

Dioxygen Affinity and Catalytic Performance of Bis-(furaldehyde) Schiff Bases Co(II) Complexes in Cyclohexene Oxidation

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Abstract: Oxygenation constants and thermodynamic parameters ΔH° and ΔS° of cobalt (II) complexes with bis-(furaldehyde) Schiff bases (**1**, **2**, **3**, **4**) were obtained by measuring saturated dioxygen uptake of these complexes in pyridine at different temperature. These complexes could activate molecular oxygen and were used as catalysts in cyclohexene oxidation. The influence of ligand structure on the dioxygen affinity and catalytic activity of the complexes were discussed.

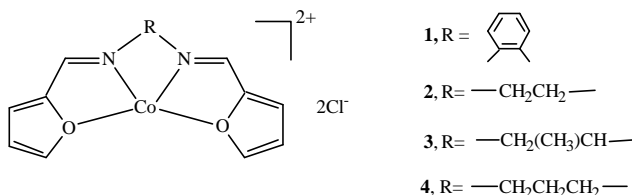
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As mimetic oxygen carrier or oxidation catalyst, Schiff base cobalt complexes such as Co (II) salen have been widely studied¹⁻⁴. However their high-price greatly limited their application. The synthesis of cheap furaldehyde Schiff bases and their complexes with Co (II), as well as the dioxygen affinity and biomimetic catalytic oxidation performance of these complexes are worth trying to study. In this paper, the saturated dioxygen uptake of cobalt complexes with different bis-(furaldehyde) Schiff bases [bis-(furaldehyde) *o*-phenylenediamine **1**, bis-(furaldehyde) ethylenediamine **2**, bis-(furaldehyde) 1, 2-diaminopropane **3**, bis-(furaldehyde) 1, 3-diaminopropane **4**] were measured. These complexes could activate molecular oxygen and were used as catalysts in cyclohexene oxidation. Oxygenation constants and thermodynamic parameters (ΔH° , ΔS°) of these complexes were calculated. The influence of temperature and bridge group R in furaldehyde Schiff bases on dioxygen affinity and catalytic activity were discussed.

The structures of bis-(furaldehyde) Schiff base cobalt complexes (**1**, **2**, **3**, **4**) were illustrated in **Scheme 1**.

20 mmol furaldehyde and 10 mmol diamino compounds were added to 30 mL ethanol under N₂ protection with stirring. After stirring 30 min, 10 mmol CoCl₂·6H₂O was added into the mixture, a blue precipitate formed, then the precipitate was filtrated and washed with ethanol and diethyl ether, dried in vacuum to give complexes (**1**, **2**, **3**, **4**). The structures of these compounds were characterized by IR, ¹HNMR and element analysis.

Scheme 1



Oxygen uptake measurement

The saturated dioxygen uptake was measured by the method reported by Xu Zheng⁵, in 40 mL pyridine solution (pyridine was also as axial ligand) with 300 mg of cobalt complex, under the conditions of 95 KPa of oxygen partial pressure and specified temperature. O_2/Co (mol/mol) is ultimately more than 0.5, so oxygenation constants were calculated according to the following equations:



$$K_{\text{O}_2} = \frac{[\text{CoLBO}_2]}{[\text{CoLB}] \times P_{\text{O}_2}}$$

L is Schiff base ligand, B is axial ligand, P_{O_2} is partial pressure of oxygen. The thermodynamic parameters ΔH° and ΔS° were calculated by the Ref. method⁵ (**Table 1**).

Oxidation of cyclohexene

1 mL cyclohexene, 3 mL 1, 2-dichloroethylene and 4×10^{-3} mmol cobalt complex were added to a 60 mL stainless steel autoclave. This system was purged with pure oxygen three times, when the system was heated to 70°C, the electromagnetic stirrer was started, and the oxygen pressure was adjusted to 10³ KPa. The reaction was lasted for 6 h. The reaction products were analyzed by GC920 with capillary column ϕ 0.25×30 m PEG 20 M and FID. Cyclohexene, 2-cyclohexene-1-ol and 2-cyclohexene-1-one were identified by standard sample, 2-cyclohexene-1-hydroperoxide was identified by washing the product mixture with 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ solution and then comparing the peaks of the product in the chromatogram.

Results and Discussion

Oxygenation of Co (II) complexes

As show in **Table 1**, dioxygen affinities are significantly influenced by the structure of the bridge group R. The oxygenation constant of the complex **1** is the highest among the four complexes. The reason is that the bridge group R in the complex **1** is connected by two —C=N— groups with two furan rings, thus a large π -conjugation system is constructed. The benzene ring in the complex **1** is a better π -donor comparing with R in

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the complexes **2**, **3**, **4**. Therefore the electron density of central metal ion and the strength of Co-O bond in the complex **1** will increase⁶. The dioxygen affinity of the complex **4** is better than that of the complexes **2** and **3**. It is possible that the bridge group in the complex **4** is 1, 3-propylene, which is more flexible than ethylene or methyl ethylene. The suitable flexibility of bridge group may be favourable for formation of a suitable steric structure.

Table 1 Oxygenation constants and thermodynamic parameter ΔH° , ΔS° of complexes

complexes	t (°C)	O ₂ /Co (mol/mol)	lnK _{O₂} (mm ⁻¹)	ΔH° (kJ·mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
1	-10	0.85	-4.86	-32.42	-163.45
	0	0.77	-5.37		
	10	0.66	-5.90		
2	-10	0.61	-6.11	-17.04	-115.32
	0	0.56	-6.34		
	10	0.49	-6.60		
3	-10	0.63	-6.02	-20.75	-115.44
	0	0.57	-6.30		
	10	0.51	-6.54		
4	-10	0.81	-5.14	-25.77	-140.67
	0	0.73	-5.56		
	10	0.63	-6.01		

It is advantageous for the formation and stability of dioxygen adduct and makes this adduct to be more stable⁷. The oxygenation constants decrease as temperature rising, so that higher temperature is not favourable for oxygenation reaction.

Catalytic oxidation of cyclohexene

The cobalt (II) complexes with bis-(furaldehyde)-Schiff bases are first used as a catalyst in the oxidation of cyclohexene. The experimental results were listed in **Table 2**.

Table 2 Oxidation of cyclohexene catalyzed by furaldehyde Schiff base complexes

complexes	Conversion (%)	Selectivity (%) [*]		
		a	b	c
1	81.27	15.37	75.42	9.21
2	72.05	15.45	76.20	8.25
3	78.32	16.14	75.50	8.36
4	79.20	15.30	76.49	8.21

^{*} a: 2-cyclohexen-1-ol, b: 2-cyclohexene-1-one, c: 2-cyclohexene-1-hydroperoxide

As show in **Table 2**, the selectivities of 2-cyclohexene-1-one formation are almost the same for the four complexes, but the catalytic activities of cobalt complexes with different bridge ligand decrease in the order: O-C₆H₄ > -(CH₂)₃- > -CH(CH₃)CH₂- > -CH₂CH₂-. It is in agreement with the order of dioxygen affinity of the complexes.

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