

Dioxygen Affinities and Biomimetic Catalytic Performance of Transition-metal Complexes with Benzoin Schiff Bases

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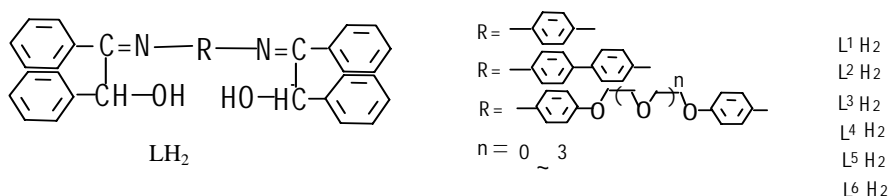
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Abstract: The oxygenation constants of transition-metal complexes with benzoin Schiff bases were measured and these complexes were first employed as models for mimicking monooxygenase in catalytic epoxidation of styrene. The highest conversion and selectivity were up to 39.6% and 100% respectively at ambient temperature and pressure. The effects of structures of the bridge group R in the ligands on the dioxygen affinities and catalytic activities to epoxidize styrene were also investigated.

Keywords: Benzoin Schiffbase, transition-metal complex, dioxygen affinity, catalytic epoxidation, monooxygenase-mimicking.

Metal porphyrin and Schiff base complex derived from salicylaldehyde as mimetic oxygenase have been widely reported^{1,2}. However, their application was greatly limited because it is difficult to synthesize them and they were easily degraded by oxidation. Thus much attention has been given to design and synthesize mimetic oxygenase models with better performance³. Although a kind of easily synthesized benzoin Schiff base complexes has been extensively investigated⁴, their dioxygen affinities and biomimetic catalytic performance have not been reported up to now. In this paper, oxygenation constants and thermodynamic parameters of several transition-metal complexes with benzoin Schiff bases were measured and they were employed to catalyze epoxidation of styrene for the first time. The influence of π -conjugation and the bridge group R in benzoin Schiff bases on the dioxygen affinity and catalytic epoxidation of styrene was also studied.

The structures of the investigated benzoin Schiff bases (L) were illustrated as following:



Diamino compounds and benzoin were added to the ethanol solution in the molar ratio of 1:2. The mixture was then heated to reflux for 2~3 hrs under the existence of

anhydrous sodium acetate to give benzoin Schiff bases, which reacted with a little excess MCl_2 in EtOH to produce complexes $M_2L^1_2 \sim M_2L^6_2$ [$M=Co(II), Mn(III)$]. They were characterized by IR, MS, 1H NMR and elemental analysis. The oxygenation constants and thermodynamic parameters, which were listed in the following **Table 1**, were determined by the known equipment and method⁵ under the condition of diglyme as solvent, $0.99 mol \cdot dm^{-3}$ of pyridine as axial ligand, $\sim 5 \times 10^{-3} mol \cdot dm^{-3}$ of concentration of complex, $8.9 \times 10^4 pa$ of oxygen partial pressure and specified temperatures.

Table 1. Oxygenation Constants and Thermodynamic Parameters ΔH° , ΔS° of Bis(benzoin Schiff bases) Complexes

Complexes	B ^{a)}	T(°C)	$\ln K_{O_2}(m^{-1})$	$-\Delta H^\circ(KJ \cdot mol^{-1})$	$\Delta S^\circ(J \cdot K^{-1} \cdot mol^{-1})$
$Co_2L^1_2$	P y	-5	-4.24	-35.69 ± 0.01	-168.42 ± 0.03
		15	-5.36		
		25	-5.85		
$Co_2L^2_2$	P y	-5	-3.82	-43.92 ± 0.03	-202.04 ± 0.02
		15	-5.19		
		25	-5.80		
$Co_2L^3_2$	P y	-5	-4.29	-48.78 ± 0.15	-217.69 ± 0.03
		15	-4.96		
		25	-5.64		
$Co_2L^4_2$	P y	-5	-2.96	-49.91 ± 0.06	-210.83 ± 0.02
		15	-4.52		
		25	-5.20		
$Co_2L^5_2$	P y	-5	-3.32	-45.54 ± 0.09	-197.58 ± 0.07
		15	-4.75		
		25	-5.38		
$Co_2L^6_2$	P y	-5	-4.05	35.87 ± 0.04	-167.50 ± 0.01
		15	-5.17		
		25	-5.66		

a) B as axial ligand

As shown in **Table 1**, dioxygen affinities were significantly influenced by the structures of bridge group R in ligands. The oxygenation constant of $Co_2L^2_2$ is higher than that of $Co_2L^1_2$. The reason is that the former is endowed with larger π -conjugation system and better π -awarding, which will increase the electron density of central metal ion and stabilize the Co-O₂ bond. When the ethoxy ether chain was introduced into R, the larger π -conjugation system was destroyed. So dioxygen affinity of $Co_2L^3_2$ was less than that of $Co_2L^2_2$. However, with the lengthening of polyethoxy ether chain, a kind of pseudo-macrocyclic polyether (elucidated as follows) such as 18-crown-6 ($n=1, Co_2L^4_2$) or 24-crown-8 ($n=2, Co_2L^5_2$) was formed. This kind of crown ether ring with special configuration will probably favor oxygen molecule to come close to active center and form the bond of Co-O₂ for its hydrophobicity of outer ethylene group and ordered arrangement of inner oxo atom⁶. When the polyethoxy ether chain was further lengthened, its flexibility was also furthered and the molecule was easily distorted so that the dioxygen affinity of complex was decreased quickly. Accordingly, the order of their dioxygen affinities is $Co_2L^4_2 > Co_2L^5_2 > Co_2L^2_2 > Co_2L^6_2 > Co_2L^1_2 \sim Co_2L^3_2$

**Dioxygen Affinities of Transition-metal Complexes
with Benzoin Schiff Bases**

847

The Mn(III) complexes of benzoin Schiff bases as mimetic monooxygenase models were first used to catalyze epoxidation of styrene. To a solution of bromobenzene (0.5mmol), imidazole (0.1mmol), styrene (0.5mmol) and iodosobenzene (1mmol) in acetonitrile(4mL) was added $Mn_2L_2Cl_2$ (0.01mmol). The result solution was vigorously stirred for 1hr at 25°C. The experimental results were analyzed by GC (SE 30 column) and summarized in **Table2**.

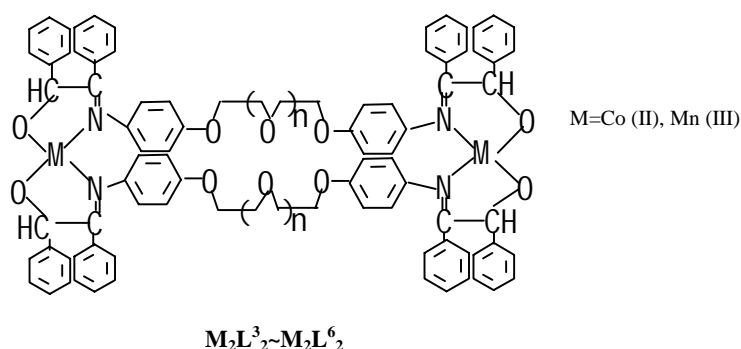


Table 2 Epoxidation of Styrene Catalyzed by Complexes of Benzoin Schiff Bases

Complexes	Conv.of styrene(%)	Yield of Epoxidation(%)	Selectivity(%)
$Mn_2L^1_2Cl_2$	25.5	25.5	100
$Mn_2L^2_2Cl_2$	28.9	28.9	100
$Mn_2L^3_2Cl_2$	32.0	32.0	100
$Mn_2L^4_2Cl_2$	36.7	36.7	100
$Mn_2L^5_2Cl_2$	39.6	39.6	100
$Mn_2L^6_2Cl_2$	31.1	28.7	92.3

*Imidazole was axial ligand

As shown in **Table 2**, the catalytic activity and selectivity of $Mn_2L^2_2Cl_2$ were still better than that of $Mn_2L^1_2Cl_2$. But they were all less than that of $Mn_2L^3_2Cl_2 \sim Mn_2L^6_2Cl_2$. The catalytic performance of $Mn_2L^4_2Cl_2$ and $Mn_2L^5_2Cl_2$ was still the best. The highest conversion and selectivity were up to 39.6% and 100% respectively. It was obviously correlated with the structures of bridge groups R in the complexes. There exists an analogous principle about the effect of the structure of R on catalytic epoxidation performance and the dioxygen affinity of M_2L_2 . Especially, the pseudo-macrocyclic ether constructed by polyethoxy group can offer large steric hindrance and hydrophobic environment which possibly favors the formation and protection of active species (Mn=O). But the pseudo-macrocyclic ether like 30-crown-10 will be formed in $Mn_2L^6_2Cl_2$ with further lengthening polyethoxy chain (n=3). As

described in a report⁷, its flexibility leads to the formation of the folded structure with a cofacial alignment of two active centers and result in forming intramolecular dimer (M-O-M) to lose activity.

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