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Dioxygen affinities and catalytic epoxidation performance of mono-Schiff base transition-metal complexes with aza-crown or morpholino pendants

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Abstract

Mono-Schiff base Co^{II} complexes, CoL_2^1–CoL_2^6 with aza-crown or morpholino pendants were synthesized. The O_2 uptake of these complexes in $MeOCH_2CH_2OMe$ solution was determined at different temperatures, and the equilibrium constants (KO_2) and thermodynamic parameters (ΔH^0, ΔS^0) for oxygenation were calculated. The corresponding Mn^{III} complexes, MnL_2^1Cl–MnL_2^6Cl, were employed to catalyze epoxidation of styrene at ambient temperature and pressures. Crown ether effects on the modulation of O_2-binding capability and the catalytic oxidation of styrene are discussed. The results indicate that the dioxygen affinities of the Co^{II} complexes are much more enhanced by aza-crown pendants than that by morpholino pendants, and the O_2-binding capabilities of CoL_2^1–CoL_2^3 with aza-crown pendants can also be enhanced by adding alkali metal (Li^+, Na^+ and K^+) cations; similarly, the catalytic activities of the Mn^{III} complexes with aza-crown pendants, MnL_2^1Cl–MnL_2^3Cl, are higher than those of the Mn^{III} complexes with morpholino pendants, MnL_2^4Cl–MnL_2^6Cl.

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. Since 1938, when Tsumaki [1] reported that Schiff base-Co^{II} complexes possess the ability to activate various molecules, especially molecular oxygen coordinated in the axial position, transition metal complexes of Schiff bases have been one of the most successful classes of synthetic oxygen carriers due to their structural similarity to those found in biological systems [2, 3]. In the past decades, a number of reports have appeared on Schiff base complexes as models for oxygen carrying metalloenzymes [4] and oxygenases [5], such as hemoglobin and cytochrome P-450 enzymes, which play important roles in the catalytic oxidation of various organic compounds [6]. Various Schiff base complexes as cytochrome P-450 models have been employed for the catalytic oxidation of olefins to epoxides and aldehydes [7–9]. However, to the best of our knowledge, very limited studies on the oxidation catalyzed by aza-crown substituted Schiff base complexes have been reported to date. Crown rings could endow functional molecules with novel performance and character, due to the hydrophobicity of the outer ethylene groups and orderly arrangement of inner oxygen atoms [10, 11]. Moreover, 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 [12]. Recent studies have indicated that crown ether-containing Schiff base complexes show much improved O_2-binding and catalytic epoxidation activity due to the special configuration and function of the crown ether ring [13]. A previous paper has reported the synthesis of MnL_2^nCl (n = 1–6) (see Figure 1) and the homogeneous direct catalytic oxidation of *p*-xylene to *p*-toluic acid by air in the presence of MnL_2^nCl under mild conditions [14]. In connection with further research aimed at the effects of an aza-crown ring appended in Schiff base complexes, and the effect of added alkali metal ions on O_2-binding activity and catalytic epoxidation performance of Schiff base Mn^{III} complexes, we now report on the synthesis and dioxygen affinities of CoL_2^n (n = 1–6) (see Figure 1), and the homogeneous catalytic epoxidation of styrene by aza-crown substituted Schiff base Mn^{III} complexes MnL_2^nCl.

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Experimental

General methods and materials

M.p's. were determined on a Yanaco MP-500 micromelting point apparatus and are uncorrected. I.r. spectra were recorded on a Nicolet-1705X spectrometer. Mass spectra were obtained on a Finnigan LCQ^{-DECA} spectrometer. Metal ion contents were measured using an IRIS-Advantage ICP emission spectrometer. Other elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Molar conductances were obtained on a DDS-11A conductivitymeter in DMF solution (1.0×10^{-3} mol l^{-1}). Molar Magnetic Susceptibilities were obtained on a T3-200 magnetic balance at 25 °C. G.c. analyses were carried on a Varian CP-3800 gas chromatograph (OV-1 column).

Materials

Mono-Schiff base ligands HL^1–HL^6 and their Mn^{III} complexes, $MnL_2{}^1Cl$–$MnL_2{}^6Cl$, were synthesized according to the literature [14]. Styrene, 1,2-epoxyethylbenzene were purchased from Sigma Chemical Co. All other analytical grade reagents were purchased from China and used without further purification.

General methods for preparation of the cobalt complexes

A solution of the ligand (2.0 mmol) and $Co(AcO)_2 \cdot 4H_2O$ (1.1 mmol) in EtOH (15 cm^3) was stirred for 2 h under a N_2 atmosphere at 70 °C, then the mixture was cooled, filtered, and washed with EtOH to give the complexes. The pure product was obtained after recrystallization from EtOH.

$CoL_2{}^1$: purple, 84% yield, m.p. 225–257 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2964, 2860, 1608, 1598, 1500, 1254, 1131, 1049 cm^{-1}; ESI-MS m/z: 1107 ($M^+ + 1$); (Found C 62.8, H 5.6, N 5.2, Cl 6.3, Co 5.4. $C_{58}H_{64}N_4O_{10}Cl_2Co$ calcd.: C 62.9, H 5.8, N 5.1, Cl 6.4, Co 5.3%). Λ_m(S cm^2 mol^{-1}): 9.53. specify Molar magnetic susceptibility $\chi_M = 7.15 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 3.83 \times 10^{-23}$ J T^{-1}.

$CoL_2{}^2$: purple, 78% yield, m.p. 231–233 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2930, 2856, 1611, 1601,1500, 1250, 1132, 1052 cm^{-1}; ESI-MS m/z: 1148 ($M^+ + 1$); (Found C 58.7, H 5.2, N 4.8, Cl 12.3, Co 5.3. $C_{56}H_{58}N_4O_{10}Cl_4Co$ calcd.: C 58.6, H 5.1, N 4.9, Cl 12.4, Co 5.1%). Λ_m(S cm^2 mol^{-1}): 8.92. Molar magnetic susceptibility $\chi_M = 7.01 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 3.79 \times 10^{-23}$ J T^{-1}.

$CoL_2{}^3$: purple, 84% yield, m.p. 262–264 °C; I.r. (KBr, cm^{-1}) ν_{max}: 3442, 2934, 2858, 1610, 1600, 1502, 1250, 1133, 1050 cm^{-1}; ESI-MS m/z: 1237 ($M^+ + 1$); (Found C 54.6, H 4.5, N 4.4, Cl 5.5, Br 12.8,Co 4.6. $C_{56}H_{58}N_4O_{10}Cl_2Br_2Co$ calcd.: C 54.4, H 4.7, N 4.5, Cl 5.7, Br12.9, Co 4.8%). Λ_m(S cm^2 mol^{-1}): 9.36. Molar magnetic susceptibility $\chi_M = 6.86 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 3.75 \times 10^{-23}$ J T^{-1}.

$CoL_2{}^4$: purple, 79% yield, m.p. 162–164 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2960, 2855, 1609,1600, 1500, 1253, 1194, 1122 cm^{-1}; ESI-MS m/z: 747 ($M^+ + 1$); (Found C 61.3, H 5.5, N 7.3, Cl 9.3, Co 7.7. $C_{38}H_{40}N_4O_4Cl_2Co$ calcd.: C 61.1, H 5.4, N 7.5, Cl 9.5, Co 7.9%). Λ_m(S cm^2 mol^{-1}): 10.15. Molar magnetic susceptibility $\chi_M = 6.57 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 3.67 \times 10^{-23}$ J T^{-1}.

$CoL_2{}^5$: purple, 79% yield, m.p. 157–159 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2940, 2855, 1611, 1600, 1501, 1254, 1200, 1121 cm^{-1}; ESI-MS m/z: 788 ($M^+ + 1$); (Found C 54.8, H 4.2, N 7.3, Cl 17.9, Co 7.6. $C_{36}H_{34}N_4O_4Cl_4Co$ calcd.: C 54.9, H 4.3, N 7.1, Cl 18.0, Co 7.5%). Λ_m(S cm^2 mol^{-1}): 12.15. Molar magnetic susceptibility $\chi_M = 6.25 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 3.58 \times 10^{-23}$ J T^{-1}.

$CoL_2{}^6$: purple, 79% yield, m.p. 167–169 °C; I.r. (KBr, cm^{-1}) ν_{max}: 2937, 2850, 1611, 1600, 1500, 1251, 1196, 1118 cm^{-1}; ESI-MS m/z: 877 ($M^+ + 1$); (Found C 49.2, H 4.0, N 6.3, Cl 8.3, Br 18.4, Co 6.8. $C_{36}H_{34}N_4O_4Cl_2Br_2Co$ calcd.: C 49.3, H 3.9, N 6.4, Cl 8.1, Br 18.3, Co 6.7%). Λ_m(S cm^2 mol^{-1}): 12.60. Molar magnetic susceptibility $\chi_M = 6.08 \times 10^{-2}$ J mol^{-1} T^{-2}, magnetic moment $\mu_m = 3.53 \times 10^{-23}$ J T^{-1}.

Oxygen uptake

The oxygenation constants and thermodynamic parameters of $CoL_2{}^1$–$CoL_2{}^6$ were determined using standard equipment and method [15]: diglyme (saturated with O_2) as solvent, 1.0 mol dm^{-3} of pyridine (saturated with O_2) as axial ligand (B), complex concentration 5×10^{-3} mol dm^{-3}, 9.7×10^4 Pa of O_2 partial pressure. The equilibrium constant (KO_2) was calculated as follows:

$$\mathrm{CoL} + \mathrm{B} \rightleftharpoons \mathrm{CoLB}$$

$$\mathrm{CoLB} + \mathrm{O_2} \rightleftharpoons \mathrm{CoLBO_2}$$

$$K\mathrm{O_2} = \frac{[\mathrm{CoLBO_2}]}{[\mathrm{CoLB}] \cdot P\mathrm{O_2}}$$

Where complexes are expressed in terms of molarities and the dioxygen concentration is expressed as partial pressure (PO_2) in Torr. ΔH^0 and ΔS^0 were calculated from equations $\Delta G^0 = -\mathrm{RTln}\ KO_2$ and $T\Delta S^0 = \Delta H^0 - \Delta G^0$. Thermodynamic parameters ΔH^0, ΔS^0 for oxygenation were determined from variation of KO_2 and $K'O_2$ over a range of temperatures.

Catalytic epoxidation of styrene

The reaction system of styrene epoxidation catalyzed by MnL_2Cl is as follows: to a solution of MeCN (5 cm^3) containing $PhCH{=}CH_2$ (0.5 mmol), PhBr (0.5 mmol, as internal standard), imidazole (0.05 mmol, as axial ligand) and MnL_2Cl catalyst (0.02 mmol), The PhIO (1.0 mmol) was added, the suspension was sealed and stirred vigorously for 1 h at 20 °C. The oxidation products were identified by g.c. analyses and confirmed by MS.

Results and discussion

Synthesis

Compared with the i.r. spectrum of the free ligand [14], those of the Schiff base Co^{II} complexes, $CoL_2{}^1$–$CoL_2{}^6$, were almost at the same frequencies, except for the C=N stretching vibration which was shifted 11–16 cm^{-1} to lower frequency and also showed an intensity greater compared to the free ligand. The absence of a OH stretching vibration ($\sim$3440 cm^{-1}) in the complexes indicated deprotonation of OH in the ligand upon complex formation, suggesting the formation of a N–O–Co coordination bond. The C–O–C stretching vibrations in the crown ether ring for the complexes were 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 [16]. The observed molar conductances of the complexes in DMF solution (1.0×10^{-3} mol l^{-1}) at 25°C showed that these mono-Schiff base Co^{II} complexes were non-electrolytes [17]. The molar magnetic susceptibility χ_M and magnetic moment μ_m of the ^{I}complexes $CoL_2{}^1$–$CoL_2{}^6$ indicated that cobalt has three non-paired electrons. These observations indicate that the cobalt in these complexes is divalent. The ESI-MS Mass spectra and elemental analysis of the complexes indicated that HL^1–HL^6 all formed 2:1(ligand/metal) complexes (CoL_2). We therefore suggest a structural formula for these Schiff base cobalt complexes as in Figure 1.

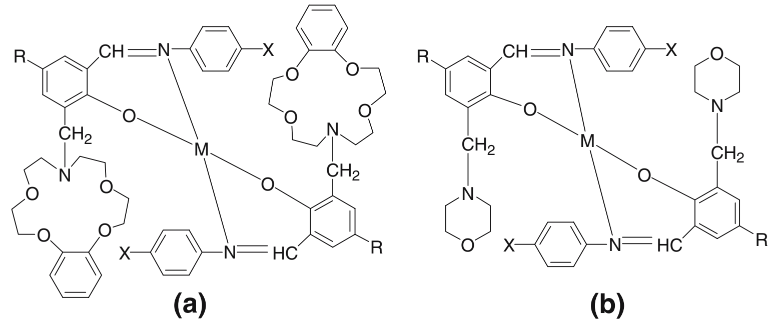
Dioxygen affinity of the cobalt (II) complexes

The equilibrium constants (KO_2) and thermodynamic parameters ΔH^0 and ΔS^0 for oxygenation of $CoL_2{}^1$–$CoL_2{}^6$ are listed in Table 1. The dioxygen affinities of these complexes were influenced greatly by both the temperature and the structures of the Schiff base ligand. Higher temperature results in a smaller oxygenation constant, perhaps due to reduced solubility of O_2 at higher temperature. Furthermore, $CoL_2{}^1$, $CoL_2{}^2$ and $CoL_2{}^3$ containing an aza-crown pendant group show much more enhanced dioxygen affinity than $CoL_2{}^4$, $CoL_2{}^5$ and $CoL_2{}^6$ which possess morpholino pendant. The results can be attributed to the macrocycle effect of the crown ring rather than the electron-donating effect of the nitrogen methylene (NCH_2) on the aromatic ring of the ligand, because the crown ring possesses a special configuration and probably favors the oxygen molecule's approach to the coordinated cobalt(II) of complexes, helping the $Co–O_2$ bond to form through its hydrophobicity ethylene groups and orderly arrangement of inner azaoxa atoms [18].

It is interesting that the addition of alkali metal salt (nitrate/$CoL_2{}^n$ (n = 1–6) = 2:1 mol/mol) to the reaction system can enhance the O_2-binding capability of $CoL_2{}^1$, $CoL_2{}^2$ and $CoL^3{}_2$, but not of $CoL_2{}^4$, $CoL_2{}^5$ and $CoL^6{}_2$. This suggests that alkali metal ions improve the O_2-binding capability only when they are coordinated with the crown ring of the complexes. Table 1 indicates that the KO_2 of complexes containing an aza-crown pendant is significantly enhanced by adding excess $NaNO_3$. However, the enhancement by adding an equal quantity of $LiNO_3$ or KNO_3 is very limited. This may be because the Li^+ ion(d = 1.36 Å) is too small to match the cavity size of aza-15-crown-5 (d = 1.7–2.2 Å), whereas K^+ ion (d = 2.66 Å) is too large, and Na^+ ion (d = 1.90 Å) matches well with the cavity size of aza-15-crown-5 [19] and so facilitates the formation and stabilization of the $Co–O_2$.

Styrene epoxidation catalyzed by the manganese(III) complexes

In order to investigate the effect of the pendant crown ether ring on the performance of the complexes as mimics for monooxygenases in catalytic oxidation, the $MnL_2{}^1Cl$–$MnL_2{}^6Cl$ complexes were employed to catalyze the epoxidation of styrene in the presence of



M= MnCl or Co
L^1 R= Cl, X=Me;
L^2 R= Cl, X=Cl;
L^3 R= Br, X=Cl

M=MnCl or Co
L^4 R= Cl, X=Me;
L^5 R= Cl, X=Cl ;
L^6 R= Br, X=Cl

Fig. 1. the structures of the Schiff base complexes.

Table 1. Equilibrium constants and thermodynamic parameters for oxygenation of CoL_2

Complex	B	T(°C)	Ions added	ln KO_2 (mm^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})
CoL_2^1	Py	−5	/	−3.27	−35.4	−159.2
		0	/	−3.56		
		10	/	−4.11		
		25	/	−4.85		
		10	$LiNO_3$	−4.05		
		10	$NaNO_3$	−3.29		
		10	KNO_3	−3.95		
CoL_2^2	Py	−5	/	−3.46	−32.8	−151.1
		0	/	−3.73		
		10	/	−4.24		
		25	/	−4.94		
		10	$LiNO_3$	−4.16		
		10	$NaNO_3$	−3.45		
		10	KNO_3	−4.11		
CoL_2^3	Py	−5	/	−3.20	−36.5	−162.9
		0	/	−3.50		
		10	/	−4.07		
		25	/	−4.85		
		10	$LiNO_3$	−4.01		
		10	$NaNO_3$	−3.25		
		10	KNO_3	−3.91		
CoL_2^4	Py	−5	/	−5.15	−26.6	−142.0
		0	/	−5.37		
		10	/	−5.78		
		25	/	−6.35		
		10	$LiNO_3$	−5.74		
		10	$NaNO_3$	−5.71		
		10	KNO_3	−5.73		
CoL_2^5	Py	−5	/	−5.21	−25.7	−139.0
		0	/	−5.42		
		10	/	−5.82		
		25	/	−6.37		
		10	$LiNO_3$	−5.80		
		10	$NaNO_3$	−5.77		
		10	KNO_3	−5.79		
CoL_2^6	Py	−5	/	−5.02	−28.1	−146.6
		0	/	−5.25		
		10	/	−5.69		
		25	/	−6.29		
		10	$LiNO_3$	−5.65		
		10	$NaNO_3$	−5.61		
		10	KNO_3	−5.63		

Table 2. Epoxidation of styrene catalyzed by Schiff base manganese(III) complexes[a]

Complex	Conversion (wt%)[b]	Epoxidation yield (%)	Selectivity (%)	TOF (h^{-1})
MnL_2^1Cl	44.4	42.1	94.8	22.2
MnL_2^2Cl	42.5	40.2	94.6	21.3
MnL_2^3Cl	41.2	38.8	94.2	20.6
MnL_2^4Cl	20.2	17.1	84.7	10.1
MnL_2^5Cl	19.8	16.9	85.4	9.9
MnL_2^6Cl	18.5	15.6	84.3	9.3

[a] Reaction time = 1 h; TOF = turnover frequency (mole $PhCH = CH_2$ converted per mol of catalyst per hour).

[b] Conversion determined by G.C. using an internal standard.

iodosylbenzene and excess imidazole, as the axial ligand, at normal pressure and 20 °C. No reaction occurs in the absence of PhIO, it shows there is no aerobic oxidation and PhIO acts as the single-oxygen donor. Styrene is readily oxidized in the presence of Schiff base manganese(III) complexes. As illustrated in Table 2, the data indicate that crown ether rings bonded to Schiff base manganese(III) complexes affected the results of the oxidation of styrene. Both conversion of styrene and the selectivity of the reaction are improved by pendant substituents. The aza-crown substituted MnL_2^1Cl, MnL_2^2Cl and MnL_2^3Cl showed more than twice the conversion of MnL_2^4Cl, MnL_2^5Cl or MnL_2^6Cl. The results may be due to the benzoaza-crown ether ring providing greater steric hindrance than does the morpholino group and, more importantly, providing a hydrophobic microenvironment around the catalytic center so as to favor the formation and protection of the active species $O = Mn(V)$ [20]. The influence of the structure of the pendant group on the catalytic activities of the manganese(III) complexes seems similar to the effects on the O_2-binding capabilities of the cobalt(II) complexes with the same ligands.

Conclusions

This study demonstrates that the presence of a pendant crown ether group in the Schiff base complexes significantly improves the O_2-binding capabilities of cobalt(II) complexes and the catalytic epoxidation performance of manganese(III) complexes. The aza-crown pendants exhibit a more significant enhancement of both of these capabilities. The addition of alkali metal (Na^+) enhances the O_2-binding capability of CoL_2^1, CoL_2^2 and CoL_2^3; on the contrary, the phenomenon was not observed for CoL_2^4, CoL_2^5 and CoL_2^6. This difference is attributed to the macrocyclic effect of benzoaza-crown ether ring, which enlarge the steric hindrance around the coordinated cobalt(II) or manganese(III) of the complexes, and so prevents the complexes being oxidized to the μ-oxodimer and losing activity. The hydrophobicity of the outer ethane groups and orderly arrangement of the inner azaoxa atoms of the crown ether ring are favorable for the formation and protection of active species of oxygenation and epoxidation.

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