
Synthesis and characterization of a new Cu(II)-carboxylate complex from aqueous media

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Abstract

A new Cu(II)-carboxylate species was synthesized in aqueous solution at the optimum pH 5. The carboxylate ligand which interacted with copper(II) is 1,2,3,4-cyclobutanetetracarboxylic acid. The new crystalline material was isolated and characterized by elemental analysis, spectroscopic techniques (FT-IR), magnetic studies and X-ray crystallography.

Keywords: Copper(II), 1,2,3,4-cyclobutanetetracarboxylic acid, materials

1. Introduction

Copper is an essential trace metal ion in all plants and animals (Gao, L et.al). It is encountered in a variety of enzymes, including the copper centers of cytochrome c oxidase and the enzyme superoxide dismutase (SOD). Moreover, it is used for biological electron transport (blue copper proteins like azurin and plastocyanin) (Cobine, P.A et. al.). In the case of most mollusks and some arthropods, hemocyanin which is a copper-containing pigment, is used as an oxygen carrier instead of hemoglobin. Even though copper is an important metalloelement, its deficiency can often produce anemia-like symptoms and it can inhibit haematopoiesis (Devereux, M et. al.). Furthermore, due to its ability to accept and donate single electrons as it changes oxidation state, copper can lead to oxidative stress (Teixeira, S.).

Copper is a metal capable of providing new species, which can be used as precursors in advanced materials (Li, D. et. al.). This fact is based on the physical properties of copper, as it is malleable and ductile, a good conductor of heat and, when very pure, a good conductor of electricity. It is also widely used in electronics (wire, electromagnets), structural engineering (pipes, statuary), household products (Cookware), coinage and finally is used for biomedical applications (isotopes $^{62}$Cu, $^{64}$Cu).

One representative acid, which can promote chemical reactivity with copper(II) in aqueous media is the low molecular mass binder 1,2,3,4-cyclobutanetetracarboxylic acid. 1,2,3,4-cyclobutanetetracarboxylic acid is a polycarboxylate ligand and is capable of coordinating with metal ions in order to produce new materials, including polymeric ones bearing specific lattice characteristics.

Synthetically, this tetracarboxylic ligand is produced by the general reaction as shown below (Figure 1):

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Figure 1. The general synthesis of 1,2,3,4-cyclobutanetetracarboxylic acid

2. Experimental Section

The aqueous synthetic chemistry of the binary system Cu(II)-1,2,3,4-cyclobutanetetracarboxylic acid was investigated. In this sense, under specific stoichiometric conditions and pH-specific reaction conditions, the arisen reactivity led to the isolation of a new crystalline material with molecular formula $[\text{Cu}]_{16}(\text{C}_8\text{H}_4\text{O}_8)_8\cdot 48\text{H}_2\text{O}$ (1). More specifically, the synthesis of I was carried out in aqueous media.

Nanopure water was used for all reaction efforts. The pH of the reaction mixture was adjusted to 5 with aqueous KOH. The addition of the base was crucial for the isolation of the new species since it helps to adjust the pH of the reaction mixture. The resulting reaction mixture was kept at room temperature. After a few days, blue crystals arose for complex I. The stoichiometric reactions for the synthesis of complex I is given below:

$$16\text{Cu(NO}_3)_2 + 8\text{HOOC} \quad \text{COOH} + 32\text{KOH} + 16\text{H}_2\text{O} \quad \text{pH 5}$$

$$[\text{Cu}]_{16}(\text{C}_8\text{H}_4\text{O}_8)_8\cdot 48\text{H}_2\text{O} + 32\text{KNO}_3$$

Reaction 1

Elemental analysis pointed to the molecular formulation of complex I. C$_{64}$H$_{128}$Cu$_{16}$O$_{112}$ (M.B. 3706.38) Anal. Calcd for I: C, 20.72; H, 3.45; Found: C, 21.32; H, 3.56%. Complex I was further characterized by FT-IR and X-Ray crystallography for one of the isolated single crystal from the reaction mixture.

The FT-IR spectrum of the complex I was recorded in KBr and reflected the presence of vibrationally active carboxylate groups. The antisymmetric stretching vibrations $\nu_{as}(\text{COO}^-)$ appear around 1564 cm$^{-1}$, whereas the symmetric stretches $\nu_s(\text{COO}^-)$ appear in the range 1425-1388 cm$^{-1}$ for complex I.

X-Ray crystallography was instrumental in revealing the three-dimensional structure of the investigated molecules. The structure of complex $[\text{Cu}]_{16}(\text{C}_8\text{H}_4\text{O}_8)_8\cdot 48\text{H}_2\text{O}$ reveals that each Cu(II) ion coordinates to two 1,2,3,4-cyclobutanetetracarboxylic ligands in an octahedral environment.

Moreover, magnetic susceptibility studies and EPR studies on I were carried out to provide valuable information on the nature of species both in the solid state and in solution. Finally, speciation studies of the binary system of Cu(II)-1,2,3,4-cyclobutanetetracarboxylic acid are expected to provide further insight into the different chemical aspects arising from variable Cu(II)-substrate stoichiometries and pH values.
3. Conclusions

In this work, the undertaken efforts targeted the comprehension of Cu(II) interactions with complex organic substrates in aqueous solutions. This fundamental contention is based on the fact that Cu(II) is capable of coordinating to polycarboxylic acids in order to provide species with distinct physicochemical properties. Hence, copper is a metal ion a) capable of coordinating with biotargets entering physiologically important binary and ternary interactions, and b) involved in precursor species assembly crucial for the synthesis of advanced materials.

To this end, the aqueous synthetic chemistry of Cu(II) with 1,2,3,4-cyclobutanetetracarboxylic acid was investigated in-depth. These efforts led to the isolation of the first species between Cu(II) and this carboxylate ligand under variable stoichiometries, pH values and bases. The physicochemical properties of the synthesized and isolated species are testimony to the chemical reactivity of copper leading to diverse lattices with distinct structural features, which can be potentially used in the discovery of new custom-designed materials.

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References

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