Universität Rostock

Traditio et Innovatio

# Polynuclear transition metal compounds made with ionic liquids

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## Introduction

New polynuclear transition metal compounds can be obtain with ionic liquids (ILs) as solvents and starting materials.[1] Our group has succeeded in the synthesis of new compounds by adding transition metal salts to ILs. So far, metals salts are limited to acetates with a “paddle wheel” structure. New polynuclear copper(II), chromium(II), or rhodium(II) acetate compounds are obtain using ionic liquids with the 1-butyl-3-methyl imidazolium ($BMIm^+$) cation and halogenides or pseudohalogenids as anions, for example chloride and thiocyanate, respectively.[2,3] In these compounds the dimere acetate structure is preserved, except in the copper cyanide salt $(BMIm)_2[Cu_4(CN)_7]$.[3] In the compound $(BMIm[Cu_2(OAc)_5][Cu(OAc)_2(H_2O)]_2*EtOH)$, which crystallizes simultaneously with the before mentioned cyanide from the same solution, coordination chains with altering “paddle wheel” acetates bridged by additional acetato ligands are observed.

Our interest is to further investigate such reaction systems. It is our goal to obtain new structures by expanding our research to other transition metal salts, for example iron(III) acetate and other ionic liquids.

## Structure

Two copper compounds can be obtained by the reaction of copper(II) acetate and BMImCN. $(BMIm)_2[Cu_4(CN)_7]$, contains copper(II) as well as copper(I) ions bridged by cyanido ligands. The reduction of a portion of the cooper(II) cations to copper(I) can be explained persumably through the formation of dicyan, as known for copper(II) cyanide. The compound has the orthorhombic space group *Pnma*. The assymetric unit contains three symmetry independent copper ions, two copper(I) and one copper(II). The formed 3D coordination polymer can be described as honeycomb structure, where the $BMIm^+$ cation is being located in the cages, shown in Figure 1.

The second compound is a pure copper(II) acetato complexe, without cyanido ligands. $BMIm[Cu_2(OAc)_5][Cu(OAc)_2(H_2O)]_2*EtOH$ crystallize in the triclinic space group $P\bar{1}$. It can be discribed as a double-salt containing two units. The first unit contains $BMIm^+$ cations and paddle wheel copper(II) acetato moieties. The copper(II) units are bridged by additional acetato ligands and therefor form chains, shown in Figure 2. In the second unit neutral paddle wheel copper(II) acetates exist. The two unites and the co-crystallized ethanol molecule are connected through hydrogen bonds.

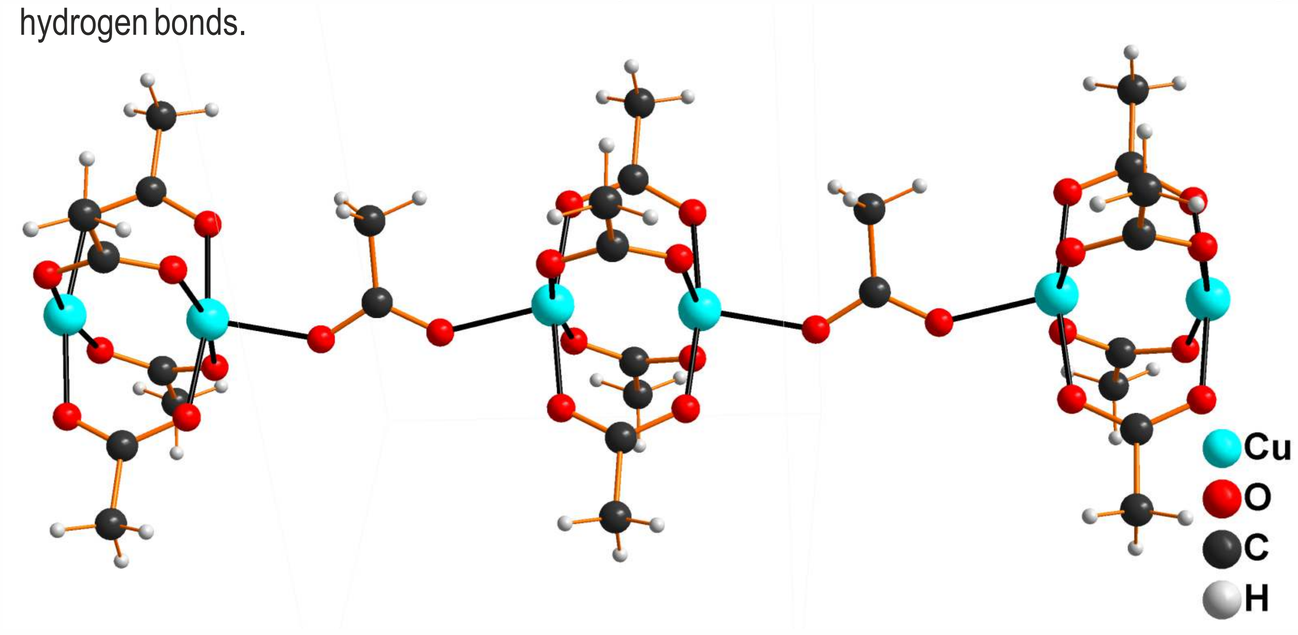


**Figure 2.** Structure of the acetate bridged paddle wheel chains, found in crystals of $(BMIm[Cu_2(OAc)_5][Cu(OAc)_2(H_2O)]_2*EtOH)$.

## Preparation

1-Butyl-3-methyl imidazolium chloride (BMImCl) is used as starting material to obtain other ILs with the $BMIm^+$ cation. BMImSCN and BMImOCN can be synthesized easily by adding KSCN or KOCN to a solution of BMImCl in dichloromethane or acetone. BMImOH is obtained through an anion-exchange process. By treating these with acetic acid or oxalic acid BMImOAc and $(BMIm)_2Oxo$ results, respectively. BMImCN is prepared by using $BMImBF_4$ and KCN in ethanol/water, according to modified literature procedure.[4]

The synthesis with an emphasis on obtaining single crystals of the new polynuclear transition metal compounds is done by slow diffusion of constituents in a small glass vial. The ionic liquids are dissolved in narrow glass tubes. The glass tubes are placed in vials containing solutions of the used transition metal salts. The arrangement is layered with solvents until both solutions are connected. For copper(II) acetate ethanol is used as solvent.

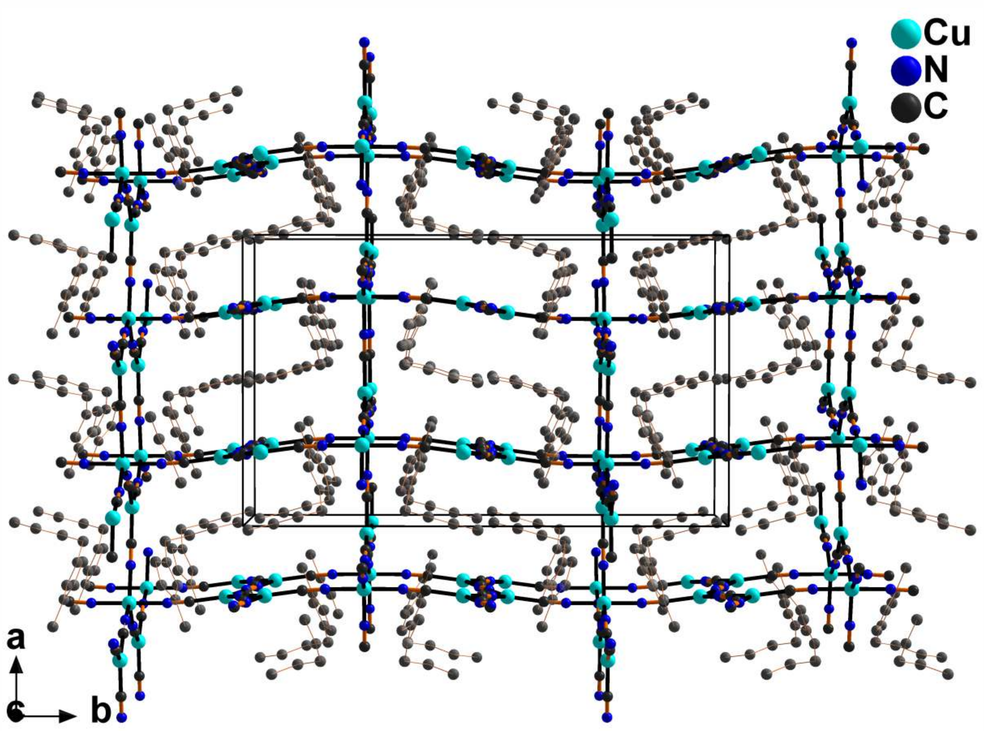


**Figure 1.** Honeycomb structure of $(BMIm)_2[Cu_4(CN)_7]$. $BMIm^+$ cations are coloured grey. Hydrogen atoms are omitted for clarity.

## Outlook

So far copper(II), chromium(II), and rhodium(II) acetates are used in chemical reactions with BMImCl, BMImBr, BMImI, $BMImF*H_2O$, BMImSCN, BMImOCN, BMImOAc and BMImCN, which lead to new polynuclear coordination polymers. Further reactions with $(BMIm)_2Oxo$, $(BMIm)_2SO_4$, $BMImNO_3$ and $(BMIm)_3PO_4$ are planned. Also, the starting transition metal salts shall be expanded to iron(III) acetate and mixed iron(III)/M(II) acetates (M = Ni, Co, Mn).

## Reference

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[3] A. Hinz, M. Köckerling, *Z. Anorg. Allg. Chem.* **2015**, *641*, 1347-1351. [4] H. Kobler, R. Munz, G. Gasser, G. Simchen, *Liebigs Ann. Chem.* **1978**, *1978*, 1937-1945.

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