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Cu(II) bipyridine and phenantroline complexes: Tailor-made catalysts for the selective oxidation of tetralin

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ABSTRACT

Mononuclear Cu(II) complexes have been synthesized, and their structure thoroughly characterized by electrospray ionization mass spectrometry (ESI-MS). These 2,2′-bipyridine and 1,10-phenantroline mononuclear Cu(II) complexes have been tested as catalysts in the partial oxidation of tetralin (1,2,3,4-tetrahydronaphthalene), using hydrogen peroxide as oxidant in acetonitrile/water as solvent.

The complexes $[Cu(bipy)_3]Cl_2\cdot 6H_2O$ (**1**), $[Cu(bipy)_2Cl]Cl\cdot 5H_2O$ (**2**), $[Cu(bipy)Cl_2]$ (**3**), $[Cu(phen)_3]Cl_2\cdot 6H_2O$ (**4**), $[Cu(phen)_2Cl]Cl\cdot 5H_2O$ (**5**), $[Cu(phen)Cl_2]$ (**6**) were able to oxidize tetralin at room temperature, at high degrees of conversion (62.1% with **2**) into α-tetralol and α-tetralon at 91% selectivity (81% in 1-tetralon).

Depending on nature and number of ligands (bipyridine or phenantroline) surrounding Cu^{2+} cation, one was able to tailor both the activity toward tetralin oxidation, and the selectivity toward 1-tetralol and 1-tetralone products, but also to raise the yield in valuable α-tetralone.

1. Introduction

Tetralone is a keto-hydronaphthalene used as a reactive intermediate, which can be converted to compounds of industrial importance, including dyes, pharmaceuticals, and agrochemicals [1–3]. Tetralone can be produced by different chemical processes, such as Friedel-Crafts acylation of aromatics with acid halide/anhydride or oxidation reactions, both involving stoichiometric amounts of either corrosive $AlCl_3$ as catalyst or $KMnO_4/K_2Cr_2O_7$ as oxidizing agent, respectively [4–8].

Recently, many efforts have been devoted to the development of environment friendly and economical processes for the selective oxidation of alkylaromatics and cycloalkanes to higher-value added ketones. In this scope, the development of homogeneous and heterogeneous catalytic systems in combination with “green” oxidizing agents like O_2 and hydrogen peroxide have been widely developed for the oxidation of tetralin [9–12].

Copper plays fundamental roles in living systems and is coordinated to the protein residues, as found in hemocyanines, which are copper-containing oxygen transport proteins from arthropods and mollusks [13]. In addition, copper is present in various enzymes involved in oxidation reactions, for instance catechol oxidase [14], dopamine monoxygenase [15,16], methane monoxygenase [17] and tyrosinase [18,19].

The use of copper complexes for the oxidation of organic compounds has been recently developed. Esmelindro et al. reported the benzene oxidation to phenol (2.2%) and 1,4-benzoquinone (6.7%) with a mononuclear Cu(II) complex, $[Cu(BMTEA)_2Cl]Cl$ (BMTEA = bis(2-thienylmethyl)-1,2-ethylenediamine), as catalyst and hydrogen peroxide as oxidant in acetonitrile at 40 °C [20]. In addition, Silva et al. reported the use of the four-centre complex $\{[Cu(BMPA)Cl_2][Cu(BMPA)(H_2O)Cl][Cu(BMPA)Cl][CuCl_4]\}$ (BMPA = bis-(2-pyridylmethyl)amine) as catalyst for cyclohexane oxidation in the presence of hydrogen peroxide in acetonitrile, yielding cyclohexanol (52.3%) and cyclohexanone (14.6%) with a catalyst turnover number of 689 [21].

Furthermore, copper complexes have also been studied for tetralin oxidation. Zhu et al. [12] have reported the liquid phase oxidation of tetralin using *tert*-butylhydroperoxide as oxidant, with a tetrameric Cu(II)-triethylamine complex at 70 °C. A degree of conversion of 72.7% was achieved with a 65.8% selectivity to α-tetralone. Velusamy and Punniyamurthy [22] described the use of a mononuclear Cu(II) complex for tetralin oxidation using H_2O_2 at 80 °C, giving α-tetralone in a 89% yield.

The aim of the present paper is to report the catalytic activity of 2,2′-bipyridine and 1,10-phenantroline Cu(II) complexes as catalysts in tetralin oxidation. The studied complexes were

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$[Cu(bipy)_3]Cl_2{\cdot}6H_2O$ (**1**), $[Cu(bipy)_2Cl]Cl{\cdot}5H_2O$ (**2**), $[Cu(bipy)Cl_2]$ (**3**), $[Cu(phen)_3]Cl_2{\cdot}6H_2O$ (**4**), $[Cu(phen)_2Cl]Cl{\cdot}5H_2O$ (**5**) and $[Cu(phen)Cl_2]$ (**6**). Based on the work developed by Canhota et al. [23], which accounted for cyclohexane oxidation with complexes **1**–**3** as catalysts, achieving yields up to 43% by using complex **3** with H_2O_2 at 50 °C, thus involving the fact that activity is strongly connected to the number of ligands coordinated to Cu(II), we envisaged the application of the complexes described herein for tetralin partial oxidation. The reactions were carried out using hydrogen peroxide as oxidant in acetonitrile/water solvent, under mild conditions (room temperature or microwave irradiation).

2. Experimental

2.1. Synthesis of the Cu(II) complexes

The complexes were synthesized based on original procedures described by Meyer [24], modified according to our latest study [25]. The synthesis of the complex $[Cu(L)_3]Cl_2$ was carried out by the addition of 3 eq. of the 2,2′-bipyridyl ligand (2,2′-bipyridine) or 1,10-phenantroline ligand in 50 mL of ethanol to 1 eq. of $CuCl_2{\cdot}2H_2O$ in 15 mL of ethanol. The mixture was then stirred for 10 min at room temperature, thus forming a precipitate after a few minutes. Finally, the solvent was evaporated slowly at room temperature, and the complex was collected.

These as-synthesized complexes **1–6** were characterized by Fourier-transform infrared spectra (FT-IR) and elemental analysis and the results were as follows:

(1) $[Cu(bipy)_3]Cl_2{\cdot}6H_2O$: Turkish blue solid. IR (KBr disc, cm^{-1}) 3069, 3051, 3028, 1604, 1597, 1566, 1492, 1442, 776. Elemental analysis calculated for $C_{30}H_{36}N_6O_6Cl_2Cu$: C, 50.60; H, 5.06; N, 11.80%. Found: C, 49.51; H, 5.41; N,11.33%.

(2) $[Cu(bipy)_2Cl]Cl{\cdot}5H_2O$: Light blue solid. IR (KBr disc, cm^{-1}): 3062, 3048, 3034, 1604, 1597, 1565, 1492, 1471, 1443, 772. Elemental analysis calculated for $C_{20}H_{26}N_4O_5C_{l2}Cu$: C, 44.69; H, 4.84; N, 10.43%. Found: C, 44.75; H, 4.70; N, 10.35%.

(3) $[Cu(bipy)Cl_2]$: Light green solid. IR (KBr disc, cm^{-1}): 3068, 3053, 3037, 1602, 1551, 1497, 1473, 1446, 777. Elemental analysis calculated for $C_{10}H_8N_2Cl_2Cu$: C, 41.27; H, 2.75; N, 9.63%. Found: C, 41.10; H, 2.59; N, 9.52%.

(4) $[Cu(phen)_3]Cl_2{\cdot}6H_2O$: Turkish-green blue solid. IR (KBr disc, cm^{-1}): 3055, 1626, 1605, 1587, 1518, 1495, 1425, 724. Elemental analysis calculated for $C_{36}H_{36}N_6O_6Cl_2Cu$: C, 55.16; H, 4,60; N, 10.70%. Found: C, 53.64; H, 4.96; N, 10.34%.

(5) $[Cu(phen)_2Cl]Cl.5H_2O$: Green solid. IR (KBr disc, cm^{-1}): 3088, 3054, 3032,1606, 1587, 1495, 1427,723. Elemental analysis calculated for $C_{24}H_{26}N_4O_5Cl_2Cu$: C, 49.26; H,4.44; N, 9.58%. Found: C, 49.25; H, 4.40; N, 9.43%.

(6) $[Cu(phen)Cl_2]$: Light green solid. IR (KBr disc, cm^{-1}): 3080, 3058, 3012, 1607, 1586, 1516, 1495, 1423,722. Elemental analysis calculated for $C_{12}H_8N_2Cl_2Cu$: C, 45.78; H, 2.54, N, 8.9%. Found: C, 45.59; H, 2.53; N, 8.78%.

2.2. Characterization and catalytic activity evaluation

FT-IR were recorded on a Nicolet Spectrometer 760 (KBr pellets). Elemental analyses were obtained using PerkinElmer 2400 CHN and a microbalance PerkinElmer AD-4 Autobalance. Electrospray ionization mass spectrometry (ESI-MS) measurements were performed on a high resolution ESI-TOF (micrOTOF, Bruker Daltonics, Bremen, Germany) mass spectrometer. Testing compounds were dissolved in methanol prior to analysis. Full scans were acquired under the following conditions: capillary, 5.5 kV; capillary exit, 100 V. All spectra shown were obtained in positive-ion mode.

The different copper complexes were tested in liquid phase tetralin oxidation either at room temperature, or under microwave-heating at 338 K for 30 min. All solvents and reagents were purchased from Aldrich or Merck. Hydrogen peroxide (H_2O_2, 30 wt% in water) was titrated by the iodometric method before use. The reactions were performed in a 20 mL round-bottomed flask, under vigorous stirring, sealed with a silicone septum under nitrogen atmosphere, using acetonitrile as solvent, H_2O_2 as oxidant and Cu(II) complexes as catalysts. The ratio acetonitrile/water was set to 8. The copper catalyst (0.007–0.009 mmol), tetralin (4.4 mmol) and hydrogen peroxide (22.2 mmol) were successively added to 10 mL acetonitrile. The reaction mixture was stirred at 293 K for 24 h for bipyridine complexes and 68 h for phenantroline complexes, respectively. Experiments were also performed with a sealed reactor under microwave heating during 30 min at 338 K (CEM Discover microwave). The reaction was quenched by the addition of 3.0 g of Na_2SO_3 and then the mixture was filtered in a silica bed to retain the catalyst. The products were analyzed by gas chromatography (HP 5890 Series II) with a capillary column (PONA, 50 m). Retention times were compared with standards and used to characterize most of the reactions products. Relative yields were calculated taking into account the response factors of the substrate (tetralin) and of the products (1-tetralone, 1-tetralol) through the use of an external standard. The turnover number (TON) was used to evaluate the catalyst performance as follows: number of substrate molecules converted per molecule of catalyst.

3. Results and discussion

3.1. Complexes characterization

3.1.1. Methodology for the design of Cu(II) complexes

Six different mononuclear Cu(II) complexes containing either 2,2′-bipyridyl or 1,10-phenantroline ligands were synthesized. The complexes differ from one another by the number of ligand molecules coordinated to central Cu(II) ion. The complexes were prepared via reaction of $CuCl_2{\cdot}2H_2O$ with 1, 2 or 3 eq. of ligands. The Cu(II) complexes described herein were synthesized by the addition of 2,2′-bipyridine or 1,10-phenanthroline in a proper metal/ligand ratio in order to form complexes **1–6** (Fig. 1), as a result of the self-assembly of Cu(II) ions with the added ligands. The most common coordination numbers of Cu(II) ions are 4, 5 and 6, but the distinction between square-planar and tetragonal distorted octahedral geometries for Cu(II) complexes is not readily evident [26].

For compounds **1** and **4**, Cu(II) is hexacoordinated to the pyridyl ligands, assuming an octahedral geometry [27,28], whereas compounds **2** and **5** assume a trigonal bipyramidal geometry as the Cu(II) ion is pentacordinated to the pyridyl and chloride ligands [29,30].

According to the literature, complex **3** can be found in two geometries: (a) distorted square pyramidal, in which one chlorine atom interacts with the Cu(II) core of a neighbor complex molecule, forming a polymer [31]; or (b) distorted octahedral, in which two chlorine atoms are interacting with a neighbor Cu(II) core [32]. However, in complex **6** Cu(II) ions are probably hexacoordinated with one 1,10-phenantroline and two chloride ions in a plane, sharing two other chlorine atoms with neighboring Cu(II) core in a perpendicular plane [33].

3.1.2. ESI-MS characterization of 2,2′-bipyridine and 1,10-phenantroline Cu(II) complexes

The resulting positive-ion mode spectra for the several complexes in methanol are depicted in Fig. 2 (bipyridine complexes) and Fig. 3 (phenantroline complexes) with the corresponding peak data and assignments presented in Tables 1 and 2. One of the most remarkable features in ESI-MS spectra of