

Dioxygen Affinities and Catalytic Oxidation Performance of Cobalt (II) Complexes with *N*-Aryl Hydroxamic Acid

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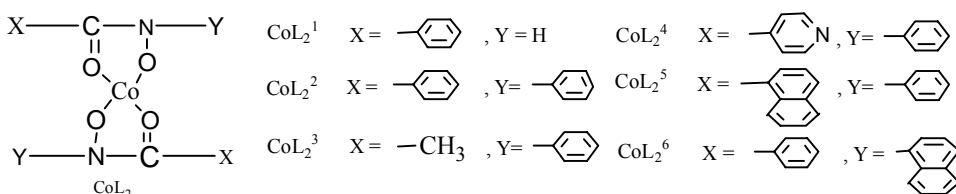
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Abstract: The oxygenation of cobalt (II) hydroxamates (CoL_2) and its catalytic performance in oxidation of *p*-xylene to *p*-toluic acid (PTA) were examined. The effects of X and Y bonded to hydroxamate group on dioxygen affinities and catalytic oxidation performance were also investigated.

Keywords: Cobalt (II) hydroxamates, dioxygen affinities, catalytic oxidation, *p*-xylene.

It is well known that the study on biomimetic oxygen carriers not only has important theoretic significance to discover the mechanism of reversible bonding, activating oxygen as well as the oxidation reaction in organism, but also has potential application in separating oxygen from air and realizing the high efficiency and selectivity of catalytic oxidation reaction under a mild condition¹. Metal- porphyrin and metal- phthalol-gaunine have been extensively used as biomimetic oxygen carriers up to now². We have discovered a kind of hydroxamates, which can be easily prepared and possess great flexible structures; and their dioxygen affinities as well as biomimetic catalytic oxidation performance have also been thoroughly studied^{3,4}. Based on our previous work, we want to investigate the effect of substituents X and Y (see **Figure 1**) bonded to hydroxamate group[-CO-N(OH)] on these properties, so another kind of interesting substituted cobalt (II) hydroxamates will be introduced in this paper. Their dioxygen affinities and catalytic oxidation of *p*-xylene will also be discussed. Further, we also try to discover some relation between dioxygen affinity and catalytic oxidation.

Figure 1 Cobalt (II) complexes with *N*-phenyl hydroxamic acid



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Except for CoL_2^2 - CoL_2^3 prepared according to published procedures⁵, the other complexes were supplied by our laboratory.

The oxygenation equilibrium constants and thermodynamic parameters (ΔH^0 and ΔS^0) presented in **Table 1** are determined according to established methodology⁶. (pyridine saturated with oxygen as solvent and axial ligand. $5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ of CoL_2 . 9.7×10^4 Pa of oxygen partial pressure and specified temperatures.)

Table 1 Oxygenation constants and thermodynamic parameters (ΔH^0 and ΔS^0)

Complexes	B	T(°C)	LnKO_2 (mm ⁻¹)	ΔH^0 (KJ.mol ⁻¹)	ΔS^0 (J.K ⁻¹ .mol ⁻¹)
CoL_2^1	Py	-5	-5.50	-28.32	-151.43
		15	-6.39		
		25	-6.67		
CoL_2^2	Py	-5	-4.86	-35.37	-172.33
		15	-5.96		
		25	-6.47		
CoL_2^3	Py	-5	-7.04	-21.22	-137.68
		15	-7.70		
		25	-8.10		
CoL_2^4	Py	-5	-5.34	-29.63	-154.87
		15	-6.25		
		25	-6.71		
CoL_2^5	Py	-5	-2.66	-49.92	-208.38
		15	-4.22		
		25	-4.89		
CoL_2^6	Py	-5	-3.02	-44.39	-190.62
		15	-4.40		
		25	-4.99		

Data in **Table 1** indicate that the oxygenation constants of CoL_2 are significantly influenced by the structure of the ligand. The dioxygen affinities of complexes in solution decrease in the order $\text{CoL}_2^5 > \text{CoL}_2^6 > \text{CoL}_2^2 > \text{CoL}_2^1 \sim \text{CoL}_2^4 > \text{CoL}_2^3$. Previous investigations suggest that π -conjugation of equatorial ligand and basicity of axial ligand exert great effect on the formation and stability of dioxygen adducts. Substituents introduced to hydroxamate group could reinforce the hydrophobic property and steric hindrance, and would be favorable to form stable 1:1 dioxygen adducts⁷. For this reason, CoL_2^2 , CoL_2^5 and CoL_2^6 in which X are aryl rings can increase electron density of central metal ion *via* π -conjugation system, which will lead to more stable Co(II)-O₂ bond. On the other hand, in the case of CoL_2^4 , the electron-withdrawing group can decrease the electron density of cobalt ion and its dioxygen affinity is the least. And in CoL_2^3 (X = CH₃), there does not exist π -conjugation system, so its dioxygen affinity is also very low. Moreover, because CoL_2^5 bears naphthalic rings each of which possesses ten π -conjugated electrons, it seems to have strong π -awarding property and its dioxygen affinity is the best. We can also observe from **Table 1** that higher the species dioxygen affinity is, lower the values of enthalpy and entropy are; consequently, ΔH^0 and ΔS^0 can be used to evaluate the oxygenation property of complexes³.

The oxygenation solution of CoL_2^2 was naturally volatilized and the separated precipitate of oxygenation complex was filtered, washed with pyridine and acetone

respectively, dried in air, to give a dark brown powder. Anal Calcd. for $C_{31}H_{25}N_3O_6Co$: C, 62.63; H, 4.21; N, 7.07; Co, 9.93. Found: C, 62.43; H, 4.32; N, 7.24; Co, 10.17. IR (KBr): 3046, 1602, 1596, 1485, 1402, 1204, 996, 921, 620 cm^{-1} . Elemental analysis indicates the formation of 1:1 (Co/O₂) oxygen adduct ($CoL_2^2 \cdot Py \cdot O_2$). Comparing with CoL_2^2 , 1204, 996, 921 cm^{-1} are new characteristic absorptions for this oxygen adduct. Absorptions at 921, 620 cm^{-1} prove the existence of pyridine, while the 1204 cm^{-1} could be ascribed to the specific vibration absorption (ν_{0-0}) of superoxide anion in this 1:1 oxygen adduct⁸.

Catalytic oxidation reaction of *p*-xylene proceeded in normal gas-liquid apparatus. Into the mixture of *p*-xylene (40 mL), $1 \times 10^{-3} mol \cdot L^{-1} CoL_2^2$, air was bubbled at the flow rate of $2.0 L \cdot L^{-1} \cdot min^{-1}$ at 110°C. Solution (0.1 mL) of reaction mixture was sampled by pipette periodically before the precipitate was separated (about 6 hours later), and diluted with ethanol (15 mL). Then the accumulative concentration of *p*-toluic acid (PTA) was calculated by standard acid-base titration.

Figure 2 Catalytic oxidation activity of CoL_2

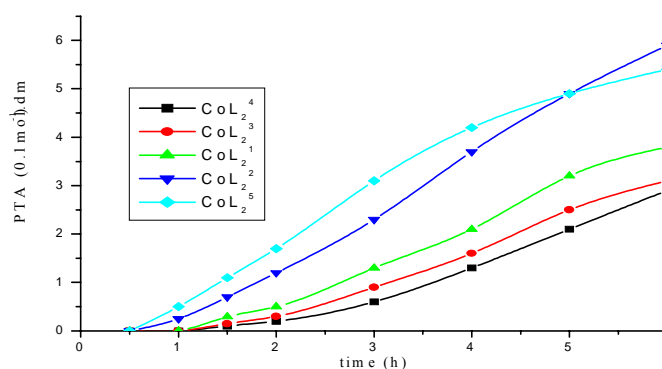


Figure 2 shows that almost all of these complexes can catalyze the oxidation of *p*-xylene. Without CoL_2 in *p*-xylene oxidation solution, PTA can hardly be detected. Especially at the initial 4 hours, the complexes which have aryl rings bonded to their hydroxamate groups and can form π -conjugation systems (such as CoL_2^5, CoL_2^6) will accelerate the rate of catalytic oxidation reaction. In contrast, the electron density of central metal ion in CoL_2^4 decreases due to the existence of pyridine group and the reaction rate is decelerated. This seems to have an analogous principle about the effect of the structure of X bonded to hydroxamate group on catalytic oxidation performance and dioxygen affinity of CoL_2 . But with catalytic oxidation proceeding, the PTA accumulative concentration that in CoL_2^5 system which has strongest dioxygenation affinity is increased slower than that in CoL_2^2 system. The reason will be explicated after further investigation.

Figure 2 also indicates that almost all catalytic oxidation have induction period. The general rule is that the stronger dioxygen affinity is, the shorter induction period is. For example, the induction periods of CoL_2^5 and CoL_2^4 are about 0.2 and 1.2 h,

respectively. And the induction period is also correlated with hydroxamate's solubility to some extent. The solubility of all Co(II) hydroxamates is poor in *p*-xylene. Only after the air is bubbled into the reaction mixture, can Co(II) hydroxamate dissolve successively and form the dark-green solution, then PTA can be detected. If $\text{CoL}_2^2 \cdot \text{Py} \cdot \text{O}_2$ instead of CoL_2^2 is added into the solution of *p*-xylene, it is easily dissolved and the oxidation reaction hardly show any induction period. In contrast, if the mixture of CoL_2^2 and *p*-xylene is stirred vigorously for 5h under N_2 atmosphere, it still cannot be dissolved and no PTA is detected. From these phenomena, it is plausible for us to infer that the procedure in which CoL_2 is dissolved is the process of which Co-O₂ bond forms, which can abstract the hydrogen atom from -CH₃ on aromatic ring and form the hydroperoxide (Co-OOH) and aryl methyl radical (Ar-CH₂•). This is the first and foremost step of the free radical oxidation of *p*-xylene.

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