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Investigation on catecholase activity of salen Co(III) octahedral complexes

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ABSTRACT

We have synthesized three octahedral Co(III) compounds in order to study their catalytic efficiency for the oxidation of 3,5-di-tertiarybutylcatechol (3,5-DTBC) into the corresponding quinone. Among the tested compounds, only one compound, **3** shows the catecholase activity. The catalytic efficiency of this compound arises from its capability to stabilise two different oxidation states of the metal centre. The initial oxidation state of cobalt ion (Co(III)) changes into Co(II) in order to accommodate the substrate. The kinetic parameters were calculated using the Michaelis-Menten equation. The catalytic loop was proposed and the byproduct formed in the cycle was experimentally determined.

1. Introduction

Metal ions especially from the transition metals have significant contribution in the biological field and also plays a pivotal role in many biological functions. The commonly observed fundamental processes in the environment as well in biology like oxygen transport, photosynthesis and nitrogen fixation are metal-centric ones [1]. Also, the smooth functioning of our body is difficult without the presence of these large number of metalloenzymes. So, it is of utmost importance to design simple as well as novel coordination compounds which are capable of mimicking the bio-activity of metalloenzymes.

Catecholase oxidase is a copper-containing enzyme found in plants and the activity of this enzyme is similar to tyrosinase [2]. The crystal structure of this enzyme including deoxy and the met forms was early reported by Krebs and co-workers and reveals the binuclear structure of the enzyme [3,4]. In catecholase oxidase, two copper atoms are present in +2 oxidation state and each metal is coordinated to four entities in order to satisfy its coordination number as four. Several attempts were made by researchers from worldwide to improve the efficiency of the catalysis by changing reaction conditions like the solvent, pH and temperature of the medium, redox potentials and the metal centre etc [5–9]. The literature reports reveal that most of the coordination compounds reported for the catalytic oxidation of 3,5-ditertiarybutylcatechol (3,5-DTBC) into the corresponding quinone are copper-based ones [10–15]. Reports on transition metal complexes other than Cu(II) atom are limited in number [1,9,16]. Also, among the non-copper coordination compounds reported, mononuclear cobalt-based catalysts are less in number [17–20].

Schiff bases [21] and their complexes [22–26] have found a wide variety of applications and the synthetic flexibility/tunability of these species still grab the interest of researchers worldwide. In the past few decades, it has been reported that Schiff bases containing Co(III) or Co(II) with different nuclearity have been increasingly used in the field of catalysis which includes industrially important reactions and also different oxidation reaction of various organic functionalities [27–35]. Also, they can bio-mimic various metalloenzymes like cyanocobalamin.

In this work, cobalt(III) complexes are exclusively selected for catecholase oxidation reaction owing to the ability of these compounds to exist in two different oxidation states and further there are only limited reports on mononuclear cobalt containing systems in this regard. We have used Co(III) octahedral complex as a model compound and an alternative for Cu(II) compounds and have also predicted the catalytic loop for the oxidation reaction.

2. Experimental

2.1. Materials and methods

The solvents used for the syntheses and catalysis are of analytical and spectroscopic grade respectively. The aldehydes,

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