

Cobalt(II) Salen Complex with Two Aza-crown Pendants and Its Analogues as Synthetic Oxygen Carriers

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Salen with two aza-crown ether pendants H_2L^1 and its analogues $H_2L^2-H_2L^4$ were successfully synthesized starting from benzo-10-aza-15-crown-5 (BN15C5) or morpholine. Their structures were characterized by IR, MS, 1H NMR and elemental analysis, and were confirmed by X-ray diffraction analysis of H_2L^1 . Moreover, the saturated oxygen uptake of their cobalt(II) complexes CoL^1-CoL^4 in diethyleneglycol dimethyl ether was determined at different temperature. The oxygenation constants (K_{O_2}) and thermodynamic parameters (ΔH° and ΔS°) were calculated. The modulation of O_2 -binding capabilities by pendant substituents were investigated as compared with the parent Schiff base complex CoL^5 (CoSalen). The results indicate that the dioxygen affinities of CoL have been much more enhanced by aza-crown pendants than that by morpholino pendants, and the O_2 -binding capabilities of CoL^1 and CoL^2 with aza-crown pendants would also be enhanced by adding alkali metal cations.

Keywords benzo-10-aza-15-crown-5, bis-Schiff base transition-metal complex, synthesis, oxygenation, alkali metal ion

Introduction

Synthetic oxygen carriers¹ are of great interest as models to mimic oxygen carrying metalloenzymes² for oxygen storage and transport. The cobalt(II) complexes of Schiff bases, such as Salen and its analogues, have been the first and the most extensively investigated due to their structural similarity to those found in biological systems.^{3,4} However, these complexes are easy to dimerize and lose activities after oxygen molecule absorption.⁵ Avdeef and coworkers⁶ demonstrated that it would be favorable to form stable oxygen adducts when these Co(II) complexes were modified by proper substituents. Thus, various substituents have been employed to improve O_2 -binding capabilities of the complexes.^{7,8} Among them, the crown ether-containing Schiff bases have attracted much attention because they can bind both alkali and transition metal guest cations through crown ether cavity and N_2O_2 donor atoms,^{9,10} and co-complexation of alkali cations close to the central transition-metal ions is known important to influence its oxygen-binding properties.⁹ Recent works have indicated that oxa-crowned Schiff base transition-metal complexes are good receptors for alkali cations^{11,12} and showed much improved O_2 -binding activity due to the special configuration and function of the crown ether ring,^{13,14} moreover, some of them can form stable Na(I) or K(I)/Co(II) hetero-nuclear complexes and solid dioxygen adducts.^{9,15} These facts inspire us to study the

influence of pendant aza-crown substituents on the O_2 -binding capabilities of Co(II) Salen and its analogues.

Herein, the synthesis of Co(II) Salen complexes with aza-crown pendants and their analogues (Scheme 1 and Scheme 2), and the study on their dioxygen affinities were described. The influence of pendant substituents, aza-crown ring and adding alkali cations on the capacities is discussed in details as compared with parent complex CoL^5 (CoSalen).

Results and discussion

Synthesis

As shown in Scheme 1, benzo-10-aza-15-crown-5 or morpholine reacts with 1 equiv. of 2-hydroxy-5-chloromethyl-benzaldehyde¹⁶ in the presence of K_2CO_3 and CH_3CN to yield aza-crown or morpholino substituted salicylaldehyde **2** (89%) and **3** (91%), which were easily condensed with diamine to give the target compounds $H_2L^1-H_2L^4$. The structure is shown in Figure 1. The crystal structure determination data of HL^1 are summarized in Table 1, and the selected bond distances and angles are listed in Table 2.

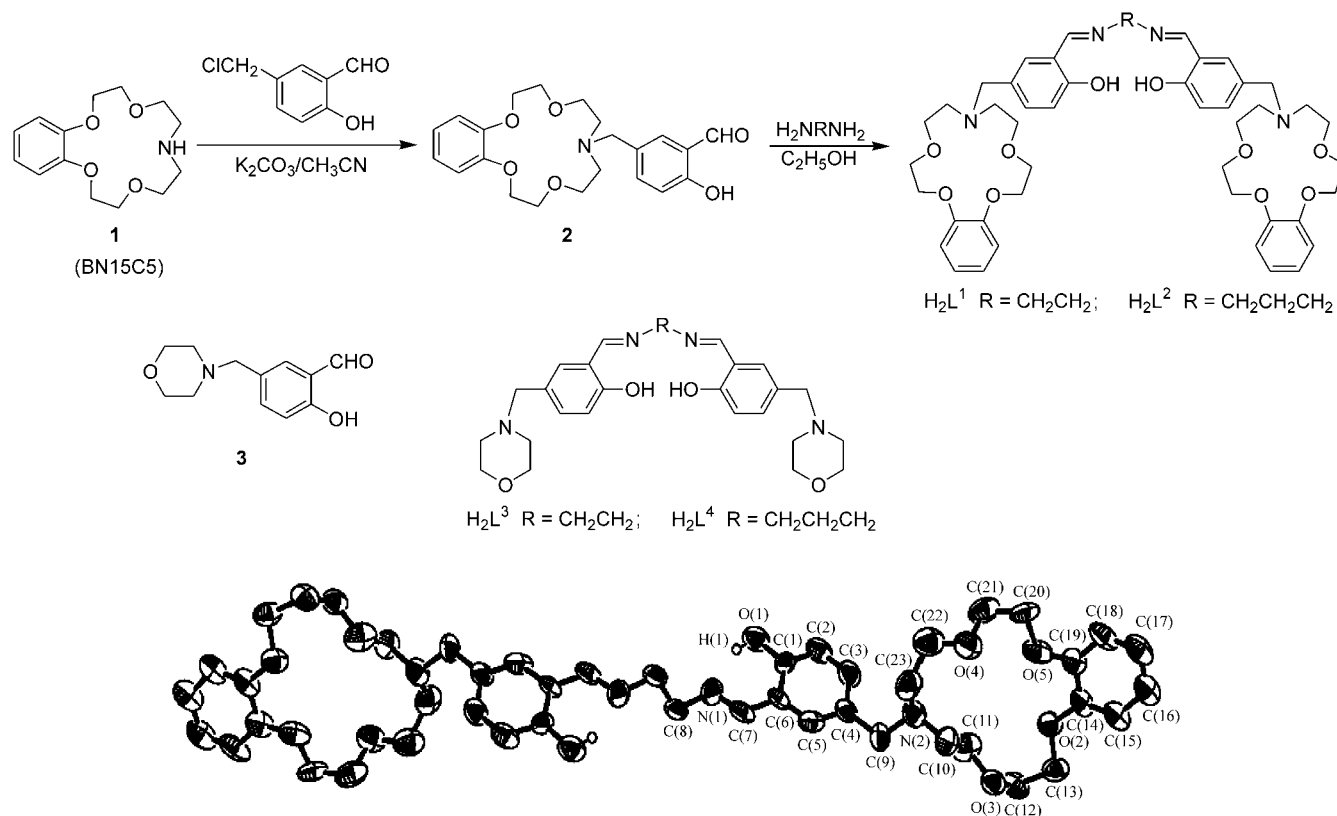
The elemental analysis and ESIMS of the complexes indicate that they are 1 : 1 (metal/ligand) complexes. Moreover, the observed molar conductances of all complexes in DMF solution ($1.00 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) are in

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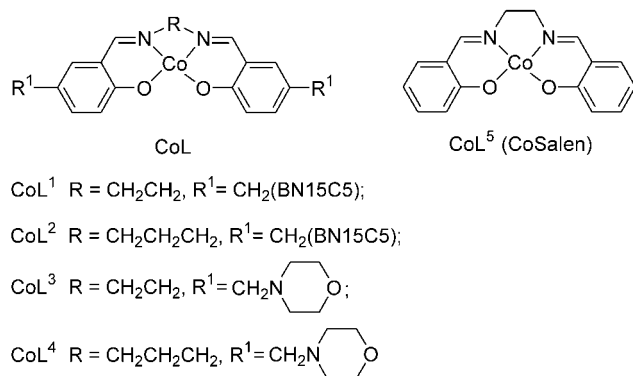
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Scheme 1

Figure 1 X-ray structure of H_2L^1 .

Scheme 2



the range of 3.85—7.53 S · cm² · mol⁻¹. This suggests that the Co(II) complexes are non-electrolytes.¹⁷ The IR spectra of the complexes showed most ligand absorptions, which are still at the same frequency except the C=N stretches shifted slightly (14—18 cm⁻¹) to lower frequencies and the OH stretches (3226—3222 cm⁻¹) disappeared after complex formation. Their structures are shown in Scheme 2.

Dioxygen affinity studies of CoL¹—CoL⁴

The oxygenation constants (K_{O_2}) and thermodynamic parameters ΔH° and ΔS° of CoL¹—CoL⁵ are given in Table 3. Table 3 shows, as compared with CoL⁵ (CoSalen), dioxygen affinity of the complexes CoL¹—CoL⁴ are obviously improved by pendant substituents in the ligands. Especially, CoL¹ and CoL² containing

Table 1 Crystallographic and structural refinement data of H_2L^1

Formula	C ₄₆ H ₅₈ N ₄ O ₁₀
Formula weight	826.96
Temperature/K	286 (2)
λ_{rad}/nm	0.071073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> /nm	0.8902(3)
<i>b</i> /nm	1.0344(3)
$\beta/(\circ)$	107.86(3)
$\gamma/(\circ)$	101.72(3)
<i>V</i> /nm ³	1.0613(6)
<i>Z</i>	1
<i>D_c</i> /(g · cm ⁻³)	1.294
No. of unique data	3282
No. of obsd. data [<i>I</i> > 2σ(<i>I</i>)]	843
<i>R</i> ₁	0.0802
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.2152

two aza-crown pendants show much more enhanced dioxygen affinity than CoL³ and CoL⁴ possessing two morpholine pendants. The results should be attributed to the macrocycle effect of crown ring rather than the electron-donating effect of two nitrogen methylene (NCH₂) on aromatic ring of the ligand, because the aza-crown ring possesses special configuration and probably favors oxygen molecule to approach the coordination center of

Table 2 Selected bond lengths (nm) and angles (°) of H₂L¹

C(1)···N(1)	0.2643(10)	C(1)-H(1)···N(1)	148.6
C(7)—N(1)	0.1285(11)	O(1)-H(1)-N(1)	144.8(6)
C(8)—N(1)	0.1464(11)	C(7)-N(1)-C(8)	122.3(8)
C(9)—N(2)	0.1431(10)	C(10)-N(2)-C(9)	113.2(8)
C(10)—N(2)	0.1424(11)	C(10)-N(2)-C(23)	111.0(8)
C(23)—N(2)	0.1477(12)	C(9)-N(2)-C(23)	110.2(9)
C(10)—C(11)	0.1517(14)	C(14)-O(2)-C(13)	114.5(8)
C(13)—O(2)	0.1448(8)	C(12)-O(3)-C(11)	113.0(9)
C(11)—O(3)	0.1451(11)	C(22)-O(4)-C(21)	110.6(8)
C(21)—O(4)	0.1450(11)	C(20)-O(5)-C(19)	117.7(7)
C(20)—O(5)	0.1497(10)		

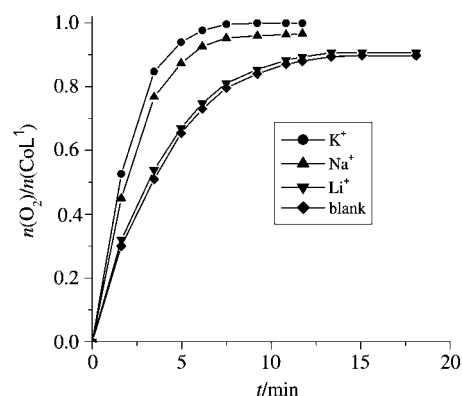
Table 3 Oxygenation constants and thermodynamic parameters (ΔH° and ΔS°) of CoL^a

CoL	B	T/°C	Ions added	$\ln K_{O_2}/\text{mm}^{-1}$	$\Delta H^\circ/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S^\circ/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
CoL ¹	Py	-5	—	-2.39	-43.80	-183.30
		0	—	-2.75		
		15	—	-3.76		
		25	—	-4.37		
		25	Li ⁺	-4.28		
		25	Na ⁺	-3.15		
CoL ²	Py	-5	—	-2.26	-45.26	-187.67
		0	—	-2.63		
		15	—	-3.67		
		25	—	-4.30		
		25	Li ⁺	-4.20		
		25	Na ⁺	-3.10		
CoL ³	Py	-5	—	-4.73	-30.12	-151.72
		0	—	-4.98		
		15	—	-5.67		
		25	—	-6.09		
		25	Li ⁺	-6.07		
		25	Na ⁺	-6.05		
CoL ⁴	Py	-5	—	-4.65	-31.06	-154.55
		0	—	-4.91		
		15	—	-5.62		
		25	—	-6.05		
		25	Li ⁺	-6.05		
		25	Na ⁺	-6.03		
CoL ⁵	Py	-5	—	-5.02	-28.50	-148.08
		0	—	-5.25		
		15	—	-5.91		
		25	—	-6.31		

^a B: base (as axial ligand); [CoL]= $5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$; [Li⁺]=[Na⁺]=[K⁺]= $1.5 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$.

the complexes to form the Co—O₂ bond through its hydrophobicity of outer ethylene groups and orderly arrangement of inner azaoxa atoms^{14,18}.

Table 3 also shows that adding alkali metal ions would improve the O₂-binding capability of CoL¹ and CoL², in contrast, in terms of CoL³ and CoL⁴, there was almost not influence. Table 3 and Figure 2 indicate that K_{O_2} , O₂-binding rate and maximum O₂ uptake of CoL¹ are visibly enhanced by the added KNO₃ and NaNO₃, however, the enhancement by adding LiNO₃ is very limited (The concentration of the alkali metal ions is 3 fold of CoL's concentration). Since aza-crown substituted Schiff base Co(II) complexes can complex with alkali cations,^{19,20} the above results may be due to that the Li⁺ ($d=0.136 \text{ nm}$) is too small to match the cavity size of 15-crown-5 ($d=0.170\text{--}0.220 \text{ nm}$), but Na⁺ ($d=0.190 \text{ nm}$) can match well the cavity, and K⁺ ($d=0.266 \text{ nm}$) would induce to form sandwich complexes as it is too large to fit in the crown ring,²¹ and then the complexation of Na⁺ or K⁺ with aza-crown ethers would favor the ion approach and control effectively the microenvironment of coordination center to help the formation and stabilization of Co—O₂.²² Furthermore, the sandwich-type K⁺ complexes with the bis(aza-crown ether) cobalt(II) complexes CoL¹ and CoL² may be more helpful for the K⁺ to approach and influence coordination center than the Na⁺. Therefore, adding K⁺ leads to a bigger K_{O_2} than adding Na⁺. To confirm the existence of the KNO₃/CoL¹ sandwich complexes in the oxygenation reaction system, we evaporated the solvent of oxygenation solution of CoL¹ and investigated the ESIMS spectra of the residue (see Figure 3). Figure 3 shows that only 1 : 1 (CoL¹/K⁺) complex [m/z 983.9 (CoL¹+KNO₃); 922.1 (CoL¹+K⁺); 883.2 (CoL¹)] was found. The results reveal that our above proposal is reasonable. The above results are also similar to Gebbink's report.²¹

**Figure 2** Influence of added alkali metal ions on dioxygen affinities of CoL¹ (25 °C).

Experimental

Melting points were determined on a Yanaco-500 micro-melting point apparatus and uncorrected. IR spectra were recorded on a Nicolet-1705X IR spec-

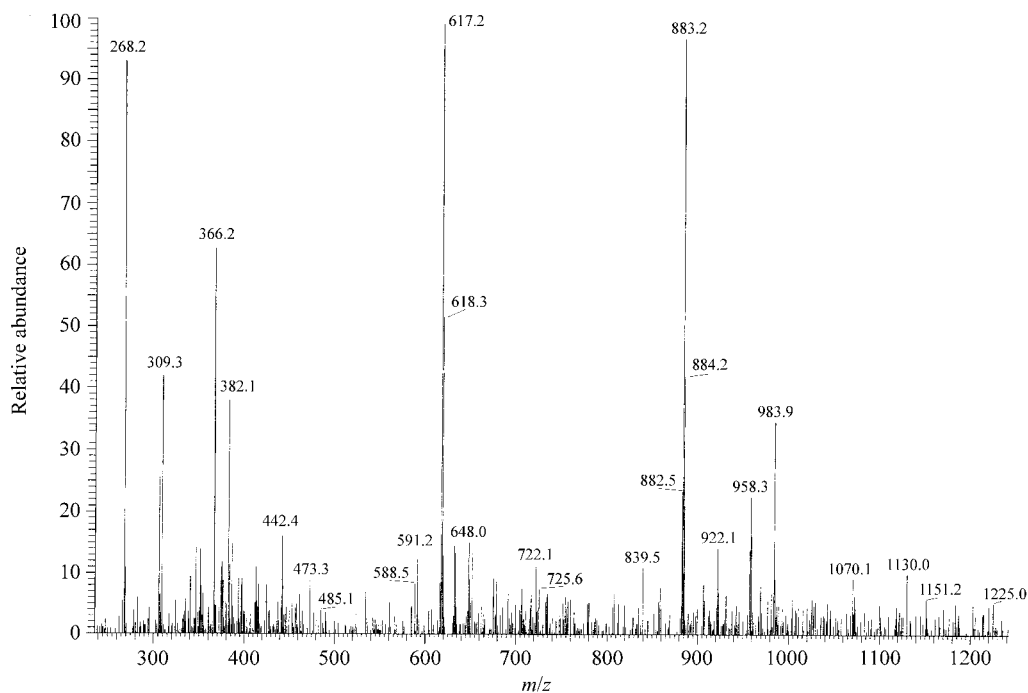


Figure 3 ESIMS spectrum of the oxygenation reactant residue with K^+ added.

trometer. 1H NMR spectra were recorded on a Bruker AC-200 MHz spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained on a Finnigan MAT 4510 spectrometer and Finnigan LCQ-DECA spectrometer. Elemental analysis was performed on a Carlo Erbo-1160 elemental analyzer. Molar conductance was obtained on a DDS-11A conductivitymeter. The Co(II) content was measured by an IRIS-Advantage ICP emission spectrometer. Silica gel (60H for TLC, Qingdao, China) was used for flash column chromatography. 2-Hydroxy-5-chloromethyl-benzaldehyde was synthesized according to literature method.¹⁶ All other reagents were of analytical grade and were used without further purification.

Synthesis of the bis-Schiff base ligands H_2L^1 — H_2L^4

Compound 2 To a stirred mixture of **1** (2.67 g, 0.01 mol) and K_2CO_3 (1.52 g, 0.011 mol) in CH_3CN (40 mL), a solution of 2-hydroxy-5-chloromethyl-benzaldehyde (1.71 g, 0.01 mol) in CH_3CN (10 mL) was added dropwise. The mixture was refluxed for 10 h. Then the reaction mixture was filtered and the solvent was evaporated. The residual mass was chromatographed on a silica gel column (eluent: ethyl acetate) to give the pure product as oil (3.57 g, 89%). 1H NMR ($CDCl_3$) δ : 10.78 (s, 1H, OH, D_2O exchangeable), 9.95 (s, 1H, HC=O), 7.42—6.81 (m, 7H, Ar-H), 4.15—3.76 (m, 14H, OCH_2 , NCH_2Ar), 2.85 (t, 4H, $J=6$ Hz, NCH_2); IR (neat) ν_{max} : 3247, 1652, 1257, 1125 cm^{-1} ; m/z : 401 (M^+). Anal. calcd for $C_{22}H_{27}NO_6$: C 65.84, H 6.73, N 3.49; found C 65.59, H 6.57, N 3.61.

Compound 3 It was prepared as described for compound **2** except starting with morpholine. 91% yield; m.p. 94—96 $^{\circ}C$; 1H NMR ($CDCl_3$) δ : 10.70 (s, 1H, OH, D_2O exchangeable), 9.92 (s, 1H, HC=O), 7.58—6.83

(m, 3H, Ar-H), 3.75—3.65 (m, 6H, OCH_2 , NCH_2Ar), 2.88—2.79 (m, 4H, CH_2N); IR (neat) ν_{max} : 3242, 1649, 1275, 1115 cm^{-1} ; MS m/z : 221 (M^+). Anal. calcd for $C_{12}H_{15}NO_3$: C 65.16, H 6.79, N 6.33; found C 64.92, H 6.97, N 6.06.

Ligand H_2L^1 Compound **2** (4.01 g, 10 mmol) in ethanol (20 mL) was added to the solution of ethylenediamine (0.6 g, 10 mmol) in ethanol (5 mL) under nitrogen, and stirred for 1 h at room temperature. The yellow precipitate was filtered and washed with ethanol. After recrystallization from ethanol, yellow crystal (7.52 g, 91%) was obtained. m.p. 118—120 $^{\circ}C$; 1H NMR ($CDCl_3$) δ : 13.12 (s, 2H, OH, D_2O exchangeable), 8.26 (s, 2H, N=CH), 7.26—6.80 (m, 14H, Ar-H), 4.13—3.62 (m, 32H, OCH_2 , NCH_2Ar , C=N CH_2), 2.79 (t, $J=6$ Hz, 8H, NCH_2); IR (KBr) ν_{max} : 3226, 1632, 1257, 1132 cm^{-1} ; ESIMS m/z : 826 (M^+). Anal. calcd for $C_{46}H_{58}N_4O_{10}$: C 66.83, H 7.02, N 6.78; found C 66.65, H 7.15, N 6.67.

Ligand H_2L^2 It was prepared using a method similar to that for HL^1 . 86% yield; m.p. 62—64 $^{\circ}C$; 1H NMR ($CDCl_3$) δ : 13.23 (s, 2H, OH, D_2O exchangeable), 8.29 (s, 2H, N=CH), 7.28—6.81 (m, 14H, Ar-H), 4.16—3.60 (m, 32H, OCH_2 , NCH_2Ar , C=N CH_2), 2.78 (t, $J=6$ Hz, 8H, NCH_2), 1.55—1.61 (m, 2H, CCH_2C); IR (KBr) ν_{max} : 3225, 1636, 1255, 1128 cm^{-1} ; ESIMS m/z : 840 (M^+). Anal. calcd for $C_{47}H_{60}N_4O_{10}$: C 67.14, H 7.14, N 6.67; found C 67.29, H 7.31, N 6.59.

Ligand H_2L^3 It was prepared using a method similar to that for HL^1 except starting with compound **3**. 83% yield; m.p. 134—136 $^{\circ}C$; 1H NMR ($CDCl_3$) δ : 13.15 (s, 2H, OH, D_2O exchangeable), 8.31 (s, 2H, CH=N), 7.15—6.84 (m, 6H, Ar-H), 3.84—3.63 (m, 16H, OCH_2 , NCH_2Ar , C=N CH_2), 2.92—2.76 (t, 8H, NCH_2); IR (KBr) ν_{max} : 3222, 1635, 1279, 1116 cm^{-1} ; MS m/z :

466 (M⁺). Anal. calcd for C₂₆H₃₄N₄O₄: C 66.95, H 7.30, N 12.02; found C 66.73, H 7.46, N 12.15.

Ligand H₂L⁴ It was prepared using a method similar to that for HL¹ except starting with compound **3**. 87% yield; m.p. 110—112 °C; ¹H NMR (CDCl₃) δ: 13.56 (s, 2H, OH, D₂O exchangeable), 8.42 (s, 2H, CH=N), 7.22—6.82 (m, 6H, Ar-H), 3.72—3.61 (m, 16H, OCH₂, NCH₂Ar, C=NCH₂), 2.92—2.76 (t, 8H, NCH₂), 1.55—1.61 (m, 2H, CCH₂C); IR (KBr) ν_{max}: 3225, 1632, 1281, 1116 cm⁻¹; MS *m/z*: 480 (M⁺). Anal. calcd for C₂₇H₃₆N₄O₄: C 67.50, H 7.50, N 11.67; found C 67.76, H 7.29, N 11.85.

General method for the synthesis of cobalt(II) bis-Schiff base complexes (CoL)

A solution of H₂L (1.0 mol) and Co(OAc)₂ · 4H₂O (1.0 mol) in EtOH (15 mL) was stirred for 2 h under N₂ at reflux, then the mixture was cooled and filtrated, washed with water and then with methanol to give the metal complexes. The pure product was obtained after recrystallization from ethanol.

CoL¹ Red, 79% yield, m.p. 235—237 °C; IR (KBr) ν_{max}: 1618, 1255, 1129 cm⁻¹; ESIMS *m/z*: 883 (M⁺). Anal. calcd for CoC₄₆H₅₆N₄O₁₀: C 62.51, H 6.34, N 6.34, Co 6.68; found C 62.63, H 6.23, N 6.47, Co 6.90. *A_m*(S · cm² · mol⁻¹): 5.66.

CoL² Red, 71% yield, m.p. 214—216 °C; IR (KBr) ν_{max}: 1618, 1256, 1126 cm⁻¹; ESIMS *m/z*: 897 (M⁺). Anal. calcd for CoC₄₇H₅₈N₄O₁₀: C 62.88, H 6.47, N 6.24, Co 6.58; found C 62.59, H 6.19, N 6.36, Co 6.75. *A_m*(S · cm² · mol⁻¹): 3.85.

CoL³ Red, 77% yield, m.p. 287—290 °C; IR (KBr) ν_{max}: 1618, 1279, 1115 cm⁻¹; MS *m/z*: 523 (M⁺). Anal. calcd for CoC₂₆H₃₂N₄O₄: C 59.66, H 6.12, N 10.71, Co 11.28; found C 59.34, H 6.41, N 10.96, Co 11.06. *A_m*(S · cm² · mol⁻¹): 7.53.

CoL⁴ Red, 72% yield, m.p. 243—245 °C; IR (KBr) ν_{max}: 1616, 1280, 1114 cm⁻¹; MS *m/z*: 537 (M⁺). Anal. calcd for CoC₂₇H₃₄N₄O₄: C 60.34, H 6.33, N 10.43, Co 10.99; found C 60.12, H 6.41, N 10.65, Co 10.63. *A_m*(S · cm² · mol⁻¹): 6.34.

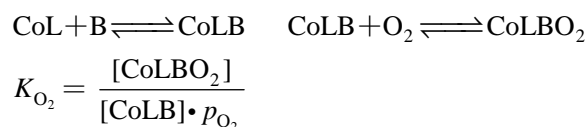
X-ray crystal structure analysis of HL¹

Data collection was performed on an Enraf-Nornius CAD-4 diffractometer with Mo Kα radiation (λ = 0.071073 nm) using the ω-2θ scan technique at 286(2) K. The structure was solved by direct methods and refined by full matrix least-squares and difference Fourier techniques with SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were theoretically added and included in the final refinement model in calculated and fixed positions with isotropic thermal parameters.

Oxygen uptake measurement

The oxygenation constants and thermodynamic parameters of CoL¹—CoL⁴ were determined by the known equipment and method:⁷ diglyme (O₂ saturated) as solvent, 1.0 mol · dm⁻³ of pyridine as axial ligand (B), 5 ×

10⁻³ mol · dm⁻³ of complexes, 97 kPa of oxygen partial pressure. The equilibrium constants (*K*_{O₂}) were calculated as follows.



where complexes are expressed in terms of molarities and the dioxygen concentration are expressed as partial pressure (*p*_{O₂}) in Torr. Thermodynamic constants Δ*H*[°] and Δ*S*[°] for the oxygenation reactions were calculated from *K*_{O₂} and *K*'_{O₂} over a range of temperatures.

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