Synthesis, Oxygenation and Catalytic Oxidation Performance of Crown Ether-Containing Schiff Base-Transition Metal Complexes

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Abstract: Mono-Schiff bases containing a crown ether ring (**HL^1**, **HL^2**, **HL^3** and **HL^4**) and their transition metal complexes were synthesized and characterized by ^{1}H NMR, IR, and mass spectroscopy as well as elemental analysis. The oxygenation constants (K_{O_2}) of Schiff base-Co(II) complexes were measured over the range of -5 to $+25\,°C$, and the values of $\Delta H°$ and $\Delta S°$ were calculated based on these K_{O_2} values. Using Mn(III)-Schiff base complexes, the biomimetic catalytic oxidation of styrene to benzaldehyde was carried out with 100% selectivity. Comparison of this complex with analogues not containing a crown ether moiety clearly demonstrated the influence of crown ether ring on the dioxygen affinities and biomimetic catalytic oxidation performance of the Schiff base complexes.

Keywords: aza-15-crown-5; benzo-15-crown-5; catalytic oxidation; dioxygen affinity; transition metal-Schiff base complexes

Introduction

Studies on dioxygen binding to transition metal complexes are of intrinsic importance, and provide opportunities to address the fundamental issues of biological oxygen carriers and oxygenases. In recent years, dioxygen binding complexes containing Fe(II), Cu(I), Ni(II) and Mn(II) have been reported,[1] but chelates of cobalt(II) offer the greatest promise because of the wide range of stabilities of cobalt-dioxygen complexes.[2] In 1938 Tsumaki reported that Schiff base-Co(II) complexes possess the ability to activate various molecules, especially molecular oxygen coordinated to the axial positions of the complexes.[3] Tsuchida demonstrated that Co-Salophen, with an elegant steric component, could form a stable 1:1 oxygen adduct because it avoids being oxidized to the μ-oxodimer *via* dimerization after absorbing the oxygen molecule.[4] Moreover, the selective oxidation of various organic compounds utilizing molecular oxygen (the most basic and abundant naturally occurring oxidant) is one of the most challenging topics in the fields of chemical and biological catalysis.[5] In the past decades, Schiff base complexes designed as cytochrome P-450 models have been employed in the catalytic oxidation of olefins with PhIO, NaClO or H_2O_2 as terminal oxidants.[6] However, to date no studies on crown ether ring-containing Schiff base complexes as catalysts for such reactions have been reported. 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.[7] Of course, crown ether-containing Schiff bases are known to bind cations in the crown ether cavity in addition to the 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 perturbing its oxygen binding properties. Herein, as part of a research program aimed at studying the effects of crown ether rings and their alkali metal complexes on the dioxygen affinities and biomimetic catalytic oxidation performance of such transition metal complexes, we have developed a series of novel Schiff base complexes bearing crown ether rings [**ML$_2^n$**, M = Co(II) or Mn(III)Cl, n = 1–5; see Figure 1].

The route for the synthesis of key intermediate of **HL^2** is shown in Scheme 1.

Reslts and Discussion

The Schiff-base ligands **HL^n** (n = 1–5) were conveniently prepared by the reaction of aromatic amines with salicylaldehyde or crown ether-functionalized salicylaldehyde. Unfortunately, due to their sterically hindered nature, the yields of the complexes were low (< 63%). In the IR spectra of **HL^n**, the characteristic frequency of Ar–OH at 3320–3220 cm^{-1} was observed, as was that for CH=N at 1620–1618 cm^{-1}. In the case of **ML$_2$**, the $\nu_{CH=N}$ of CoL_2 shifts *ca.* 10 cm^{-1} to shorter wavelength,

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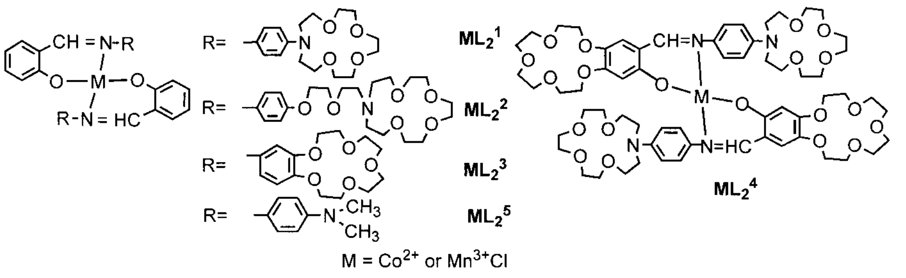
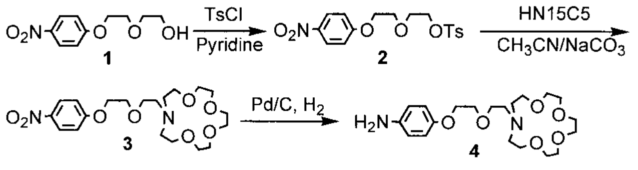


Figure 1.



Scheme 1.

and the $\nu_{CH=N}$ of **MnL$_2^n$Cl** shifts *ca.* 10 cm^{-1} to longer wavelength. Moreover the characteristic vibration of Ar–OH at 3300 cm^{-1} disappeared, but that for the vibration of $\nu_{C\text{-}O\text{-}C}$ did not change. These facts indicate that the Co^{2+} and Mn^{3+} ions only interact with the Ar–OH and CH=N groups.

The crystal structures of **HL^1**, **HL^4**,[8] and **CoL$_2^1$** are shown in Figures 2, 3 and 4, respectively. The conformations of the ligands **HL^1** and **HL^4** suggest that the aza crown ring does come closer to the coordination group compared to the benzo-crown ring. Moreover, the nitrogen atom of the CH=N moiety interacts with hydrogen atom of the Ar–OH group through an H-bond, CH=N···H-O-Ar. The crystal structure of **CoL$_2^1$** indicates the formation of a 1:2 (Co/**HL**) Co(II)-Schiff base complex, and the geometry of Co is a pseudo-tetrahedral conformation. The molecular structure of **CoL$_2^1$** 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 indicates that the aza-crown ether rings do control the coordination environment.

Since at ambient temperature, pyridine (Py) solutions of manganese complexes are oxidized in air to yield (Py)L$_2$Mn$^{(III)}$-O-Mn$^{(III)}$L$_2$(Py), the oxygenation constant (K$_{O_2}$) of Mn(III)-Schiff base complexes cannot be determined accurately.[9] Therefore we only studied the dioxygen affinities of transition metal complexes by dioxygen binding to cobalt(II) complexes. The oxygenation equilibrium constants (K$_{O_2}$) and thermodynamic parameters (ΔH° and ΔS°) of the above cobalt(II)-Schiff base complexes are listed in Table 1. As seen in Table 1, the dioxygen affinities of the cobalt(II) complexes were influenced greatly by both temperature and the structure of the Schiff base. Higher temperature results in a smaller oxygenation constant. This may be due to higher temperatures resulting in poor solubility of O$_2$. The oxygenation constants (K$_{O_2}$) of **CoL$_2^1$**, **CoL$_2^2$**, **CoL$_2^3$** and **CoL$_2^4$** with crown ether rings are larger than that of the uncrowned analogue (**CoL$_2^5$**), especially in the case of **CoL$_2^4$** that contains four crown ether rings, which shows the highest dioxygen affinity. This observation could be due to a macrocycle effect of the crown

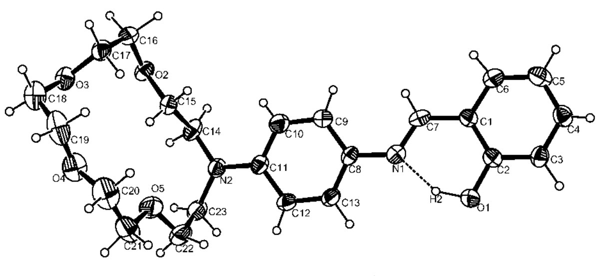


Figure 2. The crystal structure of **HL^1**.

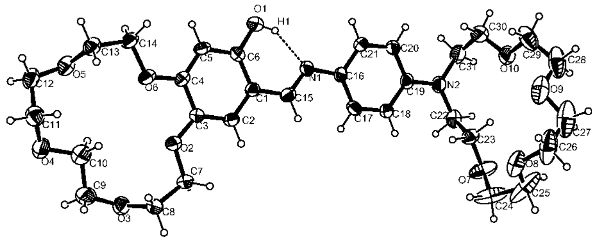


Figure 3. The crystal structure of **HL^4**.

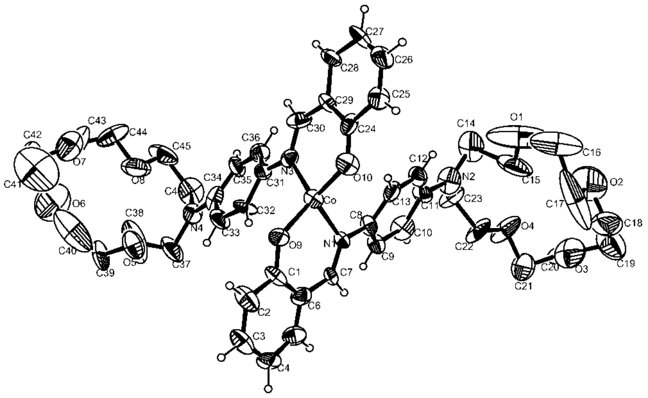


Figure 4. The crystal structure of **CoL$_2^1$**.

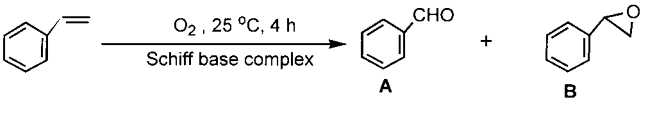
Table 1. Oxygenation constants (K_{O_2}) and thermodynamic parameters (ΔH° and ΔS°) of Co(II)-Schiff base complexes.

Complexes	B	T [°C]	Ln K_{O_2} [mm^{-1}]	ΔH° [KJ·mol^{-1}]	ΔS° [J·K^{-1}·mol^{-1}]
CoL_2^1	Py	−5	−4.22 (−4.01*)	−40.85	−228.19
		0	−4.56 (−4.36*)		
		15	−5.49 (−5.28*)		
		25	−6.06 (−5.86*)		
CoL_2^2	Py	−5	−4.03 (−3.83*)	−49.52	−258.96
		0	−4.43 (−4.22*)		
		15	−5.57 (−5.35*)		
		25	−6.27 (−6.06*)		
CoL_2^3	Py	−5	−4.27 (−4.09*)	−38.75	−220.77
		0	−4.59 (−4.42*)		
		15	−5.48 (−5.29*)		
		25	−6.02 (−5.85*)		
CoL_2^4	Py	−5	−4.02 (−3.77*)	−44.50	−240.15
		0	−4.38 (−4.14*)		
		15	−5.41 (−5.19*)		
		25	−6.03 (−5.81*)		
CoL_2^5	Py	−5	−5.62 (−5.60*)		
		0	−5.78 (−5.79*)		
		15	−6.22 (−6.23*)	−19.25	−159.21
		25	−6.48 (−6.47*)		

* The values of K_{O2} for the mixture of **CoL_2** and $NaNO_3$ (1:2, mol/mol, **CoL_2**: $NaNO_3$) were determined.

ether ring that probably facilitates the oxygen molecule to approach the coordination center of the cobalt(II) complexes and stabilize the Co−O_2 bond through the hydrophobicity of the outer ethylene group and the orderly arrangement of the inner oxygen atoms. It was also observed that the oxygenation constant for **CoL_2^2** is larger than that of **CoL_2^1**, which indicates that the flexibility of the polyether-bridged chain bonded to aza-crown ether ring may make the aza-crown ring control the coordination environment and this results in a stronger dioxygen affinity for **CoL_2^2**. It is interesting that the addition of the alkali metal salt $NaNO_3$ enhances the dioxygen affinities of crowned Schiff base-Co(II) complexes, but has little effect on that of uncrowned analogue **CoL_2^5** (see Table 1), this may be due to the alkali metal cation (Na^+), which matches well with crown ether ring and locates near to the coordination center, resulting in higher dioxygen affinity.

In order to investigate the effect of the crown ether ring on the performance of complexes as mimics of monooxygenases in catalytic oxidation reactions, the above **ML_2^n** [M = Co(II) or Mn(III)Cl, n = 1–5] were employed to catalyze the model oxidation of styrene under the conditions of normal pressure and 25 °C (see Scheme 2).



Scheme 2.

Table 2. Schiff base complexes biomimetically catalyze the oxidation of styrene to benzaldehyde.

Catalyst	Conversion [wt. %)	TOF (h^{-1})	Selectivity (wt. %)	
			A	**B**
CoL_2^1	7.5	5.6	100	0
MnL_2^1Cl	32	24	100	0
CoL_2^2	8.2	6.2	100	0
MnL_2^2Cl	38.5	28.9	100	0
CoL_2^3	5	3.7	100	0
MnL_2^3Cl	21.4	16.0	100	0
CoL_2^4	7.8	5.9	100	0
MnL_2^4Cl	36	27	100	0
CoL_2^5	1.2	1.0	5.8	94.2
MnL_2^5Cl	8	6	6.3	93.7

Legend: **A** = benzaldehyde, **B** = epoxy product, TOF = turnover frequency (mole styrene converted per mole catalyst per hour).

As illustrated in Table 2, **MnL_2^nCl** (n = 1–5) possess higher catalytic oxidation activities than **CoL_2^n** (n = 1–5) under the same reaction conditions. This may be due to the inner electronic structures of the cobalt and manganese atoms. The data indicate that crown ether rings bonded to transition metal complexes affected the results of the oxidation of styrene. The major product of oxidation of styrene catalyzed by **ML_2^5** [M = Co(II) or Mn(III)Cl] is the epoxide, and the selectivity for benzaldehyde is only *ca.* 5.8–6.3%. But for catalysts **ML_2^5** [M = Co(II) or Mn(III)Cl, n = 1–4], the only oxidation product observed comes from oxidative C=C cleavage of the olefinic moiety with the formation of benzaldehyde with up to 100% selectivity. The data in the Table 2 also indicate that crowned Schiff base complexes possess higher biomimetic catalytic activities compared to uncrowned Schiff base complexes $\mathbf{ML_2^5}$ [M = Co(II) or Mn(III)Cl]. Complexes $\mathbf{MnL_2^2Cl}$ and $\mathbf{MnL_2^4Cl}$ exhibit better performance in terms of conversion and TOF as compared to other Schiff base complexes reported by literature.[11] These results could be due to the macrocycle effect of crown ether rings whose special conformation in $\mathbf{MnL_2^nCl}$ (n = 1–4) can offer large steric hindrance and a hydrophobic environment, and possibly favor the formation of and stabilize the active Mn=O species. The possible mechanism of styrene oxidation involves free radical processes since peroxide $\mathbf{L_2^nM\text{-}OOH}$ [M = Co(II) or Mn (III)Cl, n = 1–5] could be formed from an MO_2 (M = Co or Mn) complex in the presence of acid,[12] and the above peroxide can oxidize styrene to benzaldehyde through a free hydroxyl radical intermediate, C(OOH)-C$^\bullet$ which is derived from interaction between a hydroperoxyl radical and the carbon-carbon double bond.[13]

Conclusion

In conclusion, this study indicates that crown ether rings exhibit great effects on the dioxygen affinities and biomimetic catalytic performance of transition metal-Schiff base complexes, and that the oxidation of styrene to benzaldehyde (selectivity = 100%) with molecular oxygen at 25 °C under a normal atmospheric pressure of O_2 occurs efficiently in the presence of crowned Schiff base-transition metal complexes. Further studies into the scope of this catalytic oxidation reaction are being carried out in our laboratory.

Experimental Section

Apparatus and Reagents

Melting points were determined on a Yanaco MP-500 micromelting point apparatus and are uncorrected. IR spectra were obtained on a Nicolet-1705X IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-200 MHz in $CDCl_3$ with tetramethylsilane, as the internal standard. Mass spectra were obtained on a Finnigan LCQ^{DECA} spectrometer. Elemental analyses were performed on a Carlo-Erbo 1160 elemental analyzer. Absorption spectra were recorded on a UV-Vis Tu-1901 spectrophotometer. Silica gel (60H for TLC, Qingdao, China) was used for flash column chromatography. *N,N*-Dimenthyl-[4-(2-hydroxbenzylideneimino)]aniline (**HL**^{5}),[14] *N*-(4-aminophenyl)-aza-15-crown-5 (**5**),[15] 4′-aminobenzo-15-crown-5 (**6**)[16] and 4′-formyl-5′-hydroxbenzo-15-crown-5 (**7**) (crowned salicyclaldehyde)[17] were synthesized according to published procedures. All other reagents were of analytical grade and were used without further purification. Syntheses of the new ligands are given below.

5-(4-Nitrophenyoxyl)-3-oxapentane-1-toslyate (2)

1-Hydroxy-5-(4-nitrophenyoxyl)-3-oxapentane (**1**; 22.70 g, 0.1 mol) was dissolved in pyridine (80 mL) and *p*-toluenesulfonyl chloride (19.30 g, 0.1 mol) added portionwise over 2 h as a power to the stirred, ice-cooled solution. Stirring and cooling were continued for another 4 h and then the mixture was left overnight. It was then poured onto ice (110 g) and further diluted with water (50 mL). The precipitated tosylate was filtered off and washed with water (160 mL). Recrystallization from ethanol (200 mL) gave the pure tosylate **2**; yield: 26.70 g (70%); mp 67–70 °C; ^{1}H NMR: δ = 6.87–6.70 (8H, m, ArH), 4.20–3.95 (8H, m, OCH_2CH_2O), 2.80 (3H, s, CH_3); IR (KBr): ν_{max} = 1570, 1358, 1182, 1124 cm^{-1}; MS: *m/z* = 380 (M^+ – 1); anal. calcd. for $C_{17}H_{19}NO_7S$: C 53.54, H 4.99, N 3.67; found: C 53.87, H 5.27, N, 3.44.

N-[-5-(4-Nitrophenyoxyl)-3-oxaamyl]-aza-15-crown-5 (3)

In a dry acetonitrile solution (100 mL) of monoaza-15-crown-5 (1.32 g, 6 mmol) was suspended Na_2CO_3 (12.50 mmol), and the mixture was then refluxed while stirring under a nitrogen atmosphere. To the refluxing suspension was added dropwise a dry acetonitrile solution (30 mL) of **2** (2.30 g, 6 mmol). After the addition was complete, the mixture was refluxed and monitored by TLC for 7 d. The mixture was then concentrated and water (10 mL) was added. The solution was extracted with chloroform (50 mL × 3) and the combined extract was dried over Na_2SO_4. The solvent was then removed by rotary evaporation. Chromatography of the crude product (silica gel, CH_3OH) afforded the oily product **3**; yield: 0.40 g (15%); ^{1}H NMR: δ = 6.81–6.73 (4H, m, ArH), 4.14–3.64 (22H, m, 11 × OCH_2), 3.60–3.50 (6H, m, 3 × NCH_2); IR (KBr): ν_{max} = 1601, 1564, 1368, 1225, 1124 cm^{-1}; MS: *m/z* = 428 (M^+); anal. calcd. for $C_{20}H_{32}N_2O_8$: C 56.07, H 7.48, N 6.54; found: C 56.35, H 7.59, N, 6.75.

N-[5-(4-Aminophenyoxyl)-3-oxaamyl]-aza-15-crown-5 (4)

To a suspension of 0.10 g Pd/C (10%) in 50 mL ethanol was added **3** (0.73 g, 1.7 mmol), and the mixture was hydrogenated under H_2 at 50–55 °C for 20 h. The reaction mixture was then cooled and filtered. The filtrate was evaporated to dryness and the crude product was chromatographed (silica gel, CH_3OH) to afford the slightly reddish oily product **4**; yield: 0.60 g (85%); ^{1}H NMR: δ = 6.73–6.64 (4H, m, ArH), 5.31 (2H, s, NH_2), 4.14–3.60 (22H, m, 11 × OCH_2), 3.60–3.50 (6H, m, 3 × NCH_2); IR (neat): ν_{max} = 3279, 1601, 1564, 1225, 1124 cm^{-1}; MS: *m/z* = 398 (M^+); anal. calcd. for $C_{20}H_{34}N_2O_6$: C 60.30, H 8.54, N 7.04; found: C 60.11, H 8.47, N 7.18.

N-[4-(2-Hydroxybenzylimine)]phenylaza-15-crown-5 (HL^1)

Compound **5** (0.31 g, 1.0 mmol) was dissolved in 6 mL of MeOH and the solution was mixed with a solution of 1.0 mmol of salicyclaldehyde (0.12 g, 1.0 mmol) in MeOH (6 mL) and stirred under N_2 for 2 h. The yellow precipitate was collected and washed sequentially with water and ethanol. After recrystallization from ethanol, the yellow product $\mathbf{HL^1}$ was obtained; yield: 0.35 g (85%); mp 97–100 °C; ^1H NMR ($CDCl_3$): $\delta = 13.80$ (s, 1H, OH), 8.60 (s, 1H, CH=N), 7.36–7.24 (m, 4H, Ar-H), 7.00–6.68 (m, 4H, Ar-H), 3.80–3.60 (m, 20H, OCH_2 and NCH_2); IR (KBr, film): $\nu_{max} = 3220$, 1619, 1120 cm^{-1}; MS: $m/z = 414$ (M^+); anal. calcd. for $C_{23}H_{30}N_2O_5$: C 66.67, H 7.25, N 6.76; found: C 66.95, H 7.48, N 6.49.

N-{3-Oxa-5-[4-(2-hydroxybenzylidenimine)phenoxy]-amyl}-aza-15-crown-5 (HL^2)

Compound **4** (0.40 g, 1.0 mmol) was dissolved in 6 mL of MeOH, the solution was mixed with a solution of 1.0 mmol of salicyclaldehyde (0.122 g, 1.0 mmol) in MeOH (6 mL) and stirred under N_2 for 2 h. The reaction mixture was concentrated to dryness, and chromatographed (silica gel, MeOH) to afford the oily product $\mathbf{HL^2}$; yield: 0.45 g (89%); ^1H NMR ($CDCl_3$): $\delta = 13.52$ (1H, s, OH), 8.59 (1H, s, CH=N), 7.40–7.10 (4H, m, Ar-H), 7.00–6.85 (4H, m, ArH), 4.14–3.65 (22H, m, 11 × OCH_2), 3.60–3.50 (6H, m, 3 × NCH_2); IR (neat): $\nu_{max} = 3327$, 1620, 1225, 1140 cm^{-1}; MS: $m/z = 502$ (M^+); anal. calcd. for $C_{27}H_{38}N_2O_7$: C 64.54, H 7.57, N 5.58; found: C 64.21, H 7.81, N 5.34.

4-Hydroxy-5-benzyliminemethyl-benzo-15-crown-5 (HL^3)

$\mathbf{HL^3}$ was obtained in a similar way to $\mathbf{HL^1}$ by the reaction of 4′-aminobenzo-15-crown-5 (**6**) and salicyclaldehyde; yield: 75%; mp 101–103 °C; ^1H NMR ($CDCl_3$): $\delta = 13.59$ (1H, s, OH), 8.44 (1H, s, CH=N), 7.42–7.19 (5H, m, Ar-H), 6.86 (1H, s, ArH), 6.47 (1H, s, ArH), 4.17–4.07 (8H, m, 2 × $ArOCH_2CH_2O$), 3.93–3.75 (8H, m, 2 × OCH_2CH_2O); IR (KBr, film): $\nu_{max} =$ 3227, 1628, 1225, 1140 cm^{-1}; MS: $m/z = 387$ (M^+); anal. calcd. for $C_{21}H_{25}N_2O_6$: C 65.12, H 6.46, N 3.62; found: C 65.34, H 6.59, N 3.85.

4-Hydroxy-5-[4-(*N*-aza-15-crown-5)-benzyliminemethyl]-benzo-15-crown-5 (HL^4)

$\mathbf{HL^4}$ was obtained in a similar way to $\mathbf{HL^1}$ by the reaction of 4′-formyl-5′-hydroxybenzo-15-crown-5 (**7**) and *N*-(4-aminophenyl)-aza-15-crown-5 (**6**); yield: 83%; mp 114–116 °C (lit.[8] mp 114–117 °C); ^1H NMR ($CDCl_3$): $\delta = 14.02$ (1H, s, OH), 8.41 (1H, s, CH=N), 7.21–7.16 (2H, d, J = 8 Hz, Ar-H), 6.84 (1H, s, ArH), 6.68–6.63 (2H, d, J = 10 Hz, ArH), 6.46 (1H, s, ArH), 4.16–4.07 (8H, m, 2 × $ArOCH_2CH_2O$), 3.92–3.57 (28H, m, 5 × OCH_2CH_2O and 2 × NCH_2CH_2O); IR (KBr, film): $\nu_{max} =$ 3224, 1618, 1220, 1124, 1050 cm^{-1}; MS: $m/z = 603.3$ (M^+); anal. calcd. for $C_{31}H_{44}N_2O_{10}$: C 61.59, H 7.28, N 4.64; found: C 61.79, H 7.12, N 4.53.

General Methods for Synthesis of Cobalt(II)-Schiff Base Complexes (CoL_2)

A solution of $\mathbf{HL^n}$ (2.0 mmol) and $Co(OAc)_2 \cdot 4\,H_2O$ or $MnCl_2 \cdot 4\,H_2O$ (1.1 mmol) in EtOH (15 mL) was stirred in EtOH for 2 h under N_2 at 70 °C. The mixture was then cooled, filtered, and washed with methanol to afford the transition metal complexes. Pure product was obtained after recrystallization from ethanol.

$\mathbf{CoL_2^1}$**:** dark brown; yield: 53%; mp 203–206 °C; IR (KBr, film): $\nu_{max} = 1610$, 1123 cm^{-1}; anal. calcd. for $CoC_{46}H_{58}N_4O_{10}$: C 62.37, H 6.55, N 6.32; found: C 62.55, H 6.49, N 6.18.

$\mathbf{MnL_2^1Cl}$**:** purple; yield: 58%; mp 191–194 °C; IR (KBr, film): $\nu_{max} = 1637$, 1126, 1121 cm^{-1}; anal. calcd. for $MnC_{42}H_{50}N_4O_8Cl$: C 60.80, H 6.03, N 6.76; found: C 60.61, H 5.88, N 6.93.

$\mathbf{CoL_2^2}$**:** dark brown; yield: 58%; mp 186–188 °C; IR (KBr, film): $\nu_{max} = 1611$, 1123 cm^{-1}; anal. calcd. for $CoC_{54}H_{74}N_4O_{14}$: C 64.48, H 7.36, N 5.57; found C 64.69, H 7.69, N 5.38.

$\mathbf{MnL_2^2Cl}$**:** purple; yield: 63%; mp 195–198 °C; IR (KBr, film): $\nu_{max} = 1630$, 1227, 1124 cm^{-1}; anal. calcd. for $MnC_{54}H_{74}N_4O_{14}Cl$: C 62.48, H 7.14, N 5.40; found C 62.74, H 7.03, N 5.19.

$\mathbf{CoL_2^3}$: dark brown; yield: 45%; mp 171–174 °C; IR (KBr, film): $\nu_{max} = 1616$, 1224, 1134 cm^{-1}; anal. calcd. for $CoC_{42}H_{48}N_2O_{12}$: C 60.65, H 5.78, N 3.37; found C 60.89, H 5.96, N 3.18.

$\mathbf{MnL_2^3Cl}$**:** purple. 59% yield. mp 191–194 °C. IR (KBr, film) ν_{max}: 1636, 1227, 1134 cm^{-1}. Anal. calcd for Mn $C_{42}H_{48}N_2O_{12}Cl$: C 58.40, H 5.56, N 3.24; found C 58.74, H 5.79, N, 3.48.

$\mathbf{CoL_2^4}$**:** dark brown; yield: 47%; mp 189–193 °C; IR (KBr, film): $\nu_{max} = 1611$, 1225, 1128, 1052 cm^{-1}; anal. calcd. for $CoC_{62}H_{86}N_4O_{20}$: C 58.81, H 6.79, N 4.43; found: C 58.57, H 6.53, N 4.69.

$\mathbf{MnL_2^4Cl}$**:** purple; yield: 43%; mp 248–251 °C; IR (KBr, film): $\nu_{max} = 1624$, 1223, 1126, 1053 cm^{-1}; anal. calcd. for $MnC_{62}H_{86}N_4O_{20}Cl$: C 57.39, H 6.63, N 4.32; found: C 57.63, H 6.95, N 4.17.

$\mathbf{CoL_2^5}$**:** dark brown; yield: 62%; mp 251–254 °C; IR (KBr, film): $\nu_{max} = 1610$ cm^{-1}; anal. calcd. for $CoC_{30}H_{30}N_4O_2$: C 67.04, H 5.59, N 10.43; found: C 66.75, H 5.87, N 10.19.

$\mathbf{MnL_2^5Cl}$**:** purple; yield: 57%; mp 267–271 °C; IR (KBr, film): $\nu_{max} = 1619$ cm^{-1}; anal. calcd. for $MnC_{30}H_{30}N_4O_2Cl$: C 63.32, H 5.28, N 9.85; found: C 63.06, H 5.45, N 9.62.

X-Ray Crystallography Data

Crystallographic data and experimental details are listed in Table 3.

Crystallographic data were collected using a CAD4 four-circle automated diffractometer, utilizing graphite monochromated Mokα radiation with DIFRAC. The structure was solved using the direct method and refined on F^2 using a full matrix least-squares procedure. All non-hydrogen atoms were refined anisotropically. Positions of all hydrogen atoms for $\mathbf{HL^1}$ were calculated based on geometrical factors. These hydrogens were allowed to ride on their neighboring heavy atoms during refinement, and the rest hydrogen atoms of $\mathbf{HL}^1$ were refined isotropically. The structure was solved, refined and displayed using NRCVAX and SHELX-97 grogram package.

Table 3. Crystallographic data and experimental details for **HL^1** and **CoL$_2$^{1}**.

Formula	**HL^1** ($C_{23}H_{30}N_2O_5$)	**CoL$_2$^{1}** ($CoC_{46}H_{58}N_4O_{10}$)
Formula weight	414.49	885.89
Crystal system	Orthorhombic	Monoclinic
Space group	P2$_1$nb	1α
a (Å)	8.514(3)	14.539(4)
b (Å)	9.046(3)	19.129(9)
c (Å)	27.921(7)	16.539(5)
α (°)	90.00(3)	90.00(3)
β (°)	90.00(3)	92.58(3)
γ (°)	90.00(3)	90.00(3)
V (Å^3)	2150.6(12)	4595(3)
Z	4	4
F (000)	888	1876
D_x (g cm^{-3})	1.280	1.281
Crystal size (mm)	0.32 × 0.35 × 0.40	0.20 × 0.25 × 0.28
μ (mm^{-1})	0.090	0.433
Temperature (K)	293(2)	293(2)
$2\theta_{max}$(°)	48.1	50.06
Total data	2000	4192
Independent data	1825(R_m = 0.0000)	4018(R_m = 0.0000)
Total parameters	365	4018
Goodness of fit on F^2	1.035	0.980
R [I > 20 − (I)]	0.0448	0.0609
R (all data)	0.1341	0.1738
Largest diff peak and hole (e Å^3)	0.223, −0.193	0.298, −0.224

Oxygen uptake Measurements

The values of K_{O2} were determined by the quantities (volumes) of dioxygen absorbed at equilibrium, as described in the literature.[18] Diethylene glycol dimethyl ether (saturated by O_2) was employed as solvent and pyridine (saturated by O_2) was employed as the axial base (B), which is necessary for the Schiff base complexes investigated to combine with dioxygen.[18,19] The concentration of Schiff base complexes was 3.5×10^{-3} mol · dm^{-3}, and partial pressure of dioxygen was 97 Kpa. ΔS° and ΔH° were calculated from the equations $\Delta G° = -RT \ln K_{O_2}$ and $T\Delta S° = \Delta H° - \Delta G°$. The equilibrium constants (K_{O_2}) were calculated (see Figure 5). B, p_{O_2} represent axial base and partial pressure of oxygen, respectively. Thermodynamic parameters ΔH°, ΔS° were determined from variation of K_{O_2} and K'_{O_2} over a range of temperature.

$$CoL_2 + B \rightleftharpoons CoL_2B \qquad CoL_2B + O_2 \rightleftharpoons CoL_2BO_2$$

$$Ko_2 = \frac{[CoL_2BO_2]}{[CoL_2B] \cdot p_{O_2}}$$

Figure 5.

Biomimetic Catalytic Oxidation of Styrene

The biomimetic system of manganese-Schiff base complexes-catalyzed oxidation of styrene is similar to that of manganese porphyrins-catalyzed oxidation of alkene.[20] To a solution of the imidazole co-catalyst (0.1 mmol), styrene (0.5 mmol), the reducing agent Zn (0.5 mmol), CH_3CN:CH_2Cl_2 (10 mL, 9.5:0.5, v/v) was added Co(II) or Mn (III) complex catalyst (1.0×10^{-5} mol). The mixture was vigorous stirred at 25 °C under O_2 for 30 min, and the proton donor CH_3COOH (0.086 mL) was injected. The mixture was stirred for 4 h at the same temperature and then analyzed by GC (PE-GC-9000).

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