

O₂-Binding Abilities and Catalytic Oxidation Performance of Cobalt (II) Complexes with Dihydroxamic Acid Functionalized N-pivot Lariat Ethers

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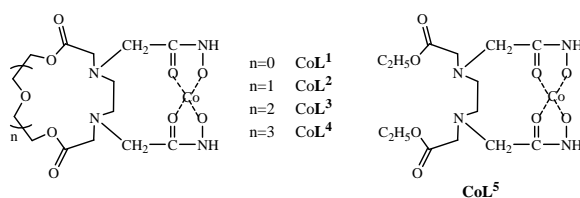
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Summary: The oxygenation constants ($\ln K_{O_2}$) and thermodynamic parameter (ΔH° , ΔS°) of Novel Co (II) complexes with dihydroxamic acids functionalized N-pivot lariat ether CoL¹~CoL⁴ and the uncrowned analogue CoL⁵ were measured. Their catalytic performance in oxidation of *p*-xylene to *p*-toluic acid (PTA) was investigated. The enhancement of O₂-binding and catalytic oxidation activities by the oxa aza crown ether ring of the cobalt complexes as well as the complexed alkali metal and alkaline-earth metal ions were discussed.

Keywords: Azacrown ether, Dihydroxamic acid, Oxygen binding, Catalytic oxidation.

Introduction

Study of new Cytochrome P450 monooxygenase model is of pretty importance to achieve a marked rate enhancement, high substrate specificity, and distinct reaction selectivity under mild oxidation conditions. In general, the active site of natural monooxygenase is regarded as a hydrophobic cavity or cleft created by folding of the polypeptide chain. To mimic the active site, macrocyclic compounds such as cyclodextrins [1], crown ether [2], cyclophanes [3] and calixarenes [4], each having an inclusion cavity as a basic skeleton of potent artificial monooxygenase, were usually employed. Our previous studies reveal that the aza crown ether substituted hydroxamic Cobalt complexes as monooxygenase model showed much more enhanced O₂-binding and catalytic oxidation activity than the uncrowned analogues [5, 6]. This inspired us to expand the models to the N-pivot lariat ether type hydroxamic cobalt complexes due to its structural flexibility. However, to the best of our knowledge, no aza crowned hydroxamic metal complexes serving as biomimetic oxygen carriers were reported yet. In this paper, we report a series novel cobalt (II) dihydroxamic acids containing aza crown ether pendants. Their O₂-binding and catalytic oxidation abilities were investigated. The effect of the aza crown pendant and the coordinated alkali metal and alkaline-earth metal ions on these activities was also discussed.



Scheme-1: Cobalt (II) dihydroxametes.

Experimental

Materials

The cobalt complexes CoL¹ ~ CoL⁵ were synthesized according to our previously report [7], their structures were characterized by IR, MS, ¹H NMR and elemental analysis, which will be published in due course. Co(AcO)₂·4H₂O, pyridine, fresh air and *p*-xylene were commercially available, pyridine *p*-xylene were purified prior to use. All other reagents were of analytical grade and used directly.

Experimental Procedure and Product Analysis

The oxygenation equilibrium constant ($\ln K_{O_2}$) and thermodynamic parameter (ΔH° , ΔS°) were determined by the reported method [9] (diglyme as solvent, 0.99 mol L⁻¹ of pyridine as axial ligand (B), 5×10⁻³ mol L⁻¹ of complexes, 9.8×10⁴ Pa partial pressure of oxygen and specific temperatures).

The catalytic oxidation of *p*-xylene to *p*-toluic acid (PTA) were carried out in a normal

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gas-liquid apparatus. Air was bubbled into the mixture of *p*-xylene (40 mL) and the cobalt complex ($1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) with $2.0 \text{ L} \cdot \text{min}^{-1}$ flow rate at $110 \text{ }^\circ\text{C}$. The reaction mixture (0.1 mL) was sampled by pipette periodically before the precipitates appeared (5 hours later), and diluted to 15 mL with ethanol. The accumulative concentration of PTA was determined by standard acid-base titration. The selective oxidation for PTA was determined by HPLC.

Results and Discussion

Dioxygen Affinities of the Cobalt (II) dihydroxamates

The oxygenation constants and thermodynamic parameters of $\text{CoL}^1 \sim \text{CoL}^5$ were presented in Table-1. The oxygenation constants were of significant difference. The order of the O-binding activity is: $\text{CoL}^3 > \text{CoL}^2 > \text{CoL}^4 > \text{CoL}^1 > \text{CoL}^5$, which should be attributed to the structural diversity. Since the only difference between the crowded cobalt complexes ($\text{CoL}^1 \sim \text{CoL}^4$) was the size of the crown ether ring (or the number of the ethyleneoxy), it could be deduced that the macrocycle effect of crown ring, which possesses special configuration, would favor oxygen molecule to approach the active center of the Co (II) complexes, and form the Co-O₂ bond through its hydrophobic outer ethylene groups and orderly arranged inner aza oxa atoms. However, CoL^4 , which possess the largest crown ring, didn't show the highest O₂-binding activities. The reason may be attributed to that too large crown ring of CoL^4 would be distorted and form steric hindrance around the active center, which is disadvantageous to the approaching of O₂⁸. Moreover, the H^0 seems to be contributed to the formation of O₂-Co (II) bond. The Co (II) complexes with smaller H^0 shows larger oxygenation constants. The relevance might be used to judge the O₂-binding activity of CoL.

Table-1: Oxygenation constants (InK_{O₂}) and thermodynamic parameters (H^0 and S^0).

Complexes	B	T(°C)	InK _{O₂} (mm ⁻¹)	H^0 (KJ.mol ⁻¹)	S^0 (J.K ⁻¹ .mol ⁻¹)
CoL ¹	Py	-5	-4.59	-36.56±0.03	-171.48±0.04
		10	-5.45		
		20	-5.98		
CoL ²	Py	-5	-3.72	-40.56±0.04	-182.27±0.05
		10	-4.68		
		20	-5.27		
CoL ³	Py	-5	-3.20	-41.78±0.04	-182.51±0.05
		10	-4.18		
		20	-4.78		
CoL ⁴	Py	-5	-3.65	-43.72±0.05	-191.37±0.03
		10	-4.69		
		20	-5.34		
CoL ⁵	Py	-5	-5.32	-29.6±0.04	-154.66±0.03
		10	-6.02		
		20	-6.45		

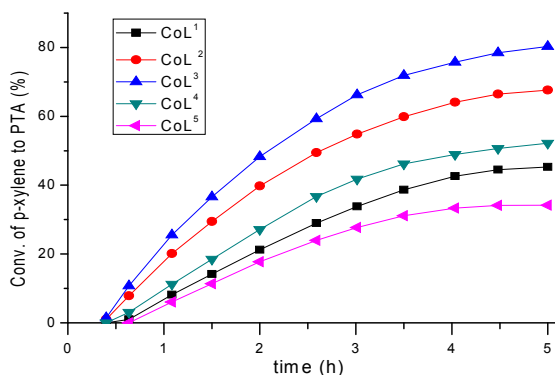
The oxygenation solution of the cobalt (II) complexes were volatilized in air at room temperature for a couple of days, the oxygen adducts of the cobalt (II) complexes could be precipitated. The oxygen adducts were filtered, and washed with pyridine and acetone respectively, dried in air to obtain a dark purple powder. The elemental analysis (take CoL^1 as an example) shows a 1:1 oxygen adduct ($\text{CoL}^1 \cdot \text{Py} \cdot \text{O}_2$) was formed. Anal. calcd. for C₁₇H₂₃CoN₅O₁₀: C 39.55, H 4.49, N 13.56, Co 11.41; found: C 39.37, H 4.62, N 13.36, Co 11.70. The characteristic vibration of IR spectra from CoL^1 and its O₂ adduct was shown in Table-2, vibration at 1205 cm^{-1} and $995, 619 \text{ cm}^{-1}$ were attributed to the formation of Co-O₂ bond and pyridine respectively [6].

Table-2: The IR spectra of CoL^1 and $\text{CoL}^1 \cdot \text{Py} \cdot \text{O}_2$.

Compounds	V _{C-O}	V _{C-N}	V _{C-O-C}	V _{N-O}	V _{O-O}	Py
CoL ¹	1595	1420	1122	982	—	—
CoL ¹ ·Py·O ₂	1576	1421	1122	975	1205	995, 619

Catalytic Oxidation of *p*-xylene to *p*-toluic acid

As shown in Fig. 1, The oxidation of *p*-xylene catalyzed by $\text{CoL}^1 \sim \text{CoL}^5$ experienced a certain induction period (0.3~0.6 h), which indicated there may be a connection between the dioxygen affinity and induction period and the coordination of molecular oxygen to the central cobalt ions is necessary to the initiation of the catalytic oxidation reaction. When the dioxygen adducts $\text{CoL} \cdot \text{Py} \cdot \text{O}_2$ were employed to the catalyze the oxidation reaction under the same conditions, it almost showed no induction period. Meanwhile, same as the order of the O₂-binding activity of $\text{CoL}^1 \sim \text{CoL}^5$, CoL^3 showed the highest catalytic oxidation activity followed by CoL^2 , and then CoL^4 and CoL^1 , the uncrowned analogue CoL^5 showed the lowest catalytic activity. This result indicated that on one hand, a proper size of crown ether ring could offer a favorable microenvironment or even some kind of substrate specificity to significantly enhance the catalytic oxidation performance of the cobalt complexes. On the other hand, the steric hindrance of the crown ether ring would shield the active center, which is not advantageous to the formation of the active oxygen affinity species and the inclusion to the substrate. It also seemed to indicate that the crown ring configuration played an important role in the modulation of the catalytic oxidation, which would be researched in our future structural studies of the cobalt complexes.

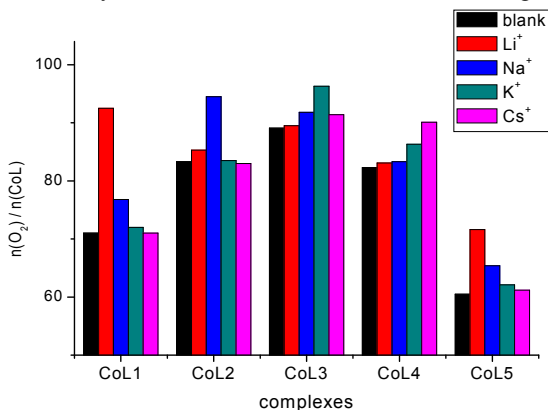


Reaction condition: Air flow rate $2.0 \text{ L L}^{-1} \cdot \text{min}^{-1}$; CoL concentration $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; Reaction temperature $110 \text{ }^\circ\text{C}$

Fig. 1: Effect of the crown ether ring on the catalytic activities of CoL.

Effect of Complexed Alkali Cations on the Dioxygen Affinity and Catalytic Oxidation Abilities of the Cobalt Complexes

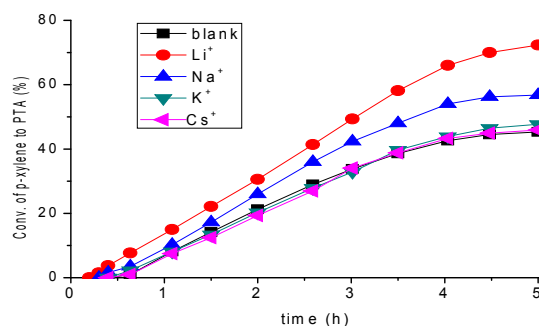
It is well known that crown ether is a very good chelator for alkaline cations, the co-complexed alkaline cations could approach the central cobalt ions, which is useful for influencing its oxygen-binding capability. To reveal the relevance between different alkaline cations and the oxygen-binding capability as well as the catalytic oxidation activity of CoL, we added stoichiometric equivalent Li^+ , Na^+ , K^+ and Cs^+ nitrate to the oxygen-binding and catalytic oxidation reaction system with the other conditions unchanged.



Alkaline cations concentration $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; Reaction temperature $20 \text{ }^\circ\text{C}$

Fig. 2: Effect of added alkaline cations on the O_2 -binding abilities of CoL.

Fig. 2 showed that the oxygen-binding abilities of CoL were enhanced by the alkaline cations to different extent. We can easily deduce that when the diameter of the alkaline cation match well with the cavity size of the crown ether of CoL, could the stable alkaline cation complex formed, the complexation would more effectively favor it to approach and control the microenvironment around the coordinated cobalt ion, and favor the formation and stabilization of Co(II)-O_2 bond. The oxygen-binding abilities of uncrowned analogue CoL^5 was visibly improved by Li^+ could be attributed to the two O atoms and two N atoms of CoL^5 side chain formed a pseudo 12-crown-4 rings which chelated much better with Li^+ than the other alkaline cations.



Reaction condition: Air flow rate $2.0 \text{ L} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$; CoL^1 concentration $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; Reaction temperature $110 \text{ }^\circ\text{C}$

Fig. 3: Effect of added alkaline cations on the catalytic activities of CoL^1 .

We also found that the effect of the alkaline cations on the catalytic oxidation of CoL were very much similar to that on their oxygen-binding mentioned above. Better the proper alkaline cations complex with the oxa-aza crown ether ring of CoL, higher its catalytic oxidation activity was. Moreover, we also found that the added alkaline cations could shorten the induction period of the catalytic oxidation. Take CoL^1 for example, the Li^+ can not only improve the PTA convention from 45.2% to 72.3% in 5 hours, but also shorten the induction period from 0.4 hour to about 0.2 hour. However, the K^+ and Cs^+ showed almost no influence on its catalytic oxidation activity and induction period. The structural studies on the heteronuclear complexes of CoL with the alkaline cation would be helpful and be our further research.

In summary, the size and the configuration

of the crown ether were key factors to influence the oxygen-binding and catalytic oxidation activities of the complexes, and the well complexation of alkaline cation with the crown ether will favor the oxygen-binding and catalytic oxidation activities.

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