

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

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Abstract: The dioxygen affinities and biomimetic catalytic performance of transition-metal complexes with (15-crown-5) salophen and its substituted derivatives were examined. The oxygenation constants of Co(II) complexes with crowned bis-Schiff bases were measured and their Mn(III) complexes were employed as models to mimic monooxygenase in catalytic epoxidation of styrene. The highest conversion and selectivity were up to 57.2% and 100% respectively at ambient temperature and pressure. The effects of crown ether ring and substituents R on the dioxygen affinities and catalytic activities were also investigated through comparing with the uncrowned analogues.

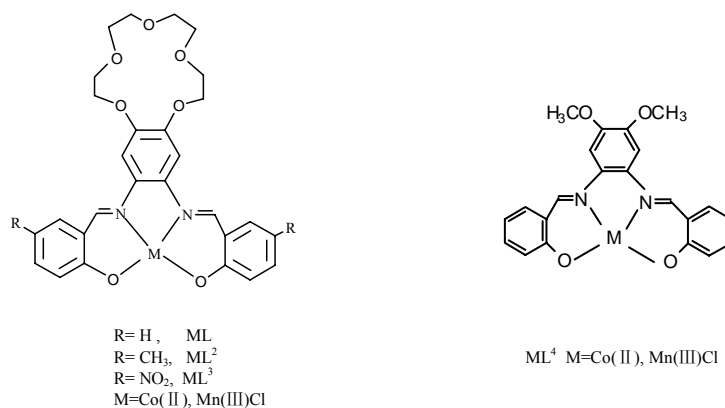
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It is well known that Cosalen can reversibly adsorb oxygen so that it can be used to separate, condense oxygen and catalyze oxidation reactions. Thus, this kind of complexes has received much attention recently^{1,2}. But these complexes are easy to dimerize and lose activities after adsorbing oxygen molecule^{3,4}. Avdeef and coworkers⁵ demonstrated that it would be favorable to form stable 1:1 oxygen adducts when these Co(II) complexes were modified by the substituents. So many new species substituted by various groups have been prepared up to now. For example, the stable dioxygen adducts of Co(II) complexes with (15-crown-5) salophen⁶ and (18-crown-6) disalophen⁷ were successfully prepared. In this report, oxygenation constants and thermodynamic parameters of (15-crown-5) salophen and its substituted derivatives ($ML^1\sim ML^3$) complexes with several transition-metals were measured. At the same time, these Mn(III) complexes were employed to catalyze the epoxidation of styrene. The effects of crown ether ring and substituents R in the ligands on the dioxygen affinities and catalytic activities, compared with that of the uncrowned analogues ML^4 , were also studied. Chemical structures of all the investigated complexes were illustrated in **Figure 1**:

The crowned bis-Schiff bases such as ligands $L^1H_2\sim L^3H_2$ have been synthesized from the condensation of salicylaldehyde or its substituted derivatives with 4',5'-diaminobenzo-15-crown-5, which was prepared from benzo-15-crown-5 *via* nitration followed by reduction in a batch⁸. Their cobalt(II) and manganese(III) complexes were obtained from the coordination of appropriate ligand with cobalt acetate or magnesium chloride according to the general methods. The uncrowned analogue was

prepared by the same method.

Figure 1. Structures of ML



The oxygenation constants and thermodynamic parameters of $CoL^1 \sim CoL^4$, which were listed in **Table 1**, were determined by the known equipment and method⁹ (diglyme as solvent, $0.99 \text{ mol} \cdot \text{dm}^{-3}$ of pyridine as axial ligand (B), $5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ of complex, $9.7 \times 10^4 \text{ Pa}$ of oxygen partial pressure and specific temperatures.).

Table 1. Oxygenation Constants and Thermodynamic Parameters ΔH^0 , ΔS^0 of $CoL^1 \sim CoL^4$.

Complexes	B	T(°C)	$\text{LnKO}_2(\text{mm}^{-1})$	$\Delta H^0(\text{KJ} \cdot \text{mol}^{-1})$	$\Delta S^0(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
CoL^1	Py	-5	-2.47	-36.81	-157.89
		10	-3.30		
		25	-4.09		
CoL^2	Py	-5	-2.12	-45.92	-188.97
		10	-3.15		
		25	-4.10		
CoL^3	Py	-5	-4.13	-36.50	-170.53
		10	-5.00		
		25	-5.82		
CoL^4	Py	-5	-4.24	-38.92	-180.48
		10	-5.17		
		25	-6.03		

As shown in **Table 1**, dioxygen affinities of these complexes were significantly influenced by the structures and electronic properties of substituents R in the ligands. The species substituted by electron-releasing groups (such as CH_3) on the aromatic rings showed high dioxygen affinities. The electron-releasing group on aromatic ring can increase electron density of central metal ion so as to stabilize the $Co-O_2$ bond *via* π -conjugation system. In contrast, the dioxygen affinity of CoL^3 was decreased by the strong electron-withdrawing effect of the nitro group. The oxygenation constants of Cobalt (II) complexes with crowned bis-Schiff bases are always higher than the uncrowned analogue CoL^4 . It indicates that the high dioxygen affinities of $CoL^1 \sim CoL^3$ seem to be attributed to the macrocyclic effect of crown ether rather than the electron-releasing effect

of two

ethyleneoxy groups (-O-CH₂CH₂-) on aromatic ring. 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 orderly arrangement of inner oxa atom¹⁰. Accordingly, the order of their dioxygen affinities is CoL²> CoL¹> CoL³> CoL⁴.

The Mn(III) complexes were employed to catalyze the epoxidation of styrene in order to investigate the biomimetic catalytic performance as monooxygenase model. To a solution of bromobenzene (0.5mmol), imidazole (0.1mmol), styrene (0.5mmol) and iodosobenzene (1.0mmol) in acetonitrile (4mL) was added MnLCl (0.01mmol). Then the mixture was vigorously stirred for 1 h at 25°C. The experimental results were analyzed by GC (SE 30 column) and summarized in **Table 2**.

Table 2. Epoxidation of styrene catalyzed by the various Mn(III) complexes

Complexes	Conv. of Styrene (%)	Yield of Epoxidation (%)	Selectivity (%)
MnL ¹ Cl	57.2	57.2	100
MnL ² Cl	43.3	43.3	100
MnL ³ Cl	21.4	21.4	100
MnL ⁴ Cl	20.5	18.9	92.3

An obvious relationship between catalytic performance of complexes and substituents on aromatic ring of salophen can be observed in **Table 2**. The catalytic activities of complexes decrease in the order MnL¹Cl> MnL²Cl> MnL³Cl> MnL⁴Cl. The highest conversion and selectivity of MnL¹Cl were up to 57.2% and 100% respectively. Surprisingly, the MnL²Cl containing two methyl groups on aromatic ring was not the best one comparing with the other investigated complexes. It is attributable that the complexes are activated toward electron-seeking oxidation attack and the catalytic activities decreased in the presence of electron-releasing groups. The catalytic performance of the Mn(III) complexes with crowned bis-Schiff bases was still higher than that of the uncrowned analogue MnL⁴Cl. This phenomena was likely similar to that in dioxygen affinities. The crown ether ring with special configuration can offer large steric hindrance and hydrophobic environment and possibly favors the formation and protection of the active species (Mn=O).

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References

1. R. D. Jones, D. A. Summerville, F. Basolo, *Chem. Rev.*, **1979**, *79*, 139.
2. E. V. Rybak-Akimova, W. Otto, P. Deardorf, R. Roesner, D. H. Busch, *Inorg. Chem.*, **1997**, *36*, 2747.
3. M. Suzuki, T. Ishikawa, A. Harada, S. Ohba, M. Sakamoto, Y. Nishida, *Polyhedron*, **1997**, *16*, 2553.

4. W. K. Wilmarth, S. Aranoff, M. Calvin, *J. Am. Chem. Soc.*, **1946**, 68, 2263.
5. A. Avdeef, W. P. Schaefer, *J. Am. Chem. Soc.*, **1976**, 98, 5153.
6. Cül, A. I. Okur, A. Cihan, N. Tan, Ö. Bakârođlu, *Synth. React. Inorg. Met-org. Chem.*, **1986**, 16, 871.
7. X. X. Lu, S. Y. Qin, *Acta Chimica Sinica*, **1999**, 57, 1364.
8. Z. H. Li, J. Z. Li, B. Sun, X. X. Lu, S. Y. Qin. *Chinese J. Org. Chem.*, **2000**, 20, 91.
9. D. Chen, A. E. Martell, *Inorg. Chem.*, **1987**, 26, 1026.
10. J. Z. Li, S. Y. Qin, Z. H. Li, H. Yang, *Acta Chimica Sinica*, **1999**, 57, 298.

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