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Chloro-bridged Cu(II) pairs linked into a 1D coordination polymer through a dinucleating imidazole-based ligand: 3D structure and magnetism

Yufei Song [a], Chiara Massera [b], Olivier Roubeau [c], Anna Maria Manotti Lanfredi [b], Jan Reedijk [a,*]

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
[b] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Universita`degli Studi di Parma, Parco Area delle Scienze 17/A, 43100 Parma, Italy
[c] Centre de Recherche Paul Pascal-CNRS UPR 8641, 115 avenue du Docteur Albert Schweitzer, 33600 Pessac, France

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Abstract

Reaction of the ligand 1,1,7,7-tetrakis(imidazol-2-yl)-2,6-diazaheptane (H_4L) with $CuCl_2$ in MeCN results in the formation of an interesting 1D polynuclear copper(II) complex with formula $[Cu_4(H_3L)(H_2L)Cl_3(H_2O)_2]Cl_2 \cdot 5H_2O$. The complex contains tetranuclear building blocks, and very interestingly, three of the four imidazole rings coordinated to Cu1 and Cu2 are dehydronated. Nevertheless, all the imidazolate rings are coordinated to Cu in a monodentate mode, although each dehydronated N is strongly hydrogen bonded to a lattice water molecule. The Cu–Cu distances between the copper(II) atoms in the tetranuclear units vary from 5.843 to 6.013 Å. The polynuclear complex, based on chloro-bridged Cu(II) pairs, is further stabilized by stacking interaction between imidazolate moieties and by a network of intermolecular hydrogen bonds. The differences between the ligand-field spectrum and the UV–Vis spectrum of the complex in MeOH indicate that the complex may partially dissociate in MeOH, as also evidenced by ESI-MS. The X-band EPR spectrum of the polycrystalline powder of the complex shows fairly broad isotropic signal centered at a $g = 2.11$, and EPR study in the MeOH solution at 77 K shows two group of signals due to $[Cu(MeOH)_6]^{2+}$ cation and the mononuclear species from the dissociated polynuclear compound. A weak antiferromagnetic interaction in dichloro-bridged Cu(II) pair dominates the magnetic behaviour of the compound.

Keywords: Polymer; Copper; Imidazole; Magnetic properties

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1. Introduction

Imidazole occurs in most of proteins as part of the side chain of histidine and constitutes the binding sites of various transition metal ions in a large number of metalloproteins [1,2]. Among them, copper–imidazole interactions are widely known and particularly interesting in biological systems [3]. For example, imidazolate, the dehydronated form of imidazole, is involved in the active site of the mixed copper–zinc enzyme, superoxide dismutase [4,5], which catalyzes the disproportionation of the harmful superoxide radical anion, acting as a bridging ligand between Cu(II) and Zn(II) ions. In order to understand the special magnetic, spectroscopic propeties and the catalytic mechanisms of copper proteins, the study and modeling of the active site of copper-containing proteins has been a

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[*] Corresponding author. Tel.: +31 71 5274450; fax: +31 71 5274671.
E-mail address: reedijk@chem.leidenuniv.nl (J. Reedijk).

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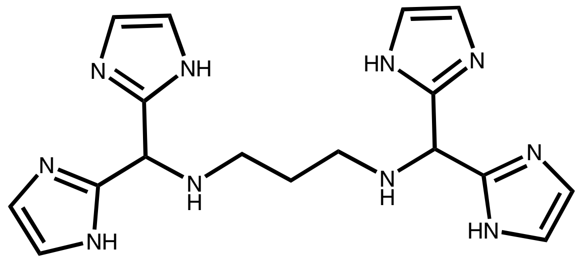

Fig. 1. The molecular structure of the ligand 1,1,7,7-tetrakis(imidazol-2-yl)-2,6 -diazaheptane (H_4L).

field of great interest within the scientific community [6–11].

Since the imidazole is ubiquitous in almost all of the copper proteins, the development of model complexes with imidazole-containing ligands have captured our interest for many years. As a continuation of the study, we present here an investigation of a new copper complex with a potential dinucleating imidazole-containing ligand, 1,1,7,7,-tetrakis(imidazol-2-yl)-2,6-diaza-heptane (H_4L) [12] (see Fig. 1).

Recently, we reported that the reaction of H_4L with $Cu(OAc)_2$ led to an unprecedented imidazolato- and acetato-bridged dodecanuclear complex [12], in which the C–N bonds in the original ligand have been oxidized to C=N bonds upon coordination with copper(II) acetate. However, when $CuCl_2$ is used for the coordination, another interesting 1D tetranuclear-based polymer is formed. In this contribution, the synthesis, crystal structure, spectroscopic and magnetic properties of the copper(II) polymeric compound have been discussed.

2. Results and discussion

The bis(imidazole-2-yl)nitromethane [13] is an interesting intermediate for the synthesis of a variety of new chelating ligands and it can be obtained in five steps by a ring-opening and double ring-closure reaction. Coupling 1,3-diaminopropane with the bis(imidazole-2-yl)-nitromethane intermediate results in the formation of a potential dinucleating ligand H_4L as shown in Fig. 1.

The polynuclear compound of formula $[Cu_4(H_3L)(H_2L)Cl_3(H_2O)_2]Cl_2 \cdot 5H_2O$ was obtained by reaction of one equivalent of the ligand H_4L with three equivalents of copper(II) chloride in acetonitrile. Diethyl ether diffusion into the acetonitrile solution resulted in the formation of blue square crystals suitable for X-ray diffraction analysis. A molecular plot representing one unit of the complex together with the atom-labeling scheme is shown in Fig. 2.

2.1. Description of structure $[Cu_4(H_3L)(H_2L)Cl_3(H_2O)_2]Cl_2 \cdot 5H_2O$

The compound consists of polymeric chains built up by dicationic subunits $[Cu_4(H_3L)(H_2L)Cl_3(H_2O)_2]^{2+}$ containing four metal ions, two nitrogen donor ligands, three coordinated chlorine atoms and two coordinated

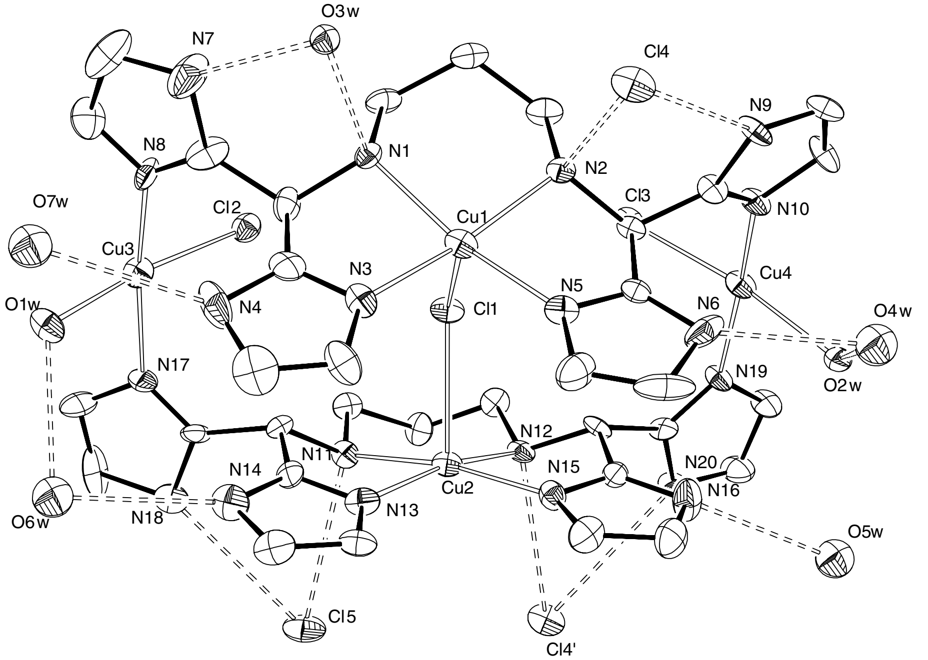

Fig. 2. Thermal ellipsoid plot (20% probability level) of the asymmetric subunit $[Cu_4(H_3L)(H_2L)Cl_3(H_2O)_2]^{2+}$ together with the two chloride counter ions, one chloride ion (Cl4′) from an adjacent subunit and the five crystallization water molecules; the hydrogen atoms have been omitted for clarity. The hydrogen bond network is indicated with dotted double lines.