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Novel cobalt(II) complexes of amino acids–Schiff bases catalyzed aerobic oxidation of various alcohols to ketones and aldehyde

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Abstract

Two cobalt(II) complexes **1** and **2** of Schiff bases derived from amino acids were synthesized and used for oxidation of benzyl alcohol with molecular oxygen at different conditions of pH, solvent, temperature and complex/alcohol molar ratio to optimize reaction conditions and to evaluate the catalytic efficiency of new cobalt Schiff base complexes. Under obtained optimum conditions, various alcohols were oxidized to corresponding aldehydes and ketones.

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The propensity of cobalt complexes to bind with molecular oxygen [1,2] and the use of more economical and environmental dioxygen–cobalt complexes for various oxidation reactions have been a subject of intensive research in the recent years [3–4]. Tsumaki discovered in 1930s that solid samples of Co(II) (salen) can bind dioxygen reversibly [5]. This caused a widespread and continuing interest in the oxygen-carrying properties of cobalt chelates, especially the complexes of Schiff base ligands [6–7]. The Schiff base transition metal complexes are attractive oxidation catalysts because of their easy synthesis and their chemical and thermal stability. Considerable attention has been paid to the preparation of transition metal complexes of Schiff bases derived from amino acids because they are considered to constitute new kinds of potential antibacterial and anticancer reagents [8].

In this article we have reported two novel cobalt(II) complexes 1 and 2 of Schiff bases derived from amino acids that have catalyzed oxidation of various alcohols to the corresponding ketones and aldehydes in excellent yields without further oxidation of aldehydes to the corresponding acids using molecular oxygen as the sole oxidant in aqueous media (Scheme 1).

First of all, oxidation of benzyl alcohol was studied as a template reaction to investigate influence of ligand structure, pH, solvent, complex concentration and temperature on catalytic activity. Furthermore, at the optimized conditions, the complexes 1 and 2 were used for oxidation of a series of alcohols.

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Ligand a and complex (catalyst) 1: $R = CH_2CO_2H$ Ligand b and complex (catalyst) 2: R = H

Scheme 1. Schematic procedure to prepare the ligands and the complexes.

1. Experimental

All the materials were supplied by Merk Chemical Co. (Darmstadt, Germany) and Fluka Co. and were used as received. The ¹H NMR measurements were carried out on an Inova 500 MHz high-resolution liquid nuclear magnetic resonance spectrometer. IR spectra were obtained with Nicolet Magna-IR 560 SXB and expressed in cm⁻¹. Elemental analyses were performed with a Vanio-EL analyzer and VISTA-MPS.

Sodium hydroxide (10 mmol) and amino acid (10 mmol) were stirred in ethanol (100 mL). When the amino acid and sodium hydroxide were dissolved, ethanol (20 mL) which dissolved phenanthrenequinone (5 mmol) was added. After reflux for 10 h, the mixture was concentrated and recrystallized from methanol to obtain the prepared solids as ligands a and b which were characterized by ¹H NMR and IR spectrometer.

To prepare complexes 1 or 2, ligands a or b (5 mmol) was mixed with $Co(OAc)_2 \cdot 4H_2O$ (5 mmol) and refluxed in MeOH (50 mL) for 3 h. The mixture was cooled and filtered. The resulting solid was washed with MeOH and ether then dried under vacuum to obtain complexes 1 and 2 characterized by elemental analyzer and IR spectrometer (Scheme 1) [9].

The general procedure for oxidation experiments was mainly the one which was described in detail by Bozell and co-workers [10]. The products were purified using column chromatography and characterized by ¹H NMR spectrometer in CDCl₃ as the solvent and TMS as internal standard.

2. Results and discussion

Complexes 1 and 2 were used as catalysts for the oxygen activation in the oxidation of benzyl alcohol in basic aqueous conditions. Oxidation reaction of benzyl alcohol using the complexes 1 and 2 at pH 11.5 and at 80 °C was considered as a standard reaction to compare the catalytic activity. Generally, complex 1 showed higher activity than complex 2 (Table 1).

The activity of the both studied complexes was very low at room temperature and practically no product was obtained even after 4 h. The activity of the complexes was increased dramatically at the temperature higher than 70 °C (Fig. 1).

The need of temperatures up to 70 $^{\circ}$ C for complexes 1 and 2 can be described by following reasons: the higher solubility of the complexes and deprotonation of the substrate which is considered to be the initial step in the oxidation of benzyl alcohols [11].

The pH has a dramatic effect on oxidation activity of the studied systems. Although, both of the prepared complexes displayed no activity at the pH lower than 7 due to low solubility, the activities of the catalysts **1** and **2** were increased dramatically upper than pH 8 and 10.5 respectively (Fig. 2).

Oxidation activity of complexes 1 and 2 in oxidation of benzyl alcohol expressed in TON^{a,b}.

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^a Benzyl alcohol = 5 mmol, complex (catalyst) = 0.005 mmol, pH 11.5, solvent = 5 mL water and 1 mL pyridine, pyridine = 1 mL (axial base), time = 4 h, temperature = 80 °C.

^b TON = mmol product/mmol complex.

Table 1



Fig. 1. The activity of complexes 1 and 2 in the oxidation of benzyl alcohol at different temperatures: benzyl alcohol = 5 mmol, complex = 0.005 - mmol, pH 11.5, solvent = 5 mL water and 1 mL pyridine, pyridine = 1 mL (axial base), time = 4 h.



Fig. 2. The effect of pH on the activity of complexes catalyzing oxidation of benzyl alcohol: benzyl alcohol = 5 mmol, complex = 0.005 mmol, temperature = 80 °C, solvent = 5 mL water and 1 mL pyridine, pyridine = 1 mL (axial base), time = 4 h.

It seems that in this reaction NaOH has two roles: deprotonation of the alcoholic substrate [12] and formation of a doubly bridged μ -peroxo species, which is thought to be the active species in oxidation processes [13].

Exploring the effect of molar ratio of benzyl alcohol/complexes on the oxidation of benzyl alcohol was performed at the different amounts of complexes, while the pH, temperature and amount of benzyl alcohol were kept constant. The enormous effect of concentration ratio of benzyl alcohol/complexes on catalytic activity suggests that the reaction is promoted by the substrate, because the substrate itself is a better axial base than OH– or pyridine (Fig. 3) [14].

As the use of protonic solvents often results in irreversible oxidation of the metal complex, much of the research on synthetic oxygen carriers has been done in aprotic solvents [14]. However, certain cobalt(II) complexes can react reversibly with dioxygen in aqueous solutions [15]. One of the requirements of this study is that the catalysts must be active in water. It was indeed observed for complexes **1** and **2** that they can catalyze the oxidation of benzyl alcohol in water at pH values higher than 8 and 10.5 respectively. The activity of the catalysts was low in methanol or ethanol. Trace amounts of aldehyde were observed in acetonitrile, toluene, acetone or dichloromethane. The water increases



Fig. 3. effect of molar ratio of benzyl alcohol/complexes on the oxidation of benzyl alcohol. Benzyl alcohol = 5 mmol, pH 11.5, solvent = 5 mL water and 1 mL pyridine, pyridine = 1 mL (axial base), time = 4 h, temperature = $80 \degree$ C.

Entry	Substrate	Time (h)	Yield %		Entry	Substrate	Time (h)	Yield %	
			Cat. 1	Cat. 2				Cat. 1	Cat. 2
1	Benzyl alcohol	4	88	84	8	Benzoin	1	100	85
2	4-Chlorobenzyl alcohol	4	84	82	9	4,4'-Dimethylbenzoin	1	100	88
3	2-Methoxybenzyl alcohol	3	94	90	10	4,4'-Dimethoxylbenzoin	1	100	100
4	2-Chlorobenzyl alcohol	4	87	81	11	4,4'-Dichlorobenzoin	1	95	92
5	2-Nitrobenzyl alcohol	4	73	70	12	Furion	1	100	82
6	1-Phenyletanol	4	85	81	13	Cyclopentanol	7	54	42
7	Diphenylmetanol	2	100	91	14	Cyclohexanol	7	43	32

Oxidation of various alcohols to ketones and aldehydes with molecular oxygen using cobalt Schiff base complexes as catalysts^a.

^a Benzyl alcohol = 5 mmol, catalyst (complex) = 0.005 mmol, pH 11.5, solvent = 5 mL water and 1 mL pyridine, pyridine = 1 mL (axial base), time = 4 h, temperature = 80 $^{\circ}$ C.

the activity as it can either receive or donate a proton from/to the reaction intermediates and that way promote the catalytic reaction [11]. Another point is that the formation of a mononuclear superoxo complex is enhanced in polar, non-aqueous solvents [16] but the dimeric μ -peroxo species must be dominated in aqueous solutions [17]. Thus, the enhanced activity in water suggests that the active species in this reaction is the dimeric μ -peroxo species [11].

The oxidation of various alcohols was examined using the prepared complexes. It was revealed that all primary alcohols and secondary alcohols were selectively oxidized to the corresponding aldehydes and ketones respectively. In general, complex **1** performed the oxidation of the all alcohols more efficiently than complex **2** (Table 2). Benzyl alcohol derivatives, benzoin derivatives and furoine were oxidized to the corresponding carbonyl compounds much faster (Table 2, entry 8–12) than aliphatic cyclic alcohols (Table 2, entry 13–14).

3. Conclusion

In summary, we have demonstrated the successful examples of cobalt Schiff base complexes that have catalyzed oxidation of various alcohols to the corresponding ketones and aldehydes in excellent yields without further oxidation of aldehydes to their corresponding acids using molecular oxygen as the sole oxidant in aqueous media. Furthermore, performance of process in aqueous media makes these catalysts environmentally interesting. Easy procedure, broad substrate applicability, high yields attained in almost short reaction times can be mentioned as advantages of this method.

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