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Synthesis of transition metal complexes with aza-crown substituted unsymmetrical salicylaldimine bis-Schiff base ligands and metal Schiff base complex catalysed oxidation of *p*-xylene to *p*-toluic acid

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Four unsymmetrical, salicylaldimine bis-Schiff bases with pendant benzo-10-aza-15-crown-5- or morpholino-groups and their 1:1 (ligand /metal) complexes with cobalt, copper and manganese have been synthesised and studied as catalysts in the aerobic oxidation of *p*-xylene to *p*-toluic acid. Significant selectivity (up to –90%) and conversion levels (up to –70%) were obtained. The effects of the pendant aza-crown ether group in Mn(III) Schiff base complexes on the oxidation of *p*-xylene were also investigated by comparison with analogues having pendant morpholino-groups.

Keywords: synthesis, benzo-10-aza-15-crown-5, unsymmetrical bis-Schiff base transition metal complexes, oxidation of *p*-xylene

Schiff bases and their metal complexes have been applied widely in the fields of coordination chemistry,[1] analytical chemistry,[2] catalytic chemistry,[3] liquid crystals and photochromism.[4,5] In recent years, there has been considerable interest in salicylaldimine Schiff base transition-metal complexes as oxygen carriers[6] and enzyme catalysis mimetics.[7,8] Many Schiff base ligands containing crown ether substituents possess different recognition sites for both alkali and transition metal guest cations;[9] for example, the Na(I)– or K(I)–Co(II) heteronuclear complexes of crowned Schiff bases can bind O_2 to form stable solid dioxygen adducts.[10,11] Our recent work has shown that dioxygen affinities and biomimetic catalytic performance of crown ether substituted salicylaldimine Schiff base transition-metal complexes are better than those of their crown-free analogues.[12] To the best of our knowledge, there are few previous studies on Schiff base complexes with pendant aza-crown groups as catalysts in aerobic oxidation of *p*-xylene to *p*-toluic acid.[13,14] In connection to our research on the effect of the bonded aza-crown ether ring in a Schiff base ligand on biomimetic catalytic properties of transition-metal complexes, we now report the synthesis of unsymmetrical salicylaldimine bis-Schiff bases with pendant benzo-10-aza-15-crown-5- or morpholino-groups and their transition metal complexes, and the homogeneous catalytic oxidation of *p*-xylene to *p*-toluic acid by air in the presence of the Schiff base complexes under mild conditions. The route for the synthesis and the structure of the unsymmetrical Schiff base complexes is shown in Fig. 1.

Experimental

Melting points were determined on a MP-500 micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-6700 spectrometer. ^1H NMR spectra were recorded on a Bruker AC-200MHz spectrometer using Me_4Si as the 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. Halogen analyses were measured using the mercury titration method[15,16] and other elementary analyses were performed on a Vario EL cube elemental analyser. Molar conductances were obtained on a DDS-11A conductivity meter.

The following compounds were prepared according to the literature:[17] (**1**) N-(2-hydroxy- 3-formyl-5-chlorobenzyl)morpholine; (**2**) N-(2-hydroxy-3-formyl-5-bromobenzyl)morpholine; (**3**) N-(2-hydroxy-3-formyl-5-chlorobenzyl)benzo-10-aza-15-crown-5; (**4**) N-(2-hydroxy-3- formyl-5-bromobenzyl)benzo-10-aza-15-crown-5; and (**5**H) Schiff base half unit.[18] Other reagents were of analytical grade and were used without further purification.

Synthesis of unsymmetrical bis-Schiff base ligands **6**H_2–**9**H_2

Schiff base ligand 6H_2: A solution of the precursor half unit (**5**H) (3.23 g, 10 mmol) and N-(2-hydroxy-3-formyl-5-chlorobenzyl)morpholine (**1**) (4.36 g, 10 mmol) in anhydrous EtOH (30 mL) was stirred for 4h under N_2 at 80 °C, then the mixture was cooled. The yellow precipitate was filtered and washed with EtOH. After recrystallisation from EtOH, yellow crystals (3.58 g, yield 64%) were obtained, m.p. 199–200 °C. ^1H NMR ($CDCl_3$) δ: 12.92 (s, 1H, OH, D_2O exchange), 10.35 (s, 1H, OH, D_2O exchange), 8.24 (s, 1H, CH=N), 7.20–6.87 (m, 14H, ArH), 3.72–3.66 (m, 6H, OCH_2, NCH_2Ar), 2.72 (t, 4H, NCH_2); IR (KBr, film) ν_{max}: 3442, 3235, 2927, 2852, 1613, 1601, 1278, 1114, 1040 cm^{-1}; ESIMS *m/z*: 560(M^++1). Anal. Calcd for $C_{31}H_{27}N_3O_3Cl_2$: C, 66.43; H, 4.86; N, 7.50; Cl, 12.65. Found: C, 66.31; H, 5.02; N, 7.35; Cl, 12.79%.

Ligand 7H_2: Prepared as described for **6**H_2 except that the starting material was N-(2-hydroxy-3-formyl-5-bromobenzyl)morpholine (**2**) instead of **1**, to give a yellow solid, yield 74%, m.p. 206–207 °C. ^1H NMR ($CDCl_3$) δ: 12.95 (s, 1H, OH, D_2O exchange), 10.41 (s, H, OH, D_2O exchange), 8.25 (s, 1H, CH=N), 7.21–6.87 (m, 14H, ArH), 3.73–3.63 (m, 6H, OCH_2, NCH_2Ar), 2.78 (t, 4H, NCH_2); IR (KBr, film) ν_{max}: 3439, 3237, 2932, 2859, 1615, 1601, 1276, 1112, 1039 cm^{-1}; ESIMS *m/z*: 605 (M^++1). Anal. Calcd for $C_{31}H_{27}N_3O_3ClBr$: C, 61.55; H, 4.50; N, 6.95; Cl, 5.86; Br, 13.21. Found: C, 61.69; H, 4.37; N, 7.09; Cl, 5.71; Br, 13.38%.

Ligand 8H_2: A solution of the precursor half unit **5**H (3.23 g, 10 mmol) and N-(2-hydroxy-3-formyl-5-chlorobenzyl)benzo-10-aza-15-crown-5 (**3**) in anhydrous EtOH (30 mL) was stirred for 5h under an N_2 atmosphere at 80 °C. The solvent was removed by evaporation and the residual mass was chromatographed on a silica gel column using $CH_3COOC_2H_5$ as an eluent to give the pure product as a yellow solid, yield 61%, m.p.187–188 °C. ^1H NMR ($CDCl_3$) δ: 12.11 (s, 1H, OH, D_2O exchange), 10.79 (s, 1H, OH, D_2O exchange), 8.29 (s, 1H, N=CH), 7.55–6.68 (m, 18H, ArH), 4.12–3.33 (m, 14H, OCH_2, NCH_2Ar), 2.85 (t, 4H, NCH_2); IR (KBr, film) ν_{max}: 3447, 3242, 2938, 2861, 1616, 1601, 1255, 1125, 1049, 928 cm^{-1}; ESIMS *m/z*: 741 (M^++1). Anal. Calcd for $C_{41}H_{39}N_3O_6Cl_2$: C, 66.49; H, 5.31; N, 5.67; Cl, 9.57. Found: C, 66.31; H, 5.48; N, 5.79; Cl, 9.68%.

Ligand 9H2: Prepared as described for **8**H_2 except that the starting material was N-(2-hydroxy-3-formyl-5-bromobenzyl)benzo-10-aza-15-crown-5 (**4**) instead of **3**, to give a yellow solid, yield 63%, m.p. 195–197 °C. ^1H NMR ($CDCl_3$) δ: 12.17 (s, 1H, OH, D_2O exchange), 10.86 (s, 1H, OH, D_2O exchange), 8.31 (s, 1H, N=CH), 7.56–6.69 (m, 18H, ArH), 4.15–3.35 (m, 14H, OCH_2, NCH_2Ar), 2.83 (t, 4H, NCH_2); IR (KBr, film) ν_{max}: 3443, 3235, 2952, 2861, 1614, 1601, 1259, 1127, 1052, 925 cm^{-1}; ESIMS *m/z*: 785(M^++1). Anal. Calcd for $C_{41}H_{39}N_3O_6ClBr$: C, 62.72; H, 5.01; N, 5.35; Cl, 4.52; Br, 10.18. Found: C, 62.91; H, 4.82; N, 5.49; Cl, 4.35; Br, 10.02.

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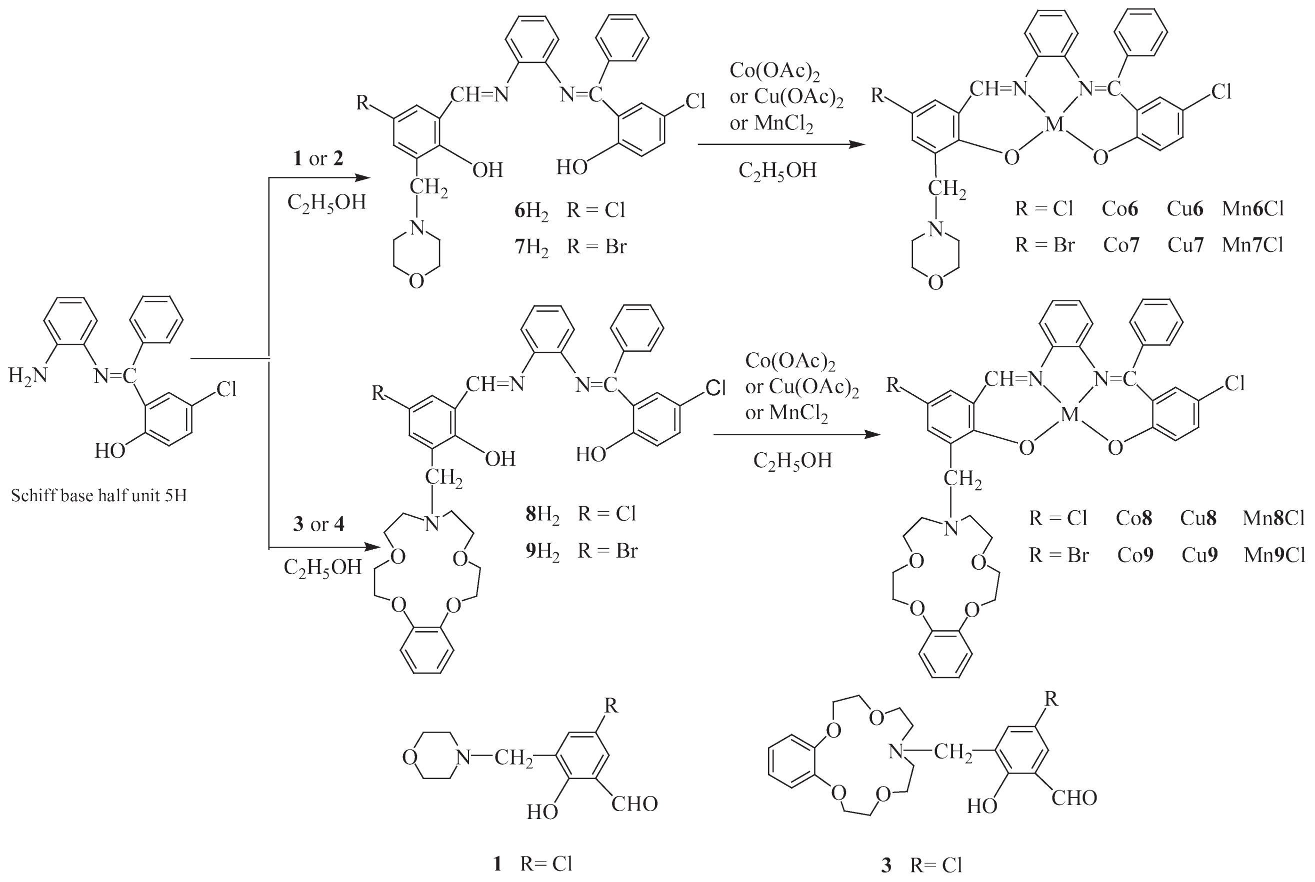


Fig. 1 The synthetic route and structure of unsymmetrical salicylaldimine Schiff base transition complexes with pendant benzo-10-aza-crown- or morpholino-groups.

Synthesis of Schiff base transition metal complexes; general procedure

A solution of unsymmetrical salicylaldimine bis-Schiff base (10 mmol) and transition metal salt [MnCl$_2$.4H$_2$O, Co(OAc).4H$_2$O or Cu(OAc).4H$_2$O] (10 mmol) in EtOH (15 mL) was stirred for 2 h under N$_2$ at 80 °C, and then the mixture was cooled, filtered, and washed with EtOH to give the complexes. The pure product was obtained by recrystallisation from EtOH.

*Mn**6**Cl*: Light yellow solid, yield 74%, m.p. 255–256 °C; IR (KBr, film) ν_{max}: 2930, 2854, 1604, 1277, 1115cm^{-1}; ESIMS *m/z*: 649 (M$^+$+1). Anal. Calcd for $C_{31}H_{25}MnN_3O_3Cl_3$: C, 57.38; H, 3.88; N, 6.48; Cl, 16.39; Mn, 8.47. Found: C, 57.46; H, 3.99; N, 6.59; Cl, 16.24; Mn, 8.64%. Λ_m(S·cm^2·mol^{-1}), 99.64.

*Co**6***: Purple solid, yield 76%; m.p. 247–249 °C; IR (KBr, film) ν_{max}: 2928, 2852,1605, 1597, 1278, 1116 cm^{-1}; ESIMS *m/z*: 617 (M$^+$+1). Anal. Calcd for $C_{31}H_{25}N_3O_3Cl_2Co$: C, 60.31; H, 4.08; N, 6.81; Cl,11.48; Co, 9.55. Found: C, 60.48; H, 4.25; N, 6.63; Cl, 11.38; Co, 9.70%. Λ_m (S·cm^2·mol^{-1}), 9.24.

*Cu**6***: Grey solid, yield 72%; m.p.>300 °C ; IR(KBr, film) ν_{max}: 2926, 2851, 1604, 6001, 1276, 1117 cm^{-1}; ESIMS *m/z*: 622 (M$^+$+1). Anal. Calcd for $C_{31}H_{25}N_3O_3Cl_2Cu$: C, 59.86; H, 4.05; N, 6.76; Cl, 11.40; Cu, 10.22. Found: C, 59.71; H, 4.23; N, 6.63; Cl, 11.59; Cu, 10.03%. Λ_m (S·cm^2·mol^{-1}), 9.83.

Mn7Cl: Light yellow solid, yield 70%; m.p. 260–261 °C; IR (KBr, film) ν_{max}: 2930, 2860, 1606, 1600, 1274, 1114 cm^{-1}. ESIMS *m/z*: 658 (M$^+$+1). Anal. Calcd for $C_{31}H_{25}N_3O_3Cl_2$ BrMn: C, 53.70; H, 3.63; N, 6.06; Cl, 10.23; Br, 11.53; Mn, 7.92. Found C, 53.84; H, 3.54; N, 6.19; Cl, 10.11; Br, 11.39; Mn, 7.76%. Λ_m (S·cm^2·mol^{-1}), 101.83.

Co7: Purple solid, yield 74%; m.p. 222–224 °C; IR (KBr, film) ν_{max}: 2928, 2861, 1605, 1600, 1275, 1115 cm^{-1}; ESIMS *m/z*: 662(M$^+$+1). Anal. Calcd for $C_{31}H_{25}N_3O_3BrClCo$: C, 56.26; H, 3.81; N, 6.35; Cl, 5.36; Br, 12.07; Co, 8.90. Found: C, 56.11; H, 3.97; N, 6.19; Cl, 5.48; Br, 11.99; Co, 9.19%. Λ_m (S·cm^2·mol^{-1}). 10.91.

Cu7: Grey solid, yield 73%; m.p. >300 °C ; IR (KBr, film) ν_{max}: 2932, 2856, 1605, 1278, 1118 cm^{-1}; ESIMS *m/z*: 666 (M$^+$+1). Anal. Calcd for $C_{31}H_{25}BrClCuN_3O_3$: C, 55.87; H, 3.78; N, 6.31; Cl, 5.32; Br, 11.99; Cu, 9.53. Found: C, 55.99; H, 3.89; N, 6.19; Cl, 5.46; Br, 12.11; Cu, 9.34%. Λ_m(S·cm^2·mol^{-1}), 9.93.

Mn8Cl: Brown solid, yield 69%; m.p. >300 °C; IR (KBr, film) ν_{max}: 2937, 2861, 1608, 1598, 1257, 1129, 1055, 928 cm^{-1}; ESIMS *m/z*: 829 (M$^+$+1). Anal. Calcd for $C_{41}H_{37}N_3O_6Cl_3Mn$: C, 59.40; H, 4.50; N, 5.07; Cl, 12.83; Mn, 6.63. Found: C, 59.17; H, 4.66; N, 5.22; Cl, 12.65; Mn, 6.51%. Λ_m (S·cm^2·mol^{-1}), 102.23.

Co8: Crimson solid, yield 68%; m.p. 252–253 °C; IR (KBr, film) ν_{max}: 2939, 2864, 1607, 1601, 1256, 1126, 1056, 926 cm^{-1}; ESIMS *m/z*: 798 (M$^+$+1). Anal. Calcd for $C_{41}H_{37}N_3O_6Cl_2Co$: C, 61.74; H, 4.68; N, 5.27; Cl, 8.89; Co, 7.39%. Found C, 61.55; H, 4.79; N, 5.15; Cl, 8.74; Co, 7.52%. Λ_m (S·cm^2·mol^{-1}). 10.64.

Cu8: Grey solid, yield 72%; m.p. >300 °C; IR (KBr, film) ν_{max}: 2938, 2864, 1609, 1601, 1257, 1128, 1054, 927 cm^{-1}; ESIMS *m/z*: 802 (M$^+$+1). Anal. Calcd for $C_{41}H_{37}N_3O_6Cl_2Cu$: C, 61.39; H, 4.65; N, 5.24; Cl, 8.84; Cu, 7.92%. Found: C, 61.53; H, 4.50; N, 5.11; Cl, 8.66; Cu, 8.09%. Λ_m (S·cm^2·mol^{-1}), 9.26.

Mn9Cl: Brown solid, yield 66%; m.p. >300 °C; IR (KBr, film) ν_{max}: 2949, 2858, 1605, 1600, 1256, 1128, 1048, 927 cm^{-1}; ESIMS *m/z*: 838 (M$^+$+1). Anal. Calcd for $C_{41}H_{37}N_3O_6Cl_2BrMn$: C, 56.38; H, 4.27; N, 4.81; Cl, 8.12; Br, 9.15; Mn, 6.29. Found: C, 56.22; H, 4.45; N, 4.67; Cl, 8.28; Br, 9.30; Mn, 6.11%. Λ_m (S·cm^2·mol^{-1}), 98.36.

Co9: Crimson, yield 69%; m.p. 257–259 °C; IR (KBr, film) ν_{max}: 2952, 2859, 1604, 1599, 1258, 1129, 1053, 928 cm^{-1}; ESIMS *m/z* 842 (M$^+$+1). Anal. Calcd for $C_{41}H_{37}N_3O_6ClBrCo$: C, 58.48; H, 4.43; N, 4.99; Cl, 4.21; Br, 9.49; Co, 7.00. Found: C, 58.65; H, 4.32; N, 5.16; Cl, 4.38; Br, 9.35; Co, 6.90%. Λ_m (S·cm^2·mol^{-1}), 10.51.

Cu9: Grey solid, yield 71%; m.p. >300 °C; IR (KBr, film) ν_{max}: 2951, 2860, 1606, 1601, 1255, 1125, 1052, 926 cm^{-1}; ESIMS *m/z*: 847 (M$^+$+1). Anal. Calcd for $C_{41}H_{37}N_3O_6ClBrCu$: C, 58.16; H, 4.40; N, 4.96; Cl, 4.19; Br, 9.44; Cu, 7.51. Found: C, 58.33; H, 4.22; N, 4.78; Cl, 4.31; Br, 9.58; Cu, 7.39%. Λ_m(S·cm^2·mol^{-1}), 9.86.

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

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 x 10^{-1} mol, 15 cm^3) and Schiff base complex (1.5 x 10^{-5} mol). The oxidation products were analysed at regular intervals by HPLC (Afilent 1100LC, Hypersil ODS 100 mm x 4.6 mm, 5mm). Authenticated standard samples were used to confirm the identity of products. The oxidation was stopped on 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*-xlene reacted and oxidation products formed by HPLC.

Results and discussion

The unsymmetrical bis-Schiff base ligands (**6**H$_2$–**9**H$_2$) were conveniently prepared by the reaction of the Schiff base half unit with crown ether-functionalised salicylaldehyde or morpholino-functionalised salicylaldehyde (Fig. 1) and characterised by IR, ^{1}H NMR, mass spectroscopy and elemental analysis. In the IR spectra of **6**H$_2$–**9**H$_2$, the characteristic absorbtions of Ar-OH at 3447–3439 cm^{-1} and 3242–3235 cm^{-1} were observed, as was that for CH=N at 1616–1613cm^{-1}. ^{1}H NMR spectra of **6**H$_2$–**9**H$_2$ show the aromatic protons as multiplets in the range 7.56–6.69 ppm, the chemical shifts of the O–H protons of the phenolic groups are in the range 12.95–12.11 ppm and 10.86–10.35 ppm, respectively.

Compared with the IR spectrum of the free ligands, those of the Schiff base transition metal complexes are almost at the same frequencies, except for the C=N stretching vibration which is shifted 7–10 cm^{-1} to a lower frequency and also shows an intensity greater than the free ligand. The absence of an OH stretching vibration (–3440 cm^{-1} and –3230 cm^{-1}) in the complexes indicates deprotonation of OH in the ligand upon complex formation, suggesting the formation of a N–O–M coordination bond (M=Co, Cu or Mn). The C–O–C stretching vibrations in the crown ether ring for the complexes are at almost the same frequency as for the free ligand. These facts suggest that the cobalt only interacts with the Ar-OH and CH=N groups.[12] The observed molar conductances of the complexes in DMF solution (1.0×10^{-3} mol L^{-1}) at 25 °C show that these unsymmetrical bis-Schiff base cobalt and copper complexes are non-electrolytes, whereas the unsymmetrical bis-Schiff base manganese complexes are electrolytes.[19] The ESI-MS mass spectra and elemental analysis of the complexes indicate that **6**H$_2$–**9**H$_2$ formed 1:1(metal/ligand) complexes. We therefore suggest structural formulae for these Schiff base transition metal complexes as shown in Fig. 1.

Oxidation of p*-xylene to PTA*

In order to investigate the effect of the central metal of the Schiff base complexes on the catalytic oxidation of *p*-xylene to PTA, Mn**9**Cl, Co**9** and Cu**9** are used as examples. The results of oxidation of *p*-xylene to PTA are shown in Fig. 2. From Fig. 2, the catalytic oxidation activity of the Mn(III) Schiff base complexes is higher than that of Co(II)- or Cu(II)-Schiff base complex analogues using the same ligand, due to the differences in 3d electronic structure of the central metal ion, which leads to a different capacity of Schiff base complexes to activate dioxygen in the reaction system.

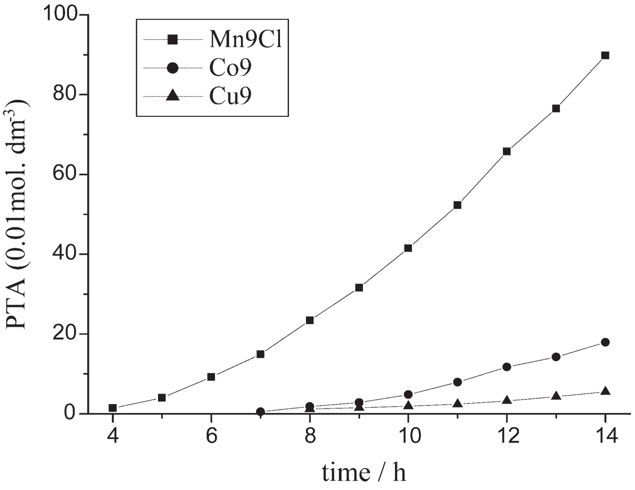


Fig. 2 The effect of central metal of Schiff base complexes on catalytic oxidation of *p*-xylene to *p*-toluic acid.

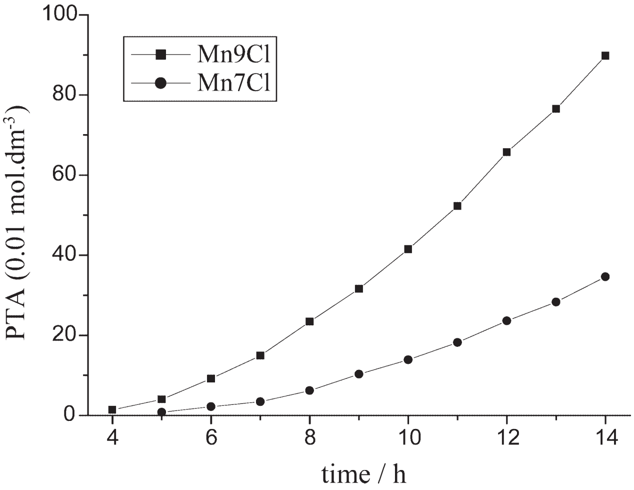


Fig. 3 The effect of aza-crown ether group on catalytic oxidation for *p*-xylene of *p*-toluic acid.

From Fig. 3, the catalytic oxidation activity of the aza-crown Mn(III) Schiff base complex (Mn**9**Cl) is higher than that of the Mn(III) morpholino-Schiff base complex (Mn**7**Cl). 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 its outer ethylene groups and orderly arrangement of the inner oxa-atoms, which facilitate the approach of the oxygen molecule to the coordination centre of the aza-crown Schiff base Mn(III) complexes.

From Fig. 4, an obvious relationship exists between the catalytic oxidation activity and the electronic properties of the

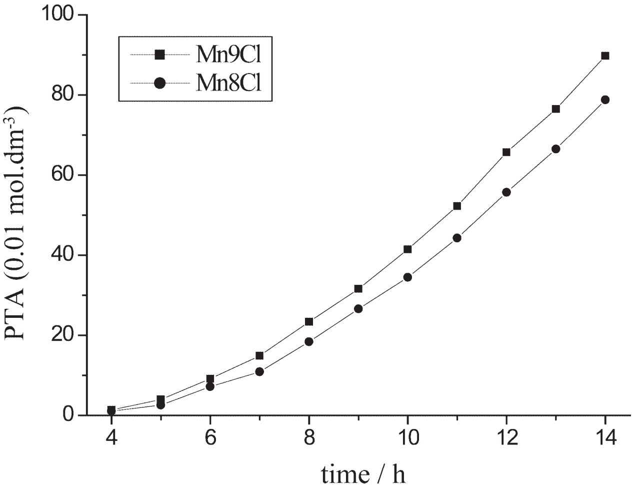
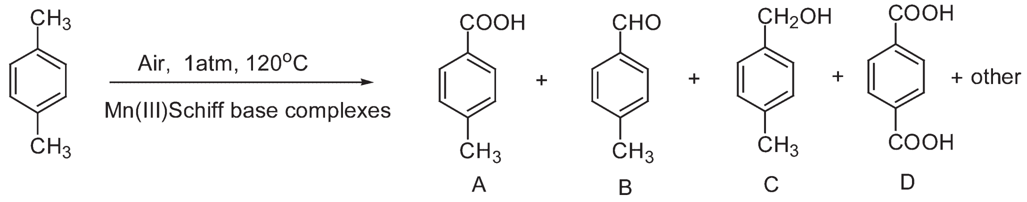


Fig. 4 The effect of aromatic substituents group on catalytic oxidation of *p*-xylene to *p*-toluic acid



Scheme 1 The catalytic oxidation products of *p*-xylene by Mn(III) Schiff base complexes.

Table 1 Schiff base Mn (III) complex catalytic oxidation of *p*-xylene to *p*-toluic acid[a]

Catalyst	Induction period /h	Conversion /wt%	TOF /h^{-1}	Selectivity for products[b]				
				A	B	C	D	Others
Mn**6**Cl	5	60	320	89.2	3.3	2.9	1.8	2.8
Mn**7**Cl	5	63	334	90.8	2.5	2.6	1.3	2.8
Mn**8**Cl	4	73	520	92.3	1.9	2.8	1.6	1.5
Mn**9**Cl	4	78	533	93.2	1.8	2.0	1.2	1.8

[a] 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 h^{-1}; Reaction temperature: 120 °C; Reaction time: 14 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).

substituent group on the aromatic rings of Mn(III) Schiff base complexes. Figure 4 shows that the catalytic oxidation activity of Mn**9**Cl, containing a Br substituent group, is higher than that of Mn**8**Cl, containing a Cl substituent group, when the structure of ligand is otherwise similar. Because the electron-donating effect of the substituent group follows the order Br>Cl, the electron density of the central metal manganese is enhanced by an electron-donating effect of the substituent group on the salicyl-aromatic ring, which facilitates the Schiff base complexes enhanced affinity for the oxygen molecule.

Comparing the catalytic oxidation activities of the Schiff base Mn(III) complexes with a pendant aza-crown group, the effect of the substituent group on 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 a pendant morpholino-group. The macrocycle effect of the aza crown ring may be significant factor for the catalytic oxidation performance of the Schiff base Mn(III) complex.

The oxidation of *p*-xylene to PTA was carried out using Mn(III) Schiff base complexes as the catalyst as shown in Scheme 1. The results of oxidation of *p*-xylene to PTA are shown in Table 1. The data in Table 1 indicate that the induction periods required for initiating the oxidation of *p*-xylene catalysed by Mn(III) Schiff base complexes are 4 h for Mn**8**Cl, 4 h for Mn**9**Cl, 5 h for Mn**6**Cl, and 5h for Mn**7**Cl, respectively. This 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 complex. Moreover, as shown in Table 1, 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 a pendant aza-crown group are also excellent in comparison with those of the oxidation of *p*-xylene catalysed by the morpholino-Mn(III) Schiff base complexes analogues. Although the conversion (–78%) for the oxidation of *p*-xylene catalysed by the Schiff base Mn(III) complexes with the 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 –93%) for the oxidation product PTA is higher than that of $Co(OAc)_2/NaBr/AcOH$, and the reaction conditions for the oxidation of *p*-xylene catalysed by aza-crown Mn(III) Schiff base complexes are milder than for other inorganic catalysts.[20,21]

Conclusion

In this paper, four unsymmetrical salicylaldimine bis-Schiff bases with pendant benzo-10-aza- 15-crown-5- or morpholino-groups and their cobalt, copper and manganese complexes have been synthesised and studied as catalysts in the aerobic oxidation of *p*-xylene to *p*-toluic acid. Significant selectivity (up to –90%) and conversion levels (up to –70%) have been obtained. The study demonstrates that the catalytic oxidation activity of Mn(III) Schiff base complexes is higher than that of Co(II)- or Cu(II)-Schiff base complex analogues. The selective oxidation of *p*-xylene to *p*-toluic acid can successfully occur in the presence of Schiff base Mn(III) complexes having a pendant aza-crown group; the catalytic oxidation activity of the aza-crown Mn(III) Schiff base complex is higher than that of the morpholino- Mn(III) Schiff base complex.

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