



Binuclear cobalt complex with Schiff base ligand: Synthesis, characterization and catalytic properties in partial oxidation of cyclohexane

Liudmila I. Rodionova^{a,*}, Andrey V. Smirnov^a, Natalya E. Borisova^a, Victor N. Khrustalev^b, Anna A. Moiseeva^a, Wolfgang Grünert^c

^a Department of Chemistry, Lomonosov Moscow State University, Lenin Hills 1/3, 119991 Moscow, Russian Federation

^b A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, 119991 Moscow, Russian Federation

^c Ruhr-Universität Bochum, P.O. Box 10 21 48, D-44801 Bochum, Germany

ARTICLE INFO

Article history:

Received 16 March 2012
Received in revised form 31 May 2012
Accepted 1 June 2012
Available online 19 June 2012

Keywords:

Cyclohexane oxidation
Binuclear cobalt complex
Schiff bases

ABSTRACT

A new binuclear cobalt complex with Schiff base ligand and amino acid was synthesized and characterized using XRD, elemental analysis, IR spectroscopy, XPS and electrochemical measurements. The presence of cobalt in the oxidation state 3+ in this complex was proved. The catalytic activity of this complex was investigated in the reaction of partial cyclohexane oxidation with air, and high activity and selectivity for cyclohexanol and cyclohexanone formation were demonstrated. The possibility of complex reuse in cyclohexane oxidation was studied and it was shown that the activity slightly decreases in a second oxidation cycle along with changes in main product distribution due to partial transfer of Co³⁺ to Co²⁺.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

One of the most promising directions of petroleum hydrocarbon feedstock conversion is its partial oxidation with air to valuable products [1]. Among these processes, the catalytic oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone becomes increasingly important due to great need of these products as precursors in caprolactam and Nylon-6 synthesis [2]. One of the first industrial alkane oxidation processes – the Du Pont adipic acid process [3], which involves homogeneous cyclohexane oxidation with air on cobalt salts, such as naphthenate or acetate, initiated an intense research activity devoted to catalytic cyclohexane oxidation over heterogeneous and homogeneous cobalt systems [4–10] using different oxidants such as air [5,6], pure oxygen [7], hydrogen peroxide [8,9] and organic hydroperoxides [10].

As cyclohexanol and cyclohexanone are more easily oxidized than the initial cyclohexane, conversion is kept at low levels (about 4–5%) to avoid the formation of side products by deeper oxidation of the cyclohexanol–cyclohexanone mixture [3]. In this connection, it is of prime importance to find new catalysts which selectively oxidize only cyclohexane.

Mono- and binuclear complexes of transitional metals with Schiff base ligands attract attention since they are structural and composition analogs of some biological active compounds [11]. Many researchers are focused on producing systems which can mi-

mic not only structural but also catalytic properties of metalloenzymes [12–15]. Based on such biological processes as methane oxidation on monooxygenase [12,13,15] or steroids oxidation on cytochrome P450 [14], new complexes for catalytic oxidation of alkanes, olefins, alcohols and aldehydes are being developed.

The detailed study of structure, state of metal and catalytic activity of such complexes can result in the elucidation of the mechanisms of biocatalyzed oxidation processes.

In this article a binuclear cobalt complex **CoL** with Schiff base ligand and L-valine will be described. The composition and structure of this complex were characterized by IR spectroscopy, elemental analysis, XRD, XPS and electrochemical measurements. The complex was tested in cyclohexane oxidation with air and showed high activity and selectivity to the cyclohexanol–cyclohexanone mixture.

2. Experimental

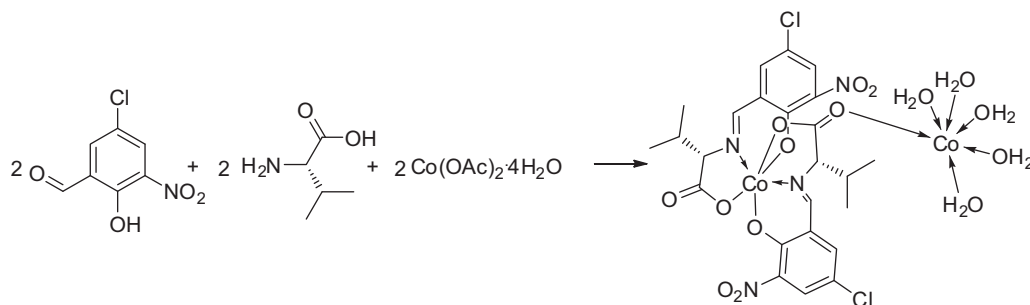
2.1. Synthesis

2.1.1. Synthesis of sodium salt of the ligand (see Scheme 2)

To the solution of 115 mg (5 mmol) of Na in anhydrous methanol (30 ml) 590 mg (5 mmol) of solid L-valine was added and the mixture was stirred until complete dissolution. After the addition of the equimolar amount of 5-chloro-2-hydroxy-3-nitrobenzaldehyde (5 mmol) the mixture was stirred for 3 h at room temperature and a dark crimson solution was formed. After evaporation of this solution, a dark red product was formed.

* Corresponding author. Tel.: +7 (495) 939 2054; fax: +7 (495) 939 3570.

E-mail address: ludmilarodionova@mail.ru (L.I. Rodionova).



Scheme 1.

Anal. Calc. for $C_{12}H_{12}ClNaN_2O_5$: C, 44.67; N, 8.68; H, 3.75; Na, 7.22. Found: C, 44.5; N, 8.92; H, 3.63; Na, 6.94%. IR (KBr, cm^{-1}): 3427, 2965, 2929, 2862, 1648, 1609, 1534, 1510, 1398, 1340, 1280, 1221. 1H NMR (400 MHz, methanol- d_4) δ ppm 1.02 (t, $J = 6.85$ Hz, 6 H) 2.40 (tq, $J = 6.60, 5.26$ Hz, 1 H) 3.98 (br, s, 1 H) 7.67 (d, $J = 2.93$ Hz, 1 H) 7.90 (s, 1 H) 8.11 (d, $J = 2.69$ Hz, 1 H) 8.48 (s, 1 H).

2.1.2. Synthesis of complex [16] (Scheme 1)

5-Chloro-2-hydroxy-3-nitrobenzaldehyde 1 g (5 mmol) and 590 mg (5 mmol) of L-valine were dissolved in 50 ml of an ethanol–water (3/1) mixture and heated for 2 h. After this period, 1.254 g (5 mmol) of solid cobalt(II) acetate tetrahydrate was added and the mixture was diluted with 50 ml of water and sonicated for 10 min to avoid precipitation of unreacted cobalt salt. The reaction mixture was filtered, washed with water and diethyl ether. The collected solid was air dried overnight and then over NaOH in a desiccator, whereupon dark brown crystals were formed.

The substance thus formed was soluble in methanol and insoluble in diethyl ether and water. The structure of complex, denoted as **CoL**, was confirmed by IR spectroscopy and X-ray diffraction.

Anal. Calc. for $C_{24}H_{32}Cl_2Co_{1.5}N_4O_{15}$: C, 37.12; N, 7.22; H, 4.12; Co, 11.4; Found: C, 36.75; N, 6.98; H, 4.04; Co, 11.7. IR (KBr, cm^{-1}): 3376, 2967, 2929, 2862, 1647, 1597, 1533, 1515, 1438, 1383, 1354, 1315, 1287, 1228, 1197, 1135.

2.2. Physical measurements

The elemental analysis (carbon, hydrogen and nitrogen) of the complex was obtained by a Thermo Flash EA 1112 series analyzer. XPS (X-ray photoelectron spectroscopy) data were recorded with the Leyboldt LH 10/100, using Magnesium $K\alpha$ excitation (1253.6 eV). The residual pressure in the spectrometer during the runs was about 10^{-8} Pa. The sample was vacuumized at liquid nitrogen temperature. The spectrometer energy scale was calibrated using Au 4f7/2 photoelectron line at 84.0 eV, the correction for surface charging was made by setting the C 1s signal of aromatic and aliphatic C to 284.5 eV. The metal content was measured using thermogravimetric analysis (TA Instruments, SDT Q600) in air flow by complex decomposition to constant mass, which was

determined as Co_3O_4 . FTIR spectra were recorded on a Nicolet Protege 460 spectrometer in KBr pellets.

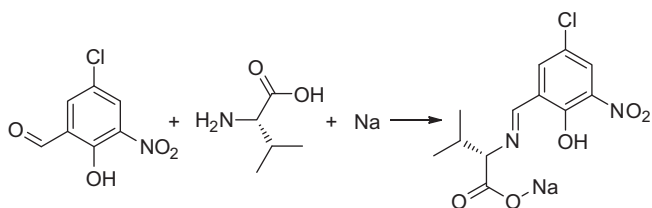
Electrochemical studies (cyclic voltammetry) were carried out on a IPC-Pro M potentiostat. A glassy-carbon disk with diameter of 2 mm was used as working electrode; a 0.1 M Bu_4NClO_4 (TBP) solution in DMF (high-purity grade) served as the supporting electrolyte; Ag/AgCl/KCl(satd.) was used as reference electrode and a platinum electrode as counter electrode. The sample concentration was 10^{-3} mol/l. All measurements were carried out under argon; the samples were dissolved in the deaerated solvent. The scan rate was 200 mV s^{-1} . All potentials are given taking into account IR-compensation.

2.2.1. X-ray crystal structure determination

A red prismatic crystal ($0.1 \times 0.1 \times 0.3$ mm³) of **CoL** ($C_{24}H_{32}N_4O_{15}Cl_2Co_{1.5} \cdot 2.5H_2O$, $M = 775.83$) is trigonal, space group $P3_121$, at $T = 100$ K: $a = 15.7626(9)$ Å, $c = 24.8669(14)$ Å, $V = 5350.7(5)$ Å³, $Z = 6$, $d_{calc} = 1.445$ g/cm³, $F(000) = 2391$, $\mu = 0.923$ mm⁻¹. A total of 51 478 reflections (7047 unique reflections, $R_{int} = 0.065$) were measured on a Bruker SMART APEX II CCD diffractometer (λ (Mo $K\alpha$)-radiation, graphite monochromator, ω and φ scan mode, $2\theta_{max} = 52^\circ$) and corrected for absorption using the SADABS program [17]. The structure was determined by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The absolute structure of **CoL** was objectively determined by the refinement of Flack parameter, which has become equal to 0.03(3). The hydrogen atoms of the water molecules were localized in the difference-Fourier map and included in the refinement with fixed positional and isotropic displacement parameters. The other hydrogen atoms were placed in the calculated positions and refined within a riding model with fixed isotropic displacement parameters ($U_{iso}(H) = 1.5U_{eq}(C)$ for the CH_3 -groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other groups). The final divergence factors were $R_1 = 0.080$ for 5218 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.206$ for all independent reflections, $S = 1.007$. All calculations were carried out using the SHELXTL program [18].

2.3. Cyclohexane oxidation

Cyclohexane (CyH) oxidation was carried out in a 100 ml stainless steel batch reactor equipped with a magnetic stirrer. In a typical experiment 0.36 mol of cyclohexane, 0.09 mol of toluene as internal standard and 6.5×10^{-6} mol of catalyst were added to the autoclave. The system was pressurized with air and then heated under permanent stirring. The operating temperature, measured by a thermocouple inside the reactor, was 140 °C. The operating pressure after heating was maintained at 25 atm. The main products, such as cyclohexanol (CyOH) and cyclohexanone (CyO), were analyzed by gas–liquid chromatography, cyclohexyl hydroperoxide (CyOOH) was detected by iodometric titration with



Scheme 2.

Download English Version:

<https://daneshyari.com/en/article/1306001>

Download Persian Version:

<https://daneshyari.com/article/1306001>

[Daneshyari.com](https://daneshyari.com)