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

Seyed Mohammad Seyedi *, Reza Sandaroos, Gholam Hossein Zohuri

Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran

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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.

Keywords: Cobalt(II) complexes; Alcohol oxidation; Aerobic oxidation

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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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* Corresponding author.
E-mail address: smseyedi@yahoo.com (S.M. Seyedi).

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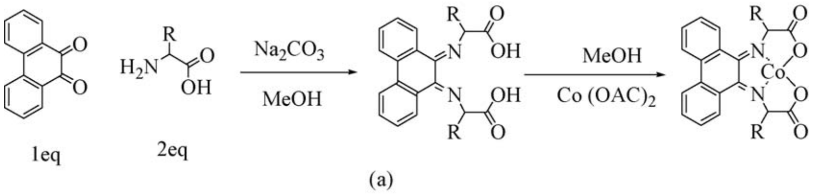

Ligand a and complex (catalyst) **1:** R = CH_2CO_2H
Ligand b and complex (catalyst) **2:** R = H

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 ^{1}H 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 ^{1}H 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 ^{1}H NMR spectrometer in $CDCl_3$ 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 °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).

Table 1
Oxidation activity of complexes **1** and **2** in oxidation of benzyl alcohol expressed in TON[a,b].

Complex	Activity (TON)
1	701
2	654

[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.