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Structures of Copper(II) imidazole complexes synthesized in ILs

Fanni Falk and Martin Köckerling

Introduction

For more than a decade ionic liquids (ILs) have encountered immense scientific attention as starting materials and reaction media. ILs containing a metal-ion are a very interesting subclass of ionic liquids, because of their possible magnetic or catalytic properties beside the typical IL properties (large electrochemical windows, low vapor pressures and so on).
Before, our work group investigated low-viscosity Co(II) metal-containing ILs with imidazolium cations.[1,2] Expanding these research to Cr(III)-ions gained low melting salts.[3] In continuation of these activities, Cu(II) salts were investigated. The first reactions of Cu(II) acetates led to new polynuclear compounds with 1D or 2D-network structures.[4] New neutral Cu(II) complexes have been obtained with imidazole ligands. Three representative examples are presented in the following sections.

Preparation

The chloride of the starting material 1-butyl-3-methylimidazolium chloride (BMImCl) was exchanged through an anion-exchanger to obtain 1-butyl-3-methylimidazolium hydroxide (BMImOH). The BMImOH was used directly without any further purification. Selected organic acids (4-hydroxybenzoic acid (PHBAH), 4-aminobenzoic acid (PABAH) and isophthalic acid (MPHTHH)) were added to an equivalent amount of BMImOH. The mixture was stirred until a homogenous solution was obtained. Then Cu(II) acetate dissolved in water was added until no further precipitation was formed. The precipitation was filtered off, washed several times with water and dried under air. Blue and violet crystals were obtained from methanolic solutions.

Results

From the reaction of BMImOH with PHBAH and Cu(II) acetate, crystals of $[Cu(H_2O)_2(MIm)(PHBA)_2]\cdot 2H_2O$ were obtained in high yield. It is a heteroleptic complex with neutral Mim and anionic PHBA ligands. Presumably, the Mim is formed through a reaction of PHBA with $BMIm^+$ with elimination of butyl 4-hydroxybenzoate. The neutral complex is mononuclear with one Mim, two PHBA and two aqua ligands in a square pyramidal environment, see Figure 1.
Even though the PABA ligand is very similar to PHBA, the mononuclear Cu(II) complex has a different composition. It contains two PABA, two Mim and one water molecules, again with a square pyramidal coordination environment of the Cu(II) ion, see Figure 2.
By the reaction with MPHTHH again a different structure was obtained. In compound **3** two MIm are coordinated to the Cu(II) ion and two MPHTH dianions in a non-chelating function. But, in contrast to compound **1** and **2**, each second carboxylic group is bonded to neighboring Cu(II) ion, i. e. compound **3** comprises a network structure, with coordinative bonds extending in two directions (2D-network, see Figure 3).

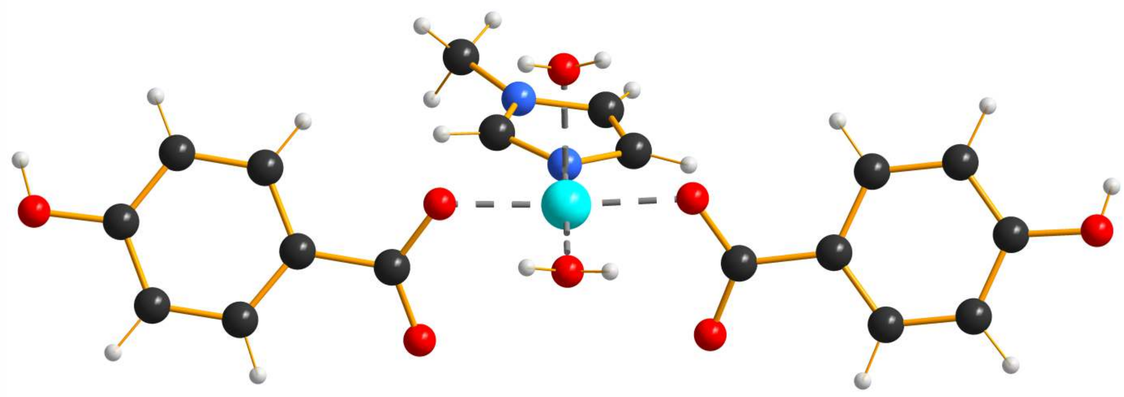

Figure 1. $[Cu(H_2O)_2(MIm)(PHBA)_2]\cdot 2H_2O$ (Compound **1**)

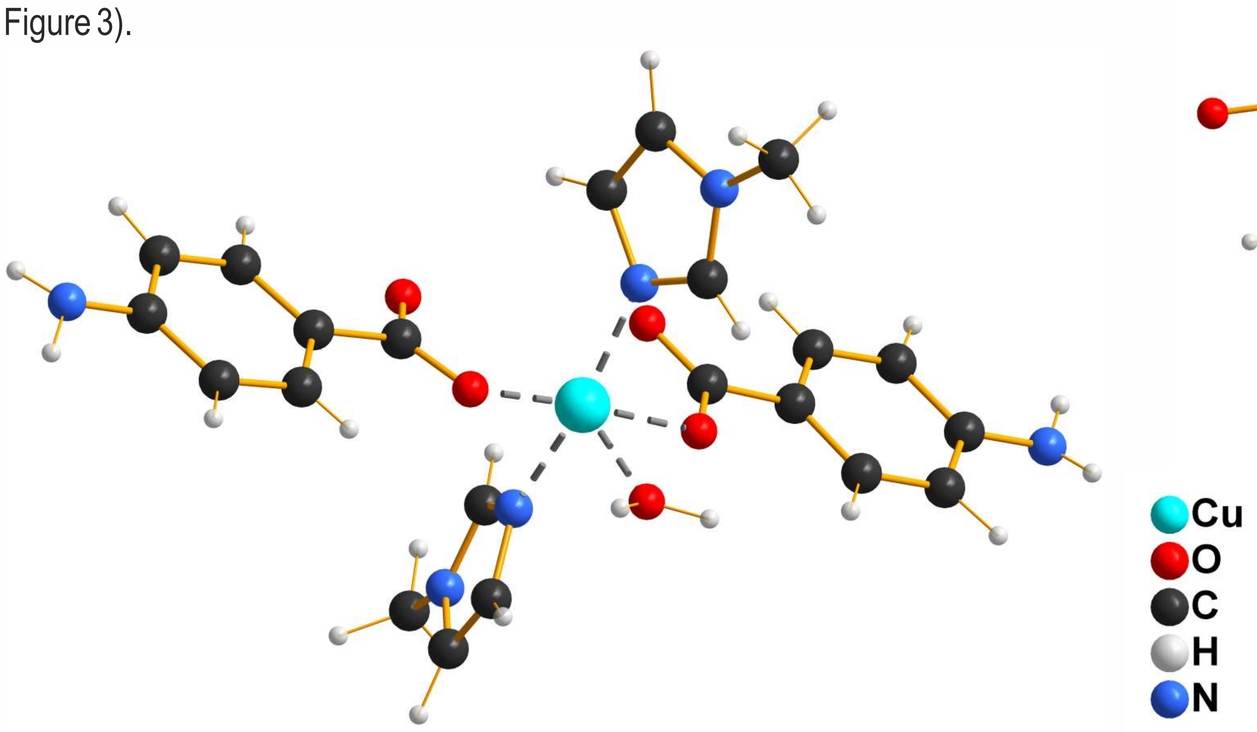

Figure 2. $[Cu(H_2O)(MIm)_2(PABA)_2]$ (Compound **2**)

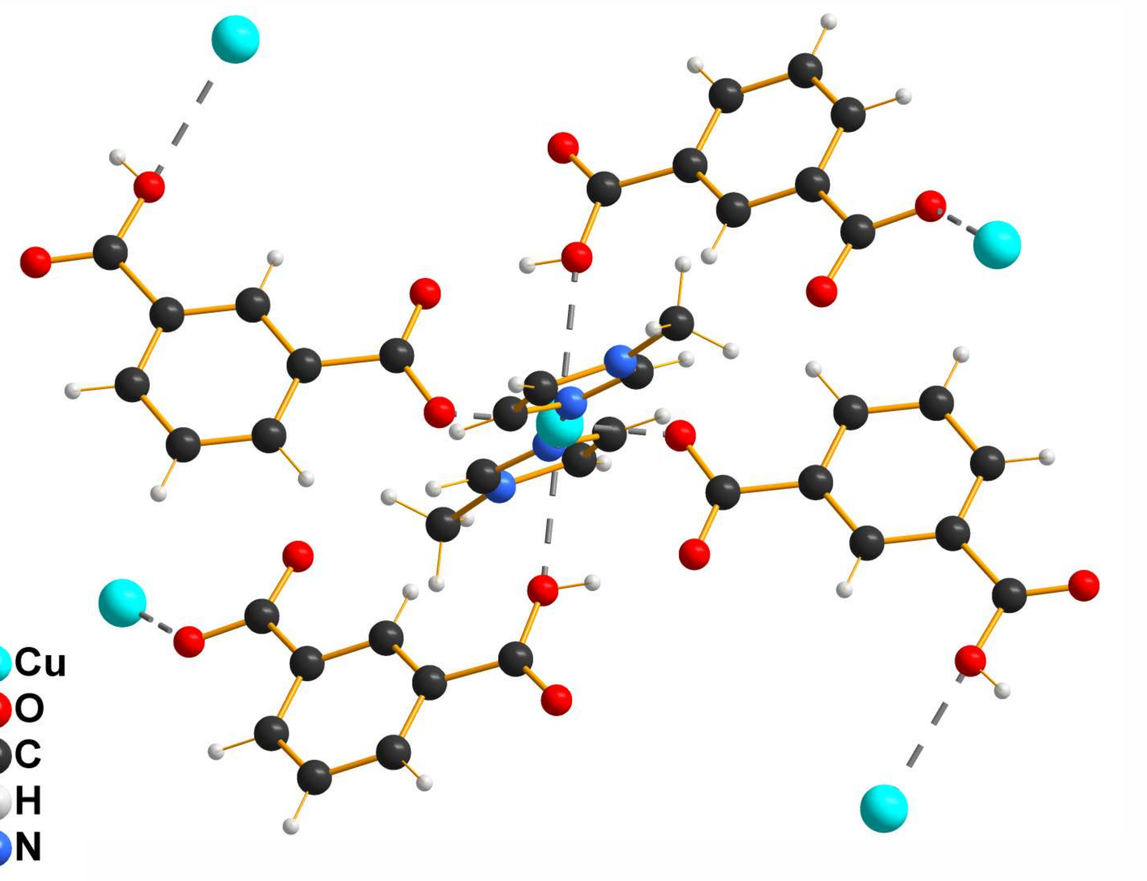

Figure 3. $[Cu(MIm)_2(MPHTH)_2]_n$ (Compound **3**)

Outlook

The coordinating variety of the organic acids to the Cu(II) ion will be further investigated, as the properties of the synthesized compounds. If the water molecule in compound **2** is exchanged by a diyne, the structure reminds of a possible intermediate in the eglinton reaction.[5] Therefore, we intend to test this compound as catalyst.

Reference

[1] T. Peppel, M. Köckerling, M. Geppert-Rybczyńska, R. V. Ralys, J. K. Lehmann, S. P. Verevkin, A. Heintz, *Angew. Chem. Int. Ed.* **2010**, *49*, 7116-7119. [2] T. Peppel, A. Hinz, P. Thiele, M. Geppert-Rybczyńska, J. K. Lehmann, M. Köckerling, *Eur. J. Inorg. Chem.* **2017**, 885-893. [3] T. Peppel, P. Thiele, M.-B. Tang, J.-T. Zhao, M. Köckerling, *Inorg. Chem.* **2015**, *54*, 982-988. [4] A. Hinz, M. Köckerling, *Z. anorg. allg. Chem.* **2015**, *641*, 1347-1351. [5] J. Jover, *J. Chem.* **2015**, *2015*, 1–8.

Department of Chemistry | Solid State Chemistry, **University of Rostock,** Albert-Einstein-Str. 3a | 18059 Rostock, Germany