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Inorganica Chimica Acta 358 (2005) 3581–3591

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Infinite zig-zag and cyclic-tetranuclear isomeric imidazolate-bridged polynuclear copper(II) complexes: Magnetic properties, catalytic activity and electrospray mass and tandem mass spectrometry characterization

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Received 16 November 2004; received in revised form 19 April 2005; accepted 16 June 2005
Available online 9 August 2005

Abstract

Two mononuclear copper(II) complexes **1** and **2** with the unsymmetrical tridentate ligands 2- and 4-[((imidazol-2-ylmethylidene)amino)ethyl]pyridine have been prepared. In alkaline solution, deprotonation of the imidazole moiety in **1** and **2** promotes self-assembly, which yielded two structurally different species. Depending on the binding site in the imidazole ring, a polymeric complex with an infinite zig-zag-chain **3**, or a cyclic-tetranuclear complex **4** is formed, as shown by spectroscopic and spectrometric analysis. Herein, structural characterization of these isomeric polynuclear complexes was performed by electrospray mass (ESI-MS) and tandem mass spectrometric experiments (ESI-MS/MS). Each isomer was shown to be stable in methanolic solutions and to display unique mass spectra with characteristic multiply charged molecular and fragment ions, corroborating previous data by EPR measurements. Magnetic data in the solid state fit a typical curve for an one-dimensional infinite regular chain system, with $J = -(32.4 \pm 1.2)\ \mathrm{cm}^{-1}$ and $g = 2.03$ for **3**, and that of a cyclic-tetranuclear structure with $J = -(55.5 \pm 0.4)\ \mathrm{cm}^{-1}$ and $g = 2.29$ for **4**. In the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) by molecular oxygen, both complexes were shown to act as efficient catalysts, exhibiting very similar ratios: $k_{\mathrm{cat}}/K_{\mathrm{M}} = 9.12 \times 10^6\ \mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{min}^{-1}$ for **3** and $8.73 \times 10^6\ \mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{min}^{-1}$ for **4**. These similar ratios indicate that interactions between the metal centres in **3** or **4** and the substrate in solution occur predominantly at the outside of the catalyst framework.

Keywords: Copper(II) complexes; ESI mass spectrometry; Magnetic properties; Catalytic activity

1. Introduction

Continuing interest in the synthesis and characterization of polynuclear copper(II) complexes derives from the efforts to understand their many varied physicochemical properties such as electrochemical, optical, magnetic, mechanical, and catalytic activity, which constitute important characteristics for its potential applications [1]. On the other hand, multicopper proteins such as laccase, ascorbate oxidase and ceruloplasmin show a trinuclear copper cluster in addition to other metal domains, in which interactions between the metal centres are important factors for its peculiar reactivity, promoting very rapid electron transfers [2]. Therefore,

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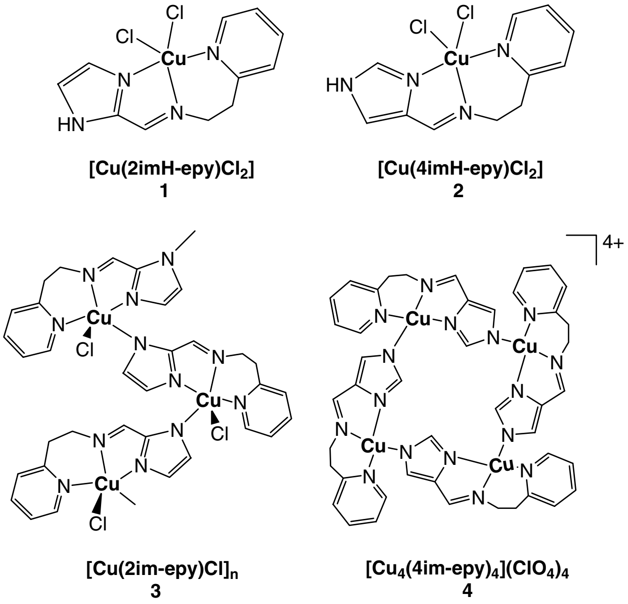
doi:10.1016/j.ica.2005.06.006

polynuclear copper(II) complexes could also be helpful for better elucidation of the cooperative action between metal centres in the active sites of such enzymes [3].

Copper(II) complexes with imine ligands containing imidazolate-bridging groups have been used as precursors of assemblies based on supramolecular coordination chemistry, leading to highly ordered, symmetrical molecular or supramolecular structures [4]. Matsumoto and coworkers, for instance, verified the influence of substituents in the imidazole ring on the deprotonation and interconversion between monomer and assembled oligomers by inputting external information, specifically a change of pH [4,5]. Substituents in the imidazole ring apparently have a marked effect on ring size and in the structural orientation of these complexes, since different architectures were realized, for example: cyclic tetramers [5,6] and hexamers [5], as well as 1D chains [6,7].

Although the syntheses and characterization of polynuclear coordination complexes have been extensively investigated in the last years, mainly in solid state [4–8], the stability and reactivity of these oligomeric species in solution are relatively unknown, generally due to problems of solubility in specific solvents. MS characterization of such complexes has also been a difficult task. Electrospray mass spectrometry (ESI-MS) [9] using the soft electrospray ionization technique, which is able to gently transfer pre-formed ions [10] directly from solution to the gas phase, has become a major technique for mass and structural analysis of a large variety of both neutral and ionic metallic complexes [11], and we have been using extensively such technique for fine structural analysis of metalo-organic species [12]. ESI-MS has also been used to characterize polynuclear complexes. As a typical example, Stoeckli-Evans and coworkers self-assembled two new tetranuclear copper(II) and nickel(II) complexes from the ligand pyrazin-2,3-dicarboxylic acid bis[(pyridine-2-ylmethyl)-amide] with multiple anion encapsulation, and used ESI-MS to estimate their stability in methanol and water solvents [13]. ESI-MS shows that anions are not essential for the formation of the macrocyclic complexes as proposed previously [14], suggesting that the formation of the tetranuclear species is ruled primarily by the design of suitable ligands and the choice of appropriate metal ions.

We have previously reported the synthesis and characterization of some new copper(II) complexes containing imidazolate group incorporated in the imine ligand, as precursors of dinuclear and polynuclear species, designed to act as oxidation catalysts in homogeneous solution [15]. In this work, we wish to investigate the stability and reactivity of these polynuclear complexes in solution, and have therefore prepared **3** and **4** (Scheme 1), two species with different structural orientations about the binding position of the imidazole ring. These two complexes are particularly interesting, since they show a sterical influence of the heterocyclic ligand in the building of the final molecular architecture.



Scheme 1.

2. Experimental

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled very carefully, only in small amounts.

2.1. Syntheses of complexes

2.1.1. [Cu(2imH-epy)Cl$_2$] (*1*) and [Cu(4imH-epy)Cl$_2$] (*2*)

2-(aminoethyl)pyridine (0.13 ml, 1 mmol) in methanol (10 ml) was added dropwise to a solution of 2-imidazolecarboxaldehyde (96 mg, 1 mmol) or 4-imidazolecarboxaldehyde (0.19 g, 2 mmol) in methanol (15 ml), and the mixture was stirred at 55 °C, for 1 h. A methanolic solution (10 ml) of $CuCl_2 \cdot 2H_2O$ (170 mg, 1 mmol) was then added at once. After several hours of standing, a green powder precipitate was observed for **1** or a blue one for **2**, which was collected by filtration, washed with small amounts of methanol and diethyl ether, and finally dried in vacuum under P_2O_5. The obtained yield was 78% for [Cu(2imH-epy)Cl$_2$] and 47% for [Cu(4imH-epy)Cl$_2$]. *Anal.* Calc. for compound **1**, $C_{11}H_{12}N_4CuCl_2$: C, 39.47; H, 3.61; N, 16.73; Cl, 21.18. Found: C, 39.69; H, 3.64; N, 16.68; Cl, 20.93%. $\Lambda_M = 212\ S\ cm^2\ mol^{-1}$ in water, and $\Lambda_M = 42\ S\ cm^2\ mol^{-1}$ in DMF. UV–Vis, λ_{max}/nm, (ε/l $mol^{-1}\ cm^{-1}$) in water: 256 (8060), 304 (9280), 670 (47). UV–Vis, λ_{max}/nm, in solid: 692. FTIR (KBr, cm^{-1}): 3142–3125 ($\nu_{N–H}$); 1628 ($\nu_{C=N}$); 1607, 1482, 1439 ($\nu_{C=C}$, $\nu_{C=N}$ (pyridine ring)). *Anal.* Calc. for compound **2**, $C_{11}H_{12}N_4CuCl_2 \cdot H_2O$: C, 37.45; H, 4.00; N, 15.88.