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Dioxygen affinities and catalytic oxidation performance of unsymmetrical bis-Schiff base transition-metal complexes with aza-crown pendant groups

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Co^{II} and Mn^{III} complexes with aza-crown substituted, unsymmetrical bis-Schiff base ligands have been synthesised starting from monoaza-15-crown-5 or benzo-10-aza-15-crown-5. The saturated oxygen uptakes of the Co^{II} complexes **[CoL^1]–[CoL^4]** in diethyleneglycol/dimethyl ether solution were determined at different temperatures. The oxygenation constant (Ko_2) and thermodynamic parameters ($\Delta H°$, $\Delta S°$) were calculated. The Mn^{III} complexes (**[MnL^{1}Cl]–[MnL^{4}Cl]**) were employed to catalyse styrene oxidation using molecular oxygen at ambient temperature and pressure. The modulation of O_2-binding capabilities and catalytic oxidation performance by the aza-crown ether pendant groups in **[ML^3]** and **[ML^4]** were investigated as compared with the parent complexes **[ML^1]** and morpholino-substituted analogue **[ML^2]**. The results indicate that the dioxygen affinities and catalytic oxidation activities of **[CoL^3]** and **[CoL^4]** have been much more enhanced by aza-crown pendants. Moreover, the O_2-binding capabilities of **[CoL^3]** and **[CoL^4]** were also improved by adding alkali metal cations (Li^+, Na^+ and K^+) to the system, and adding Na^+ shows the most significant enhancement of dioxygen affinities. Likewise, **[MnL^{3}Cl]** and **[MnL^{4}Cl]** exhibit the best catalytic activities: the conversion of styrene to benzaldehyde are up to 41.2% and 45.8% with more than 99% selectivity.

Keywords: unsymmetrical bis-Schiff bases, aza-crown ether, transition-metal complexes, dioxygen affinities, catalytic oxidation

The transition-metal complexes of Schiff bases represent one of the most successful classes of synthetic oxygen carrier due to their structural similarity to those found in biological systems.[1,2] They have been extensively studied as models of dioxygen-carrying metalloenzymes[3] and oxygenases,[4] such as hemoglobin and cytochrome P–450,[5] which play important roles in the catalytic oxidation of organic substrates.[6] However, many of these complexes easily dimerise and lose activity after O_2 absorption.[7] Avdeef and coworkers[8] demonstrated that formation of stable dioxygen adducts would be favoured if these complexes were modified by proper substituents to obtain additional stereo hindrance and hydrophobicity. Thus, various substituents have been employed to improve O_2-binding capabilities and catalytic oxidation activities of the complexes.[9-11] Among them, crown ether-containing Schiff bases have attracted much attention because they can bind both alkali and transition metal guest cations through the crown ether cavity and the N_2O_2 donor atoms.[12-15] In addition, co-complexation of alkali cations close to the central transition-metal ion is known to be important in influencing its dioxygen-binding properties.[16] Our recent works have indicated that symmetrical axa-crowned bis-Schiff bases transition-metal complexes are good receptors for alkali cations[17] and showed much improved O_2-binding activity and catalytic oxidation activity due to the special configuration and function of the crown ether ring. Moreover, adding alkali metal cations (Li^+, Na^+ and K^+) will also favour their O_2-binding activity.

However, to the best of our knowledge, no reports about O_2-binding activity and biomimetic catalytic oxidation performance of crown ether-containing unsymmetrical Schiff base complexes have appeared. As an extension of our former studies,[18] we herein report a facile way to prepare unsymmetrical bis-Schiff base complexes bearing aza-crown ethers and discus the influence of the aza-crown pendant on the O_2-binding activity and catalytic oxidation performance.

Experimental

Melting points were determined on a Yanaco-500 micro-melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet-1705X IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-200 MHz spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained on Finnigan MAT 4510 or Finnigan LCQ^{-DECA} spectrometers. Elemental analysis was performed on a Carlo Erbo-1160 elemental analyser. Molar conductance was obtained on a DDS–11A conductivity meter. GC analysis was carried out on a Varian CP-3800 gas chromatograph (OV-1 column). The Co^{II} and Mn^{III} contents were obtained on a IRIS-Advantage ICP emission spectrometer. N-(3-formyl-4-hydroxybenzyl)morpholine (**2b**) and N-(3-formyl-4-hydroxybenzyl)benzo- 10-aza-15-crown-5 (**2d**) were prepared according to our report.[14] 2-hydroxy-5-chloromethyl-benzaldehyde,[19] monoaza-15-crown-5,[20] compounds **[CoL^1]** and **[MnL^{1}Cl]** were synthesised according to the literature method.[21]

Synthesis of N-(3-formyl-4-hydroxybenzyl aza-15-crown-5 (**2c**): To a stirred mixture of aza-15-crown-5 (0.01 mol) and K_2CO_3 (0.011 mol) in acetonitrile (40 ml), a solution of 2-hydroxy-5-chloromethylbenzaldehyde (0.01 mol) in acetonitrile (10 ml) was added dropwise. The mixture was refluxed for 10 h, cooled and filtered. The solvent was evaporated and the residual mass was chromatographed on a silica gel column (eluent: ethyl acetate) to give the pure product as an oil, 86% yield. IR (neat) ν_{max}: 3256, 1658, 1256, 1126 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ10.68(s, 1H, OH, D_2O exchangeable), 9.96(s, 1H, CH=N), 7.42–6.81 (m, 3H, ArH), 4.12–3.68(m, 18H, OCH_2, NCH_2Ar), 2.86 (t, 4H, $J = 5.5$ Hz, NCH_2); MS (*m/z*): 353 (M^+). Anal. Calcd for $C_{18}H_{27}NO_6$: C 61.19, H 7.65, N 3.97. Found: C 61.30, H 7.51, N 4.04%.

General method for synthesis of unsymmetrical bis-Schiff base ligands **HL^2–HL^4**

A mixture of compound **1** (10 mmol and **2b–d** (10 mmol) were dissolved in methanol (50 ml) and refluxed for 6 h under N_2, then cooled and filtered to give the crude product as an orange solid. The crude product was dissolved in the minimum of ethyl acetate and then chromatographed on a silica gel column (eluent : ethyl acetate) to give the pure product as a yellow solid.

HL^2: Yellow crystals; Yield 82%. m.p.178–180 °C. ^{1}H NMR ($CDCl_3$) δ14.12 (s, 2H, OH, D_2O exchange), 8.22 (s, 1H, CH=N), 7.15–6.86 (m, 15H, ArH), 3.71–3.65 (m, 6H, OCH_2, NCH_2Ar), 2.92–2.76 (t, 4H, NCH_2); IR(KBr) ν_{max}: 3445, 1608, 1280, 1156 cm^{-1}; MS *m/z*: 526(M^+). Anal. Calcd for $C_{31}H_{28}N_3O_3Cl$: C 70.72, H 5.32, N 7.98. Found C 70.91, H 5.17, N 7.75%.

HL^3: Yellow crystals; Yield 61%. m.p. 126–128 °C. ^{1}H NMR ($CDCl_3$) δ: 14.11(s, 2H, OH, D_2O exchange), 8.25(s, 1H, N=CH), 7.22–6.85(m, 15H, ArH), 4.10–3.33(m, 18H, OCH_2, NCH_2Ar), 2.81(t, $J = 5.6$ Hz, 4H, NCH_2); IR(KBr) ν_{max}: 3441, 1608, 1255, 1133; ESIMS *m/z*: 658 (M^+). Anal. Calcd. For $C_{37}H_{40}N_3O_6Cl$: C 67.48, H 6.08, N 6.38. Found C 67.65, H 6.11, N 6.26%.

HL^4: Yellow crystals; Yield 66%. m.p.144–146 °C. ^{1}H NMR($CDCl_3$) δ: 14.28(s, 2H, OH, D_2O exchange), 8.35(s, 1H, N=CH), 7.52–6.66(m, 19H, ArH), 4.12–3.31(m, 14H, OCH_2, NCH_2Ar), 2.81(t, $J = 5.6$ Hz, 4H, NCH_2); IR(KBr) ν_{max}: 3443, 1608, 1256, 1131; ESIMS *m/z*: 706 (M^+). Anal. Calcd. For $C_{41}H_{40}N_3O_6Cl$: C 69.69, H 5.67, N 5.98. Found C 69.82, H 5.46, N 5.74%.

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General method for synthesis of Co(II)/Mn(III) unsymmetrical bis-Schiff base complexes **ML**

A solution of **HL^2–HL^4** (1.0 mol) and $Co(OAc)_2 \cdot 4H_2O$ or $MnCl_2 \cdot 6H_2O$(1.0 mol) in methanol (15 ml) was stirred for 2 h under N_2 at reflux, then the mixture was cooled and filtered, washed with methanol and then with diethyl ether to give the metal complexes. The pure product was obtained after recrystallisation from ethanol.

[CoL^2]: Red solid, 71% yield, IR (KBr) ν_{max}: 1616, 1281, 1156 cm^{-1}; MS *m/z*: 583(M$^+$). Anal. Calcd for $C_{31}H_{26}N_3O_3ClCo$: C 63.81, H 4.46, N 7.20, Co 10.12. Found C 63.59, H 4.25, N 7.38, Co 10.04%. Λ_m(S·cm^2·mol^{-1}): 4.33.

[CoL^3]: Red solid, 79% yield, IR(KBr) ν_{max}: 1620, 1255, 1132; ESIMS *m/z*: 715(M$^+$). Anal. Calcd. for $C_{37}H_{38}N_3O_6CoCl$: C 62.09, H 5.31, N 5.87, Co 8.25. Found C 61.93, H 5.22, N 5.90, Co 8.39%. Λ_m(S·cm^2·mol^{-1}): 6.82.

[CoL^4]: Red solid, 85% yield, IR(KBr) ν_{max}: 1618, 1252, 1131; ESIMS *m/z*: 763(M$^+$). Anal. Calcd. for $C_{41}H_{38}N_3O_6CoCl$: C 64.48, H 4.98, N 5.50, Co 7.73. Found C 64.35, H 5.25, N 5.32, Co 7.47%. Λ_m(S·cm^2·mol^{-1}): 5.26.

[MnL^{2}Cl]: Brown solid, 81% yield, m.p.>300 °C. IR (KBr) ν_{max}: 1617, 1278, 1155 cm^{-1}; ESIMS *m/z*: 614(M$^+$). Anal. Calcd for $C_{31}H_{26}N_3O_3Cl_2Mn$: C 60.49, H 4.23, N 6.83, Mn 8.96. Found C 60.22, H 4.31, N 6.58, Mn 8.73%. Λ_m(S·cm^2·mol^{-1}): 93.44.

[MnL^{3}Cl]: Brown solid, 87% yield, m.p.>300 °C. IR(KBr) ν_{max}: 1620, 1254, 1130; ESIMS *m/z*: 746(M$^+$). Anal. Calcd. for $C_{37}H_{38}N_3O_6MnCl_2$: C 59.52, H 5.09, N 5.63, Mn 7.37. Found C 60.02, H 5.11, N 5.70, Mn 7.21%. Λ_m(S·cm^2·mol^{-1}): 82.04.

[MnL^{4}Cl]: Brown solid, 82% yield, m.p.>300 °C. IR(KBr) ν_{max}: 1618, 1255, 1128; ESIMS *m/z*: 794(M$^+$); Anal. Calcd. for $C_{41}H_{38}N_3O_6Cl_2Mn$: C 61.89, H 4.78, N 5.28, Mn 6.93. Found C 62.07, H 4.53, N 5.03, Mn 7.11%. Λ_m(S·cm^2·mol^{-1}): 79.68

Oxygen uptake measurements

The oxygenation constants and thermodynamic parameters of **[CoL^1]–[CoL^4]** were determined by the known equipment and method:[22,23] diglyme (O_2 saturated) as solvent, 1.0 mol·dm^{-3} of pyridine as axial ligand (B), 5 × 10^{-3} mol·dm^{-3} of complexes, 9.7 × 10^4 Pa of oxygen partial pressure. The equilibrium constant (Ko_2) was calculated as follows.

$$\mathrm{CoL} + \mathrm{B} \rightleftharpoons \mathrm{CoLB} \qquad \mathrm{CoLB} + \mathrm{O_2} \rightleftharpoons \mathrm{CoLBO_2} \quad \mathrm{Ko_2} = \frac{[\mathrm{CoLBO_2}]}{[\mathrm{CoLB}] \cdot \mathrm{Po_2}}$$

Complexes are expressed in terms of molarities and the dioxygen concentration are expressed as partial pressure (Po_2) in torr. Thermodynamic parameters $\Delta H°$and $\Delta S°$ for the oxygenation reactions were calculated from Ko_2 and $K'o_2$ over a range of temperatures.

Catalytic oxidation of styrene

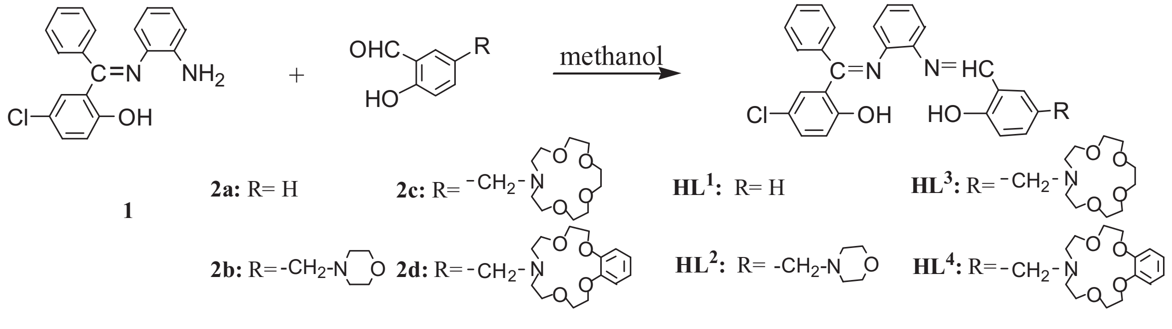
To a solution of styrene(1.0 mmol), the imidazole as co-catalyst (0.1 mmol), reducing agent Zn (1.0 mmol) and $CH_3CN:CH_2Cl_2$ (15 ml, 9.5:0.5, v/v) was added [MnLCl] as catalyst (0.01 mmol). Then the mixture was vigorously stirred at 25 °C under O_2 for 0.5 h, and the proton donor acetic acid (0.069 ml, 1.1 mmol) was injected. The mixture was stirred for 1.5 h at 25 °C. The oxidation products were identified by GC analyses and confirmed by MS.

Result and discussion

All of the unsymmetrical bis-Schiff base ligands **HL^2–HL^4** have been conveniently prepared by condensation of the semi-ligand **1** and morpholine or aza-crown ether substituted salicylaldehyde. The procedure is illustrated in Scheme 1. The elemental analyses and ESIMS of the complexes indicate that they are 1:1 (metal/ligand) complexes. Moreover, the molar conductance of all complexes in DMF solution (10^{-3} mol·dm^{-3}) are respectively in the 4.33–6.82 range (cobalt complexes) and 79.68–93.44 range (manganese complexes) S·cm^2·mol^{-1}at 25 °C. The facts suggest the cobalt^{II} complexes are non-electrolytes and manganese^{III} complexes are 1:1 electrolytes.[24] The IR spectra show most ligand absorptions are still in the same frequency except the C=N stretch absorption shifts slightly (8–12 cm^{-1}) to higher frequency, which is different from that of the symmetrical analogues we previously reported.[25] The OH stretches (*ca* 3442 cm^{-1}) disappear after complex formation. The proposed structure is shown in Fig. 1.

Considering that the pyridine (Py) solutions of **[MnL^{1}Cl]–[MnL^{4}Cl]** are readily oxidised in air to yield [(Py)L_2Mn(III)-O-Mn(III)L_2(Py)] at ambient temperature, the oxygenation constants (Ko_2) of **[MnL^{1}Cl]–[MnL^{4}Cl]** cannot be accurately determined.[26] We have only studied the dioxygen affinities of **[CoL^1]–[CoL^4]**. The oxygenation constants (Ko_2) and thermodynamic parameters ΔH^0 and ΔS^0 of **[CoL^1]–[CoL^4]** are given in Table 1. It shows, as compared with **[CoL^1]** and **[CoL^2]**, the dioxygen affinity of aza-cowned complexes **[CoL^3]** and **[CoL^4]** are obviously improved. This result is due to the aza-crown pendants increasing the steric hindrance and hydrophobicity of the complexes. Furthermore, the macrocycle effect of aza-crown ring, rather than the morpholino-substituents, which possesses a special configuration, probably allows the O_2 molecule to approach the coordinated Co^{II} of the complexes, and then form the Co–O_2 bond through the hydrophobicity of the outer ethylene groups and the orderly arrangement of the inner aza-oxa atoms.[18]

Table 1 also shows that adding alkali metal ions (as $LiNO_3$, $NaNO_3$ and KNO_3) to the oxygenation system (the concentration of the alkali metal ions is equal to the CoL concentration) improves the O_2-binding capability of **[CoL^3]** and **[CoL^4]**. In contrast, in terms of the uncrowned analogs **[CoL^1]** and **[CoL^2]**, there was almost no influence. This result reveals that alkali metal ions improve the O_2-



Scheme 1

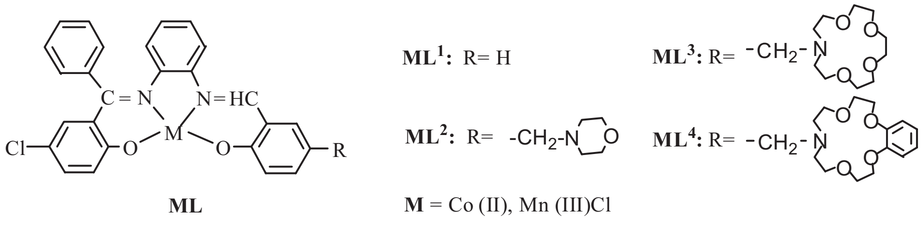


Fig. 1 Structure of the unsymmetrical Schiff base complexes ML.

Table 1 Oxygenation constants and thermodynamic parameters ($\Delta H°$ and $\Delta S°$) of CoL

CoL	B	T/°C	Ions added	$\ln K_{O_2}$/mm^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
[CoL^1]	Py	–5	–	–4.36	–36.25	–171.51
		0	–	–4.64		
		15	–	–5.45		
		25	–	–5.94		
[CoL^2]	Py	–5	–	–3.12	–41.12	–179.37
		0	–	–3.44		
		15	–	–4.33		
		25	–	–4.83		
		25	Li^+	–4.82		
		25	Na^+	–4.83		
		25	K^+	–4.82		
[CoL^3]	Py	–5	–	–2.83	–42.51	–182.11
		0	–	–3.19		
		15	–	–3.85		
		25	–	–4.75		
		25	Li^+	–4.67		
		25	Na^+	–3.68		
		25	K^+	–4.39		
[CoL^4]	Py	–5	–	–2.32	–44.34	–172.72
		0	–	–2.65		
		15	–	–3.64		
		25	–	–4.31		
		25	Li^+	–4.22		
		25	Na^+	–3.25		
		25	K^+	–3.99		

Table 2 Catalytic oxidation of styrene catalysed by [MnLCl]

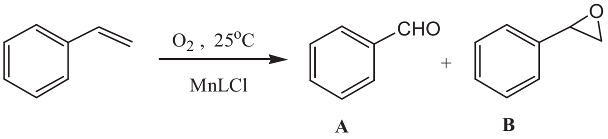
Catalyst	Convention/wt.%	TOF/h^{-1}	Selectivity/wt.%	
			A	**B**
[MnL^{1}Cl]	11.6	5.80	6.7	93.3
[MnL^{2}Cl]	13.3	6.65	8.4	91.6
[MnL^{3}Cl]	41.2	20.6	99.1	0.9
[MnL^{3}Cl] + Na^+	47.1	23.6	99.2	0.8
[MnL^{4}Cl]	45.8	22.9	99.3	0.7
[MnL^{4}Cl] + Na^+	53.5	26.8	99.2	0.8

A = benzaldehyde, **B** = epoxy product TOF = Turnover frequency (mole styrene converted per mol catalyst per hour).

binding capability only when they are coordinated with the crown rings of the complexes. Table 1 also indicates that the O_2-binding capabilities of **[CoL^3]** and **[CoL^4]** are visibly enhanced by adding $NaNO_3$. However, the enhancement by adding equal $LiNO_3$ and KNO_3 is very limited. Since aza-crown substituted Schiff base Co(II) complexes can complex with alkali cations,[27] the above results may be due to the fact that Na^+ (d = 1.90Å) matches much better with the cavity size of 15-crown-5 (d = 1.7–2.2Å) than does Li^+ (d = 1.36Å) or K^+ (d = 2.66Å). Thus the efficient complexation of Na^+ with aza-crown ethers would favour this cation to approach and control effectively the microenviroment around the coordinated Co^{II} and facilitate the formation and stabilisation of Co–O_2.[28]

Kochi's report demonstrated that Mn^{III}-Schiff complexes are high-active catalysts for olefin oxidation.[4] Herein, we describe **[MnL^{1}Cl]**–[**MnL^4**Cl] catalysing styrene oxidation (Scheme 2). As illustrated in Table 2, the aza-crowned **[ML^3]** and **[ML^4]** show higher catalytic oxidation activities than the uncrowned analogues **[ML^1]** and **[ML^2]**. The result may be due to the macrocycle effect of the azacrown rings. The special conformation of azacrown rings in **[ML^3]** and **[ML^4]** can offer large steric hindrance and a hydrophobic environment and favour the formation and protection of the active oxidation species (Mn = O). Table 2 also illustrates that adding Na^+ (as $NaNO_3$ and in the same concentration as **[ML^3]** and **[ML^4]**) to the complexes **[ML^3]** and **[ML^4]** enhances the catalytic oxidation activities. This result also shows that the Na^+ complex, with the azacrown ring, may advantage the active oxidation species (Mn = O).

An interesting fact is that aza-crowned **[ML^3]** and **[ML^4]** show different catalytic selectivity from that of uncrown analogues **[ML^1]** and **[ML^2]**. The major product of styrene oxidation catalysed by **[ML^3]** and **[ML^4]** comes from oxidative C=C cleavage of the olefinic moiety to form phenyl aldehyde with more than 99% selectivity. In contrast, the major product of styrene oxidation catalysed by **[ML^1]** and **[ML^2]** is epoxide with about 90% selectivity. This fact indicates that the azacrown ring, which possesses special configuration and steric hindrance in the Mn^{III} complexes, plays a critical role in the formation of phenyl aldehyde. Further studies of the catalytic oxidation mechanism are being carried out in our lab.



Scheme 2

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