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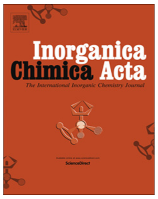

Research paper

Copper(II) complexes with an arylhydrazone of methyl 2-cyanoacetate as effective catalysts in the microwave-assisted oxidation of cyclohexane

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ABSTRACT

Reaction of sodium (E/Z)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl)benzene-sulfonate (NaHL) with copper(II) nitrate hydrate in the presence of imidazole (im) in methanol affords [CuL(im)(H_2O)] (**1**). Complex **1** is characterized by IR spectroscopy and ESI-MS spectrometry, elemental and single crystal X-ray crystal structural analyses. The coordination environment of the central copper(II) is nearly intermediate between ideal square-based pyramidal and trigonal bipyramidal geometry, three sites being occupied by the L^{2-} ligand, which chelates in the O, N, O fashion, while two other sites are filled with the water and imidazole molecules. Extensive intermolecular hydrogen bonds between the L^{2-}, water and imidazole ligands lead to a 3D supramolecular network. **1** and known Cu(II) complexes [Cu(H_2O)$_2$L]·H_2O (**2**), [Cu(H_2O)(py)L]·H_2O (**3**) and [Cu_3(μ_3-OH)(NO_3)(CH_3OH)(μ_2-X)$_3$(μ_2-HL)] (**4**) act as effective catalysts in the oxidation of cyclohexane to cyclohexanol and cyclohexanone, using low power microwave (MW) irradiation, under mild conditions. Without a promoter, the activity of the catalyst reached a turnover number of 1.44×10^3 and a turnover frequency of $1.98 \times 10^3\ h^{-1}$, after 2 h, at 50 °C.

1. Introduction

Arylhydrazones of active methylene compounds (AHAMC) bear hydrazone, carbonyl and cyano moieties and thus provide a rich organic and coordination chemistry [1,2]. Usually the AHAMC ligands are prepared by the Japp-Klingemann reaction [3]. Nucleophilic additions to cyano group(s) of the obtained hydrazone compounds lead to new AHAMC ligands [4]. AHAMC and their complexes have been found to possess a wide variety of useful properties, such as sensor or analytical reagents, spin-coating films, optical storage media, catalysts, etc [1,5]. The modification of the active methylene fragment or aromatic moiety can be used as a synthetic approach for the regulation of properties of those ligands and their coordination compounds. For instance, introduction of hydrophilic polar groups, such as sulfo or carboxy group(s), to AHAMC can increase the solubility of the obtained complexes and provide an acidic medium in the peroxidative oxidation of alkanes [6].

Acidic medium can also be created/organized by using an axillary ligand which has an acidic proton, for example, imidazole (im).

Their application in the functionalization of inert C—H bonds of hydrocarbons with a metal catalyst and an oxidant is a promising area of catalysis [2f,4a,4b,6]. Alkanes are attractive substrates for added value organic chemicals (alcohols, ketones, aldehydes and carboxylic acids). Unfortunately, their low reactivity constitutes a considerable limitation towards their broad application for direct syntheses of oxygenated products under relatively mild conditions [7]. However, the use of an appropriate metal catalyst, namely a copper complex [8], that promotes the catalytic functionalization of the non-activated C—H bonds of hydrocarbons has been one of the goals of some of us [7,9]. We chose cyclohexane oxidation as the model reaction to test our complexes, which constitutes an important step for Nylon 6 and Nylon 6,6 production, a main industrial process [10].

Thus, in this work we combine the above mentioned approaches towards the following aims: i) to synthesize a new

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copper(II) complex, [CuL(im)(H_2O)] **(1)**, derived from sodium (*E*/*Z*)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl) benzenesulfonate (NaHL) and imidazole (im) ligands and ii) to apply **1** and known Cu(II) complexes, [Cu(H_2O)2L]·H_2O (2), [Cu(H_2O)(Py)L]·H_2O (3), [Cu_3(μ_3-OH)(NO_3)(CH_3OH)(μ_2-X)$_3$(μ_2-HL)] (4) [4], as catalysts for the peroxidative oxidation of cyclohexane.

2. Results and discussion

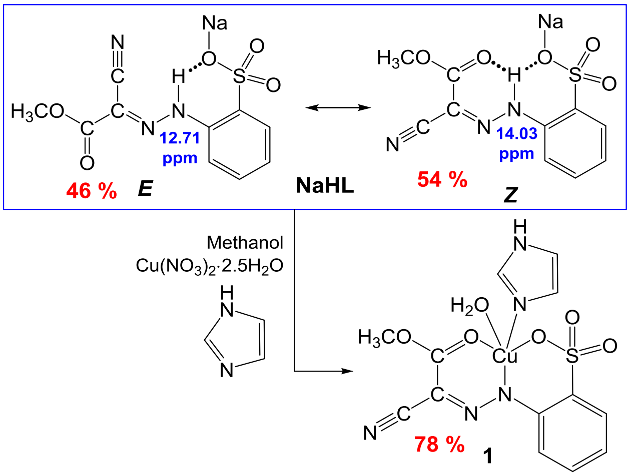
2.1. Synthesis and characterization of 1

The synthesis and characterization of sodium (*E*/*Z*)-2-(2-(1-cyano-2-methoxy-oxoethylidene)hydrazinyl) benzenesulfonate (NaHL) (Scheme 1) was reported earlier by us [4a] and will not be discussed here. Reaction of copper(II) nitrate hydrate with NaHL in the presence of imidazole (im) in a methanol solution leads to the mononuclear compound [CuL(im)(H_2O)] (**1**) (Scheme 1). **1** was characterized by elemental analysis, IR spectroscopy, ESI-MS and single crystal X-ray diffraction. The IR spectrum of **1** displays bands at 3448 *ν*(O–H), 2222 *ν*(C≡N), 1646 *ν*(C=O) and 1579 *ν*(C=N) cm^{-1} which are significantly shifted in relation to those of the free ligand [3475 *ν*(OH), 2209 *ν*(C≡N), 1710 *ν*(C=O), 1628 *ν*(C=O···H), 1596 *ν*(C=N)] [4a]. Elemental analysis and ESI-MS in methanol (peak at *m*/*z* 431.7 [Mr+H]$^+$) support the proposed formulation of **1** as a monomer.

2.2. Description of the X-ray crystal structure

The asymmetric unit of the title compound (Fig. 1) contains one monomeric unit of the title compound, in which the Cu(II) ion is coordinated by the L^{2-} ligand together with one water molecule and one imidazole ligand. The Cu atom adopts a five-coordinated geometry defined by three oxygen atoms O1, O4 and OW1 belonging to the sulfonate group, ester group and water molecule and two nitrogen atoms N1 in the hydrazo group and N4 of imidazole entity.

The geometry around the Cu^{II} centre in the monomeric unit can be described as distorted trigonal bipyramidal. Considering that the complex presents a coordination number of 5, the parameter was calculated for the complex to measure the grade of distortion, and its value varies from 0 (in regular square-based pyramidal geometry) to 1 (in regular trigonal bipyramidal geometry) [11]. In the title complex the calculated τ value is equal to 0.40. This value is lower than 0.5 and shows that in the title compound the geometry around the copper atom is nearly intermediate between the two ideal coordination geometries. The apical positions are occupied by the N donor atoms N1 and N4; the bond lengths are located at 1.976(3) Å and 1.956(3) Å, respectively. The angle of N4–Cu1–N1 is with 179.12(11)° close to 180°. The equatorial positions of the trigonal plane are occupied by the O donor atoms O4, OW1 and O1 (Fig. 2). The bond lengths are Cu1–O1 = 1.991(2), Cu1–O4 = 1.978(2) and Cu1–OW1 = 2.234(2) Å.



Scheme 1. Synthesis of **1**.

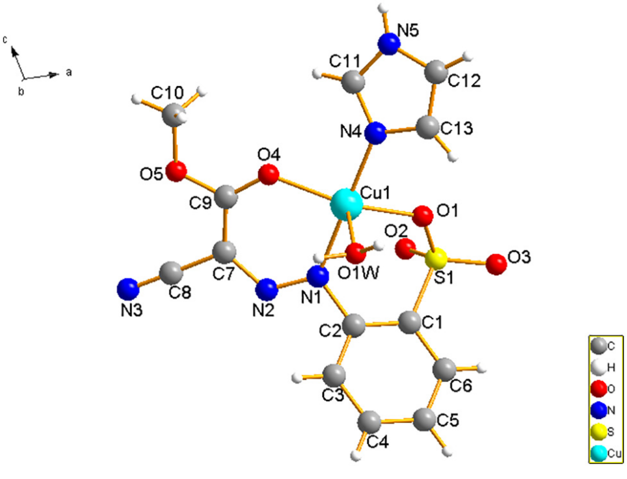


Fig. 1. Asymmetric unit of **1**.

The copper ion forms two fused six-membered metallacycles, Cu1-O1-S1-C1-C2-N1 and Cu1-O4-C9-C7-N2-N1. Consistent with electron delocalization in these metallacycles are the N1–N2, C7–N2, and C9=O4 bond lengths of 1.295(3), 1.344(4), and 1.241(4) Å (see Table S1), respectively. The crystal structure is stabilized by weak intermolecular hydrogen bonding interactions (Fig. 3; Table S2) between the coordinated water molecule, the imidazol entities and the nitrile or sulfonate bridging group. Within the intermolecular hydrogen bonds; O1W – H2···N3^{ii}, N5–H5A···O3^{iii} and O1W–H1···O2^{i}, the donor-acceptor distances are equal to 2.873(1), 3.047(1) and 2.744(1) Å, respectively.

2.3. Catalytic oxidation of cyclohexane

The catalytic study focused on the use of cyclohexane as model substrate for the investigation of the catalytic performance of **1** and known Cu(II) complexes, [Cu(H_2O)$_2$L]·H_2O (**2**), [Cu(H_2O)(py)L]·H_2O (**3**) and [Cu_3(μ_3-OH)(NO_3)(CH_3OH)(μ_2-X)$_3$(μ_2-HL)] (**4**), derived from the same ligand (Scheme 2) [4a], in oxidation reactions of cycloalkanes using *tert*-butyl hydroperoxide (TBHP, 70% aq.

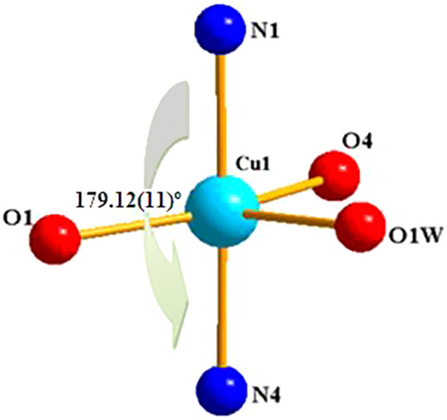


Fig. 2. Schematic drawing of coordination geometry of Cu(II) in **1**.