($M^+ + 1$); Anal. calcd. for $C_{25}H_{24}N_3O_3Cl$: C, 66.74; H, 5.34; N, 9.34; Cl, 7.90; found: C, 66.56; H, 5.52; N, 9.12; Cl, 7.99%.

Ligand H_2L^6

H_2L^6 was prepared as described for (H_2L^4) except staring with half unit (*HL* [3]) instead of *HL* [1] to give yellow solid, yield 78%, m.p. 175–177°C. ^{1}H NMR($CDCl_3$) δ: 12.99 (s, 2H, OH, D_2O exchange), 8.53 (s, 1H, N═CH), 8.41 (s, 1H, N═CH), 7.56–6.89 (m, 10H, ArH), 3.70–3.47 (m, 6H, OCH_2, NCH_2Ar), 2.69 (t, $J = 5.2$ Hz, 4H, NCH_2); IR (KBr, film) ν_{max}: 3238, 2932, 2854, 1614, 1596, 1500, 1271, 1192, 1042 cm^{-1}; ESI-MS m/z: 495 ($M^+ + 1$); Anal. calcd. for $C_{25}H_{24}N_3O_3Br$: C, 60.73; H, 4.86; N, 8.50; Br, 16.19; found: C, 60.57; H, 5.02; N, 8.32; Br, 16.37%.

General Methods for Preparation of Manganese Complexes

A solution of ligand (1.0 mmol) and $MnCl_2.4H_2O$ (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.

MnL^{1}Cl: Brown, 78% yield, m.p. 241–243°C. IR (KBr, film) ν_{max}: 2935, 2862, 1607, 1603, 1492, 1255, 1127, 1050, 932 cm^{-1}; ESI-MS m/z: 685 ($M^+ + 1$); Anal. calcd. for $C_{35}H_{35}N_3ClO_6Mn$: C, 61.45; H, 5.12; N, 6.14; Cl, 5.19; Mn, 8.05; found: C, 61.30; H, 5.31; N, 6.29; Cl, 5.04; Mn, 8.28; Λ_m(S·cm^2·mol^{-1}): 114.50. Molar magnetic susceptibility $\chi_M = 1.06 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.66 \times 10^{-23}$ J T^{-1}.

MnL^{2}Cl: Brown, 74% yield, m.p. >300°C. IR (KBr, film) ν_{max}: 2925, 2864, 1606, 1600, 1501, 1253, 1129, 1051, 930 cm^{-1}; ESI-MS m/z: 719 ($M^+ + 1$); Anal. calcd. for $C_{35}H_{34}N_3Cl_2O_6Mn$: C, 58.50; H, 4.74; N, 5.85; Cl, 9.89; Mn, 7.66; found: C, 58.31; H, 4.91; N, 5.69; Cl, 9.84; Mn, 7.83; Λ_m(S·cm^2 mol^{-1}): 111.82. Molar magnetic susceptibility $\chi_M = 1.11 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.67 \times 10^{-23}$ J T^{-1}.

MnL^{3}Cl: Brown, 74% yield, m.p. 210 ~ 211°C. IR (KBr, film) ν_{max}: 2927, 2864, 1605, 1601, 1502, 1254, 1130, 1053, 926 cm^{-1}; ESI-MS m/z: 764 ($M^+ + 1$); Anal. calcd. for $C_{35}H_{34}N_3ClBrO_6Mn$: C, 55.08; H, 4.46; N, 5.51; Cl, 4.66; Br, 10.49; Mn, 7.21; found: C, 55.25; H, 4.31; N, 5.46; Cl, 4.84; Br, 10.38; Mn, 7.38; Λ_m(S·cm^2·mol^{-1}): 115.72. Molar magnetic susceptibility $\chi_M = 1.03 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.60 \times 10^{-23}$ J T^{-1}.

MnL^{4}Cl: Brown, 71% yield, m.p. 256–258°C. IR (KBr, film) ν_{max}: 2928, 2856, 1606, 1600, 1500, 1271, 1193, 1040 cm^{-1}; ESI-MS m/z: 505 ($M^+ + 1$); Anal. calcd. for $C_{25}H_{23}N_3O_3ClO_3Mn$: C, 59.28; H, 4.57; N, 8.34; Cl, 7.05; Mn, 10.92; found: C, 59.45; H, 4.39; N, 8.17; Cl, 7.24; Mn, 10.78; Λ_m(S·cm^2·mol^{-1}): 105.89. Molar magnetic susceptibility $\chi_M = 9.81 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.49 \times 10^{-23}$ J T^{-1}.

MnL^{5}Cl: Brown, 75% yield, m.p. 274–276°C. IR (KBr, film) ν_{max}: 2925, 2851, 1606, 1600, 1500, 1271, 1186, 1043 cm^{-1}; ESI-MS m/z: 539 ($M^+ + 1$); Anal. calcd. for $C_{25}H_{22}N_3Cl_2O_3Mn$: C, 55.76; H, 4.09; N, 7.81; Cl, 13.20; Mn, 10.22; found: C, 55.58; H, 4.26; N, 7.67; Cl, 13.29; Mn, 10.08; Λ_m(S·cm^2·mol^{-1}): 114.81. Molar magnetic susceptibility $\chi_M = 1.00 \times 10^{-1}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.53 \times 10^{-23}$ J T^{-1}.

MnL^{6}Cl: Brown, 78% yield, m.p. >300°C. IR (KBr, film) ν_{max}: 2928, 2855, 1606, 1599, 1500, 1272, 1194, 1044 cm^{-1}; ESI-MS m/z: 583 (M^+); Anal. calcd. for $C_{25}H_{22}N_3ClBrO_3Mn$: C, 51.50; H, 3.78; N, 7.21; Cl, 6.09, Br, 13.73; Mn, 9.44; found: C, 51.38; H, 3.86; N, 7.39; Cl, 6.21; Br, 13.86; Mn, 9.53; Λ_m(S·cm^2·mol^{-1}): 108.32. Molar magnetic susceptibility $\chi_M = 9.49 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 4.41 \times 10^{-23}$ J T^{-1}.

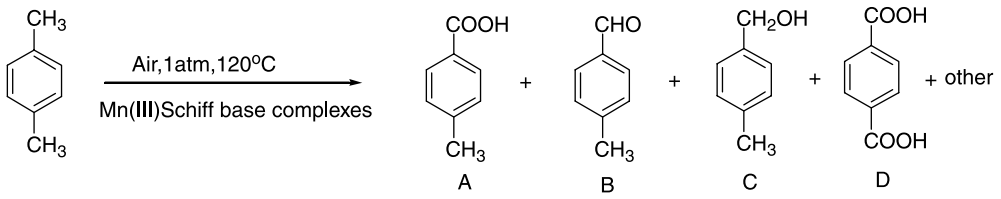
General Procedure for the Oxidation of p-Xylene to p-Toluic Acid (PTA) with Air

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 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.

RESULTS AND DISCUSSION

Synthesis

The Schiff base half units (HL^1–HL^3), which were synthesized via mono condensation of 1,2-phenylenediamine and salicylaldehyde or substituted salicylaldehyde by controlling reaction condition, were the key intermediate for synthesis of unsymmetrical salicylaldimine bis-Schiff bases. Unsymmetrical bis-Schiff base ligands (H_2L^1–H_2L^6) were conveniently prepared by the reaction of the Schiff base half units with crown ether-functionalized salicylaldehyde or morpholino-functionalized salicylaldehyde and characterized by IR, ^{1}H NMR, Mass spectroscopy and elemental analysis. Compared with the IR spectra of the ligands, these complexes have almost similar spectra, except for the C=N stretching vibration which shifted slightly (8–11 cm^{-1}) to lower frequency and its intensity was greater than that of free ligand. Moreover, the characteristic vibration of Ar-OH at ~3230 cm^{-1} disappeared, but the C-O-C stretching vibrations did not change after complexes formed. These facts indicate 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 **H_2L^1–H_2L^6** formed 1:1 (ligand/metal) complexes, respectively. The above-mentioned facts showed that Schiff base ligand can coordinate with manganese ion as in Scheme 1.



SCHEME 2 The oxidation of p-xylene to p-toluic acid catalyzed by Mn(III) Schiff base complexes.

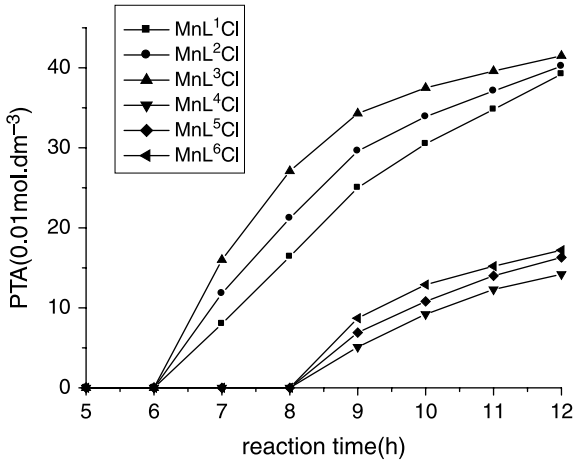


FIGURE 1 Accumulated content of PTA plotted against reaction time.

Oxidation of p-Xylene

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

The plot of the accumulated content of PTA *vs.* reaction time (Fig. 1) indicated that the induction periods required for initiating the oxidation of *p*-xylene catalyzed by the aza-crown Mn(III) Schiff base complexes (~6.0 h for MnL^1Cl, MnL^2Cl and MnL^3Cl) are shorter than those for the oxidation of *p*-xylene catalyzed by the morpholino Mn(III) Schiff base complexes (~8.0 h for MnL^4Cl, MnL^5Cl and MnL^6Cl). The time for PTA to reach the maximum concentration during the oxidation of *p*-xylene catalyzed by the aza-crown Mn(III) Schiff base complexes is also shorter than that for morpholino Mn(III) Schiff base complexes. This may be due to the presence of the aza-crown ring which can control more efficiently the microenvironment of the active center than morpholino group owing to crown ring's hydrophobicity of the outer ethylene groups and orderly arrangement of inner oxa atoms and facilitate the oxygen molecule to approach the coordination center of the aza-crown Schiff base Mn(III) complexes [16].

Moreover, as shown in Table I, it can be seen that the selectivity for PTA, conversion and turnover frequency (TOF) for the oxidation of *p*-xylene catalyzed by the Schiff base Mn(III) complexes with pendant aza-crown group are also more excellent than those of the oxidation of *p*-xylene catalyzed by the morpholino Mn(III) Schiff base complexes analogues. Although the conversion (~40%) for the oxidation of *p*-xylene catalyzed 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 condition for the oxidation of *p*-xylene catalyzed by the aza-crown Mn(III) Schiff base complexes is milder than that of other inorganic catalysts [3,4]. Comparing the catalytic oxidation activities of Schiff base Mn(III) complexes with pendant aza-crown group, the effect of substituent group of aromatic ring on the oxidation of *p*-xylene seems small, and the same phenomenon was also observed for the Schiff base Mn(III) complexes with pendant morpholino group.

Table II also shows that the addition of alkali metal nitrate (nitrate/MnL^nCl = 2:1 mol/mol) can enhance the catalytic activity of Schiff base Mn(III) complexes

TABLE I Mn(III) Schiff base complexes catalytic oxidation for p-xylene to PTA[†]

					Selectivity for products[‡]				
Entry	Catalyst	Induction period (h)	Convn. (wt %)	TOF	A	B	C	D	others
1	MnL^1Cl	5.8 h	38	255	89.4	2.1	2.5	2.7	3.3
2	MnL^2Cl	6.2 h	39	262	90.2	1.9	4.1	0.9	2.9
3	MnL^3Cl	6.0 h	44	296	88.9	2.5	2.0	2.8	3.8
4	MnL^4Cl	8.9 h	13	87	84.4	2.8	4.8	2.1	5.9
5	MnL^5Cl	9.1 h	16	108	82.5	3.2	3.6	3.0	6.7
6	MnL^6Cl	9.0 h	15	101	86.0	4.3	3.9	2.0	3.8

[†] Condition: 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: 2.4 L L^{-1} h^{-1}; Reaction temp.: 120°C; Reaction time: 12 h.
[‡] 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 hour).

TABLE II Effect of addition of alkali metal nitrate on Mn(III) Schiff base complexes catalytic oxidation for *p*-xylene to PTA[†]

Entry	Catalyst	Convn. (wt %)	TOF	Selectivity for products[‡]				
				A	B	C	D	others
1	$NaNO_3$	0	0	0	0	0	0	0
2	$MnL^1Cl + LiNO_3$	45	302	91.6	2.3	2.8	1.7	1.6
3	$MnL^1Cl + NaNO_3$	57	383	92.9	1.9	2.2	1.3	1.7
4	$MnL^1Cl + KNO_3$	47	316	92.3	1.9	2.3	2.0	1.5
5	$MnL^2Cl + LiNO_3$	47	316	90.9	2.4	2.8	2.1	1.8
6	$MnL^2Cl + NaNO_3$	59	396	92.8	1.9	1.8	1.7	1.7
7	$MnL^2Cl + KNO_3$	51	343	91.9	2.4	1.2	2.3	2.2
8	$MnL^3Cl + LiNO_3$	49	329	91.5	2.3	2.1	2.5	1.6
9	$MnL^3Cl + NaNO_3$	60	403	93.5	1.6	1.8	1.5	1.6
10	$MnL^3Cl + KNO_3$	51	343	91.3	2.2	1.6	2.5	2.4
11	$MnL^4Cl + LiNO_3$	14	94	83.6	3.3	5.4	1.3	6.4
12	$MnL^4Cl + NaNO_3$	15	101	84.5	3.3	4.8	2.1	5.3
13	$MnL^4Cl + KNO_3$	15	101	84.4	2.6	4.7	2.6	5.7
14	$MnL^5Cl + LiNO_3$	16	108	83.7	4.7	2.4	2.4	6.8
15	$MnL^5Cl + NaNO_3$	18	121	83.2	3.5	4.4	3.5	5.4
16	$MnL^5Cl + KNO_3$	18	121	83.6	4.1	3.4	3.2	5.7
17	$MnL^6Cl + LiNO_3$	17	114	82.8	4.4	5.1	2.3	5.4
18	$MnL^6Cl + NaNO_3$	18	121	83.5	3.9	4.6	2.7	5.3
19	$MnL^6Cl + KNO_3$	19	128	84.3	3.2	4.2	3.2	5.1

[†] Reaction conditions are the same as those in Table I.
[‡] 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 hour).

with pendant aza-crown group (MnL^1Cl–MnL^3Cl), and the TOF values were significantly improved. In contrast, for MnL^4Cl–MnL^6Cl, the TOF values were improved a little. Especially in the case of addition of $NaNO_3$ the catalytic activity is visibly enhancement (see Entry 3, 6 and 9). This may be due to that the dimension of the Li^+ (d = 0.136 nm) is too small to match the cavity size of crown ring (N-15-C-5) (d = 0.17–0.22 nm), and the dimension of K^+ (d = 0.266 nm) [18] is too large to fit in the cavity size of crown ring, But Na^+ (d = 0.19 nm) [18] can matched well with cavity size of crown ring and was located near to the coordination center. Moreover, the positive charge of Na^+ can enhance the molecular oxygen to be activated to some degree.

CONCLUSION

In this paper, a series of novel unsymmetrical 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. 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 group, which display a much better catalytic activity than the Schiff base Mn(III) complexes with pendant morpholino group 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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