



Influence of anions and solvents on distinct coordination chemistry of cobalt and effect of coordination spheres on the biomimetic oxidation of *o*-aminophenols

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ABSTRACT

The present work reports the synthesis and structural characterizations of five new cobalt complexes (1–5) resulting from a N₃O donor ligand, a Schiff base condensation product of *N,N*-dimethyldipropylenetriamine and 3-ethoxysalicylaldehyde, and their catalytic activity for the aerobic oxidation of various substrates, namely *o*-aminophenols and catechol. X-ray structural studies reveal that the Schiff base ligand can bind the metal centre either in the tetradentate fashion using all the available donor sites of the monoanionic deprotonated form (in 2 and 3) or in the tridentate fashion using the zwitterionic form of the Schiff base ligand with pendent quaternary amine nitrogen (in 1 and 4). Additionally, the monoanionic deprotonated ligand can bind the metal centre in the tridentate fashion (in 4 and 5) where the pendent tertiary amine nitrogen is involved in the intramolecular hydrogen bonding. All these adaptabilities associated with this triamine make it appealing candidate for exploration of the coordination chemistry with diverse structures. All complexes except compound 1 are efficient functional models for phenoxazinone synthase, and as expected the availability of labile sites at the first coordination sphere for the substrate, *o*-aminophenol, binding is the governing factor for higher catalytic activity in 2 and 3. Requisite of the hydrogen bond acceptor centre as well as proton abstraction centre at the second coordination sphere behind the facile oxidation of the substrate were also explored (reactivity of 1 versus 4 and 5). Moreover, the broader catalytic ability of these complexes was examined with substituted aminophenol and catechol as substrates, and the results were assembled and analysed. Furthermore, emphasis was given to get insight into the mechanistic pathway of functioning phenoxazinone synthase activity, well supported by the mass spectral study.

1. Introduction

Oxidation reaction plays a vital role in organic chemistry for the synthesis of fine organic chemicals as well as in manufacture of large-scale petrochemical compounds [1,2]. The majority of these industrial processes involve the stoichiometric oxidation with traditional oxidants, such as permanganate, dichromate and heavy metal oxides, thereby producing vast wastes which are causing environmental pollution. Pressure from society has placed restrictions on such industrial oxidation methods, with emphasis on the need for sustainable and environmentally friendly processes. As a result, a greater attention has been given on the development of novel and efficient catalytic processes with use of molecular oxygen as a sole oxidant, which is environmentally benign and show a high efficiency per weight of oxidant. However, the direct oxidation of organic substrates by molecular

oxygen is a challenging task because of its kinetic restriction that is associated with conversion of triplet ground state to singlet state of oxygen, and most of the time selectivity does not reach to the desired level [3–6]. Nature has developed several metallo-oxidases to make controlled aerobic oxidations under highly mild conditions in which metalloenzymes activate molecular oxygen for the synthesis of numerous biochemically important compounds with great regio- and stereo-selectivity [7–9]. Bioinorganic chemists have paid a lot attention in unravelling the catalytic mechanism of these enzymes by means of a synthetic analogue approach [10–12]. This approach helps to get insight into the structures of the active sites and reactive intermediates and the mechanistic details of dioxygen activation and oxidation reactions occurring at the active sites [13–19]. Mechanistic studies are clearly a means of developing better synthetic methods, which in turn help in searching efficient catalysts as alternatives of traditional toxic

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industrial catalysts. Therefore, the application of various oxidative transformations involving metal catalysis to specific transformations of different organic substrates, such as aromatic hydrocarbons, alkanes, and oxygen-containing compounds, by molecular dioxygen and their mechanistic exploration is the subject of growing interest [20].

We are now involved in developing biomimetic catalysts for the oxidation of 3,5-di-*tert*-butylcatechol and *o*-aminophenol by molecular dioxygen, modelling the structures and functions of catechol oxidase [21,22] and phenoxazinone synthase [23,24]. The latter is a multi-copper metalloenzyme that catalyses the oxidative coupling of a wide variety of substituted *o*-aminophenols to phenoxazinone chromophore in the final step for the biosynthesis of actinomycin D in aerobic condition [25]. This potent antineoplastic agent actinomycin D is well known for its wide clinical application for the treatment of many tumours, including Wilm's tumour, where the phenoxazinone chromophore intercalates with DNA base-pairs, thereby abnormal functioning can be stopped by preventing the DNA dependent RNA synthesis [26,27]. The active site structures of several oxidase enzymes and the structures of their efficient synthetic analogues with transition metals [21–25,28–36] clearly suggest that the functional models must have labile or vacant coordination sites available for substrate binding as a primary requirement for the efficient *in vitro* catalysis. Therefore, the ligands with fewer donor centres could be the buffering choice for the development of synthetic analogues. Transition metal complexes with Schiff base ligands have been provided a large number of enzymatic models mainly because of their synthetic simplicity, and thereby fine tuning of the catalytic activity may be achieved by modification of the coordination environment at the metal centre by judicious choice of amine and carbonyl parts of the Schiff bases. It is also well known that the extraordinary catalytic activity of metalloenzymes is mainly regulated by the participation of protein chain through the substrate recognition and stabilisation of the intermediates exploiting various noncovalent forces [37–39]. Therefore, the design and synthesis of coordination compounds beyond the first coordination sphere could be the right way of developing efficient biomimetic catalysts.

We have now started developing coordination chemistry with the Schiff base ligands derived from the triamine *N,N*-dimethyldipropylenetriamine as the coordination chemistry with this amine was almost unexplored [40]. Moreover, this amine may readily produce N_3O donor Schiff base ligands when reacts with salicylaldehyde or its derivative. Such ligands by the reaction with transition metal ions could produce synthetic analogues having either vacant or labile position(s) available for substrate binding. Furthermore, the presence of different kind of functionality in the Schiff base ligands derived from this amine, namely imine, amines (both secondary and tertiary), and phenol (from salicylaldehyde part), may allow fine tuning of the ligand field around the metal centre, leading to significant modification of the catalytic efficiency. In continuation to our long standing interest in searching better biomimetic catalysts [21–24], in this present work, Schiff base HL (Scheme 1) derived from *N,N*-dimethyldipropylenetriamine and 3-ethoxysalicylaldehyde was allowed to react with cobalt(II) salts in the presence of different counter ions, and finally we ended up with the isolation of five new cobalt complexes, $[Co(HL)_2](ClO_4)_3 \cdot 2H_2O$ (1), $[Co(L)(N_3)_2]$ (2), $[Co(L)(NCS)_2]$ (3), $[Co(HL)(L)][Co(NCS)_4] \cdot 0.5CH_3OH$ (4) and $[Co(L)_2]_2[Co(NCO)_4]$ (5). Their structural diversities and biomimetic catalytic activities with various substrates such as *o*-aminophenol, 2-amino-5-methylphenol and 3,5-di-*tert*-butylcatechol in aerobic condition have been critically analysed. Remarkably, the influence of solvents and counter ions on the diverse coordination chemistry of cobalt was observed. Moreover, the flexible donor property associated with *N,N*-dimethyldipropylenetriamine part of the Schiff base was also explored. Further emphasis was also given to get insight into the structure-property correlation to justify the reactivity trend of the complexes.

2. Experimental section

2.1. Materials and physical measurements

Reagent or analytical grade chemicals such as cobalt(II) nitrate hexahydrate, cobalt(II) perchlorate hexahydrate, *o*-aminophenol (OAPH), 2-amino-5-methylphenol, 3-ethoxysalicylaldehyde, and *N,N*-dimethyldipropylenetriamine were purchased from commercial sources and used as received. Solvents were also reagent grade and used without further purification.

Caution! Azide and perchlorate salts of metal complexes especially with organic ligands are potentially explosive. Only a small quantity of material should be prepared at a time and it should be handled with great care.

Elemental analyses for carbon, hydrogen and nitrogen were performed using a Perkin-Elmer 240C elemental analyser. IR spectra were recorded on a PerkinElmer Spectrum Two FTIR spectrophotometer in the range 400–4000 cm^{-1} with the samples prepared as KBr pellets. UV–vis spectrophotometric studies were carried out in an Agilent Carry-60 diode array UV–vis spectrophotometer at room temperature. Cyclic voltammetric studies were performed at room temperature in methanol with tetrabutylammonium perchlorate as a supporting electrolyte on a CH Instrument electrochemical workstation model CHI630E with three-electrodes assembly comprising of a platinum working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. Electrospray ionization mass spectra (ESI–MS positive) were recorded in a Micromass Q-tof-Micro Quadrupole mass spectrophotometer.

2.2. Synthesis of the Schiff-base ligand (HL)

Tetradentate N_3O donor Schiff base ligand (HL) was synthesized by the condensation reaction of 1.0 mmol of *N,N*-Dimethyldipropylenetriamine (159 mg) and 1.0 mmol of 3-ethoxysalicylaldehyde (166 mg) in 20 ml of methanol (or acetonitrile). Mixture of these reactants in methanol was allowed to reflux for *ca.* 1 h, and then cooled. The *in situ* prepared Schiff base ligand was used directly for the synthesis of the subsequent metal complexes as described below.

2.3. Synthesis of $[Co(HL)_2](ClO_4)_3 \cdot 2H_2O$ (1)

Addition of $Co(ClO_4)_2 \cdot 6H_2O$ (0.730 g, 2.0 mmol) dissolved in 20 ml of methanol to the Schiff base ligand HL (2.0 mmol) solution at room temperature instantly produced a dark-brown solution. The mixture was stirred in air for 30 min during which time light brown powders separated out from the solution. It was collected by filtration and washed with mother liquor followed by methanol/ether and finally air dried. Yield: 0.867 g (85%). Dark-brown crystals suitable for X-ray analysis were obtained from slow evaporation of acetonitrile-methanol mixture of the complex at ambient temperature within few days. Anal. Calcd. for $C_{70}H_{128}Co_2N_{12}O_{35}Cl_6$: C 41.45%, H 6.36%, N 8.29%. Found: C 41.28%, H 6.42%, N 8.35%. FTIR (KBr, cm^{-1}): $\nu(N_3)$ 2050 vs; $\nu(C=N)$ 1632 s; $\nu(ClO_4)$ 624 s, 1104 vs.

2.4. Synthesis of $[Co(L)(N_3)_2]$ (2)

$Co(NO_3)_2 \cdot 6H_2O$ (291 mg, 1.0 mmol) and Schiff base ligand HL (1.0 mmol) were mixed together in 40 ml acetonitrile, and to the mixture 2 ml aqueous solution of sodium azide (130 mg, 2.0 mmol) was added with stirring. The resulting solution was then heated to reflux for about 30 min during which time colour of the solution changed to dark brown. The reaction mixture was then filtered and kept at ambient temperature for slow evaporation. Analytically pure dark-brown crystals suitable for X-ray diffraction study were separated out from the solution after few days, which was collected by filtration and washed with methanol/ether and air dried. Yield: 392 mg (86%). Anal. Calcd.

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