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Solvothermal Synthesis of a Stable Coordination Polymer with Copper-I−Copper-II Dimer Units: $[Cu_4\{1,4\text{-}C_6H_4(COO)_2\}_3(4,4'\text{-bipy})_2]_n$

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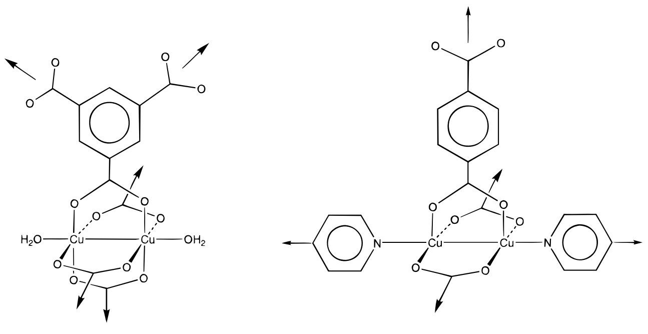
Metal coordination polymer chemistry is a growing field, its exploration driven in part by the search for novel magnetic materials[1,2] as well as for new microporous phases[3] and catalysts[4] which are complementary to zeolites. Recently, we reported the solvothermal synthesis of a highly porous yet stable coordination polymer from copper ions and trimesic acid $[Cu_3\{1,3,5\text{-}C_6H_3\text{-}(COO)_3\}_2(H_2O)_3]_n$, **1**.[5] Central to the stability of **1** is the structural rigidity of its $[Cu_2(\mu\text{-}O_2CR)_4L_2]$ dimer units (Figure 1). A recent report by Japanese workers of a related sorption polymer $[Cu\text{-}\{1,4\text{-}C_6H_4(COO)_2\}(H_2O)_x]_n$,[6] prompted us to explore the solvothermal chemistry of the copper terephthalate system.

Herein we report that under solvothermal or hydrothermal conditions, reaction of copper(II) nitrate, terephthalic acid, and 4,4′-bipyridine[7] results in the formation of an air-stable, open-framework coordination polymer with mixed-valence $[Cu_2]^{3+}$ dimer subunits, $[Cu_4\{1,4\text{-}C_6H_4(COO)_2\}_3(4,4'\text{-bipy})_2]_n$, **2**. We believe that the polymer represents the trapping through "supramolecular precipitation" of the unstable Cu(I)−Cu(II) dimers which are produced under the reducing conditions prevalent in the reaction media at high temperatures.

Compound **2** is formed phase-pure as small dark-blue blocks of ~100 μm dimension in ~65% yield from a solvothermal reaction (180 °C, 1 day) of $[Cu(NO_3)_2]\cdot H_2O$, $[1,4\text{-}C_6H_4(COOH)_2]$ and [4,4′-bipy] of 1:1:1 ratio in 50% aqueous ethanol. Larger crystal specimens up to 1 mm are formed, although in much reduced yield (~20% of the isolated solids) from a parallel hydrothermal reaction with copper sulfate. The dark coloration suggested a rather novel structure for **2** which was confirmed by single-crystal diffraction.[8]

Rather than the expected "paddle-wheel" arrangement of four bridging carboxylates, found in **1**, an open-framework polymer containing dimeric $[Cu_2(\mu\text{-}O_2CR)_3L_2]$ units with only three carboxylate bridges is found in compound **2**. (Figure 2) Once the framework atoms had been refined, difference Fourier maps revealed no peaks of chemical significance, residual electron density maxima and minima were +0.92/−0.97 e Å^{-3}, both less than 1 Å from Cu. The necessity to charge balance the ligands in **2**, indicate that the metals have a mixed Cu(I)−Cu(II) formulation. Other structural evidence for this comes from the unusually short Cu−Cu separation of 2.442(1) Å. This is consistent with the majority of $[Cu_2]^{3+}$ complexes determined previously,[9−11] which also have short "bonds".[12] Furthermore the bond valence sums indicate equivalence of the Cu centers and a delocalized 1.5+ "oxidation state" for each site.[13]



1 **2**

Figure 1. Connectivity diagrams for coordination polymers **1** and **2**.

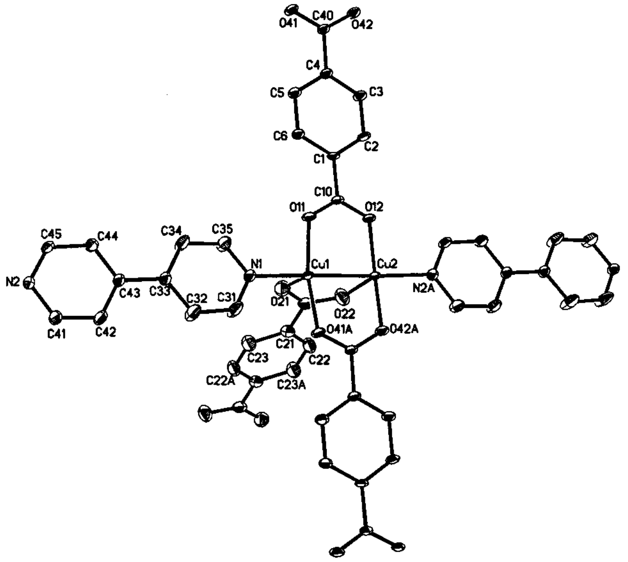


Figure 2. Thermal probability ellipsoid (40%) for **2**.

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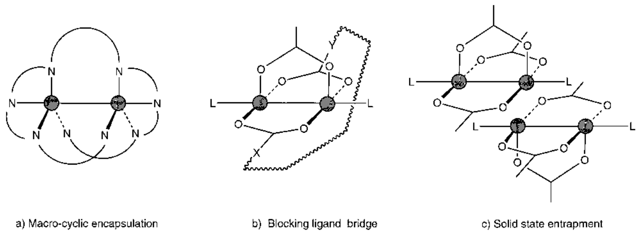

a) Macro-cyclic encapsulation b) Blocking ligand bridge c) Solid state entrapment

Figure 3. Kinetic stabilization for mixed valence Cu(I)−Cu(II) dimers. (a) $[Cu_2(\text{'}N_8\text{'})]^{3+}$ refs 9 and 10, (b) $[Cu_2(O_2CR)_3L_2]$ ref 11, (c) compound **2**.

Mixed-valence Cu(I)−Cu(II) chemistry is of importance to certain metallo-enzyme systems, such as cytochrome *c* oxidase and nitrous oxide reductase. These contain Cu_A centers which are fully delocalized $[Cu_2]^{3+}$ dimers (class III) bridged by cysteine units.[14] Two approaches to forming stable model complexes containing class III centers may be contrasted with formation of **2**. The first involves encapsulation by multidentate amine ligands, such as the nonoazacryptands.(Figure 3a)[9,10] More recently, Lippard et al. have reported $[Cu_2(XDK)(O_2CCF_3)(THF)_2]$ a complex with tri-carboxylate bridges, whereby one side of the dimer is sterically blocked from completing its coordination sphere (Figure 3b).[11] In both of the above cases the metal dimer core is inaccessible to further ligand attack. In **2** this “kinetic” stabilization comes about from the entrapment of the dimer units within the body of the coordination polymer crystal.

Other physical studies on **2** also support its novel mixed-valence formulation. In keeping with the strong absorptions found for other $[Cu_2]^{3+}$ dimers,[9−11] the diffuse reflectance UV−vis spectrum for **2** (dilution to 0.1% w/w with NaCl) shows broad intense absorption throughout the entire visible−near-IR region. The only notable window lies between 400 and 500 nm, which accounts for the dark blue color of the solid. Final and conclusive evidence for the electronic structure of **2** comes from study of its temperature-dependent magnetic susceptibility.[15] At 6.5 kOe (0.65 T) a plot of $1/\chi$ versus T obeys the Curie−Weiss Law, $[\chi = C/(T - \Theta)]$ showing **2** to be paramagnetic between 4 and 300 K. The value of the magnetic moment is calculated to be 1.73 μ_B per $[Cu_2]$ formula unit, consistent with one unpaired electron per dimer. The Weiss constant Θ is close to zero and thus indicates little coupling between the $S = {}^1/_2$ spins through the 4,4′-bipyridine linkers.[16]

The formation of **2** has two key aspects, reduction of Cu^{2+} and polymer crystallization. At high-temperature both the ethanol solvent and the 4,4′-bipyridine base may serve as effective reducing agents for Cu(II) to Cu(I). In the reaction to form **1**, which involved trimesic acid and Cu^{2+}, we showed that use of 50% aqueous ethanol at 180 °C for 1−2 days, produced particulates of copper metal along with the product microcrystals. The extent of this deposition increased with time. In the solvothermal reaction of terephthalic acid and Cu^{2+} no bulk Cu was formed, presumably since reduced copper species become incorporated into crystals of **2**. Ethanol is thus an effective agent for the reduction of the Cu(II) though is not essential to the process. The quantitative formation of the polymer $[Cu^IBr(4,4'\text{-bipy})]$ by Li and co-workers[17] from hydrothermal reaction of copper(II)bromide and excess 4,4′-bipyridine, conclusively shows that the latter can also provide the reducing power necessary to form Cu(I).

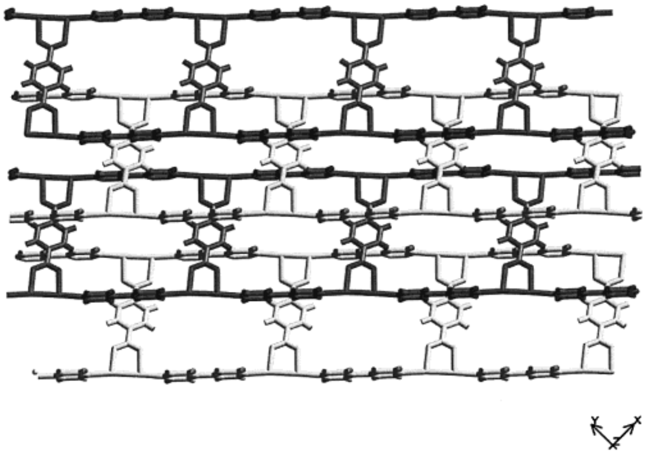

Figure 4. Packing diagram for **2** along [001] showing interpenetrating polymer networks.

Crystallization of **2** follows the formation of individual $[Cu_2]^{3+}$ dimers. Due to the multifunctional nature of the terephthalate and 4,4′-bipyridine ligands these dimers will start to aggregate in solution and, upon reaching a critical size, precipitate and serve to template further crystal growth. Both the reductive formation of the $[Cu_2]^{3+}$ units and their polymerization to **2** occur at high temperature. No crystals of **2** are found when the reagents are heated to 180 °C for 1 h and cooled to room temperature.

The overall packing in **2** is shown in Figure 4. The crystal structure, like many open-framework metal coordination polymers, involves interpenetration of one molecular assembly with another.[18] These pack efficiently together in space and hence as the crystals grow results in the “solid state” entrapment of the Cu(I)−Cu(II) dimers. A remarkable feature of the structure is that $[Cu_2]$ dimers of neighboring chains are in van der Waals contact with each other (Cu(1)- - -Cu(1)′ = 3.98 Å), with no intervening atoms. The solid has little porosity, and there are no guest solvent molecules in the crystal. Furthermore, the ligands are stable and rigid; thus, there is no simple kinetic pathway for decomposition of **2**.[19]

In this instance the entrapment of the $[Cu_2]^{3+}$ species does not appear to have resulted in any novel cooperative magnetic properties in the polymer. However, the formation of **2** implies other molecular magnetic systems with unusual or unstable REDOX states[20] might be accessed through similar in-situ “trapping” within kinetically stable solids.

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Supporting Information Available: Tables and figures (PDF). A crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) EHMO studies have been carried out on a model complex of **2**. These are in general agreement with those in refs 10a and 11.

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