

## Solvothermal Synthesis of a Stable Coordination Polymer with Copper-I–Copper-II Dimer Units: $[\text{Cu}_4\{1,4\text{-C}_6\text{H}_4(\text{COO})_2\}_3(4,4'\text{-bipy})_2]_n$

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Metal coordination polymer chemistry is a growing field, its exploration driven in part by the search for novel magnetic materials<sup>1,2</sup> as well as for new microporous phases<sup>3</sup> and catalysts<sup>4</sup> 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  $[\text{Cu}_3\{1,3,5\text{-C}_6\text{H}_3(\text{COO})_3\}_2(\text{H}_2\text{O})_3]_n$ , **1**.<sup>5</sup> Central to the stability of **1** is the structural rigidity of its  $[\text{Cu}_2(\mu\text{-O}_2\text{CR})_4\text{L}_2]$  dimer units (Figure 1). A recent report by Japanese workers of a related sorption polymer  $[\text{Cu}\{1,4\text{-C}_6\text{H}_4(\text{COO})_2\}(\text{H}_2\text{O})_x]_n$ ,<sup>6</sup> 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<sup>7</sup> results in the formation of an air-stable, open-framework coordination polymer with mixed-valence  $[\text{Cu}_2]^{3+}$  dimer subunits,  $[\text{Cu}_4\{1,4\text{-C}_6\text{H}_4(\text{COO})_2\}_3(4,4'\text{-bipy})_2]_n$ , **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  $\sim 100\ \mu\text{m}$  dimension in  $\sim 65\%$  yield from a solvothermal reaction (180 °C, 1 day) of  $[\text{Cu}(\text{NO}_3)_2]\cdot\text{H}_2\text{O}$ ,  $[1,4\text{-C}_6\text{H}_4(\text{COOH})_2]$  and  $[4,4'\text{-bipy}]$  of 1:1:1 ratio in 50% aqueous ethanol. Larger crystal specimens up to 1 mm are formed, although in much reduced yield ( $\sim 20\%$  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.<sup>8</sup>

Rather than the expected "paddle-wheel" arrangement of four bridging carboxylates, found in **1**, an open-framework polymer containing dimeric  $[\text{Cu}_2(\mu\text{-O}_2\text{CR})_3\text{L}_2]$  units with only three carboxylate bridges is found in compound **2**. (Figure 2) Once

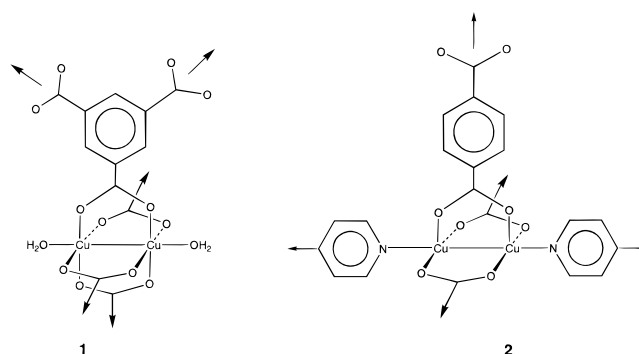


Figure 1. Connectivity diagrams for coordination polymers **1** and **2**.

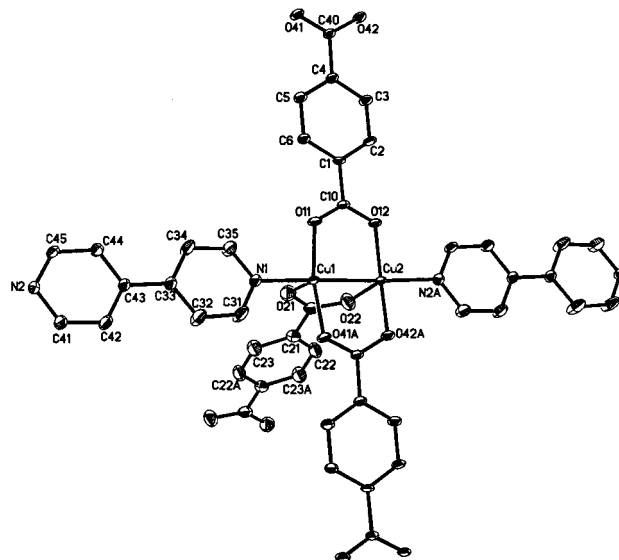


Figure 2. Thermal probability ellipsoid (40%) for **2**.

the framework atoms had been refined, difference Fourier maps revealed no peaks of chemical significance, residual electron density maxima and minima were  $+0.92/-0.97\ \text{e}\ \text{\AA}^{-3}$ , both less than  $1\ \text{\AA}$  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  $[\text{Cu}_2]^{3+}$  complexes determined previously,<sup>9–11</sup> which also have short "bonds".<sup>12</sup> Furthermore the bond valence sums indicate equivalence of the Cu centers and a delocalized 1.5+ "oxidation state" for each site.<sup>13</sup>

(8) Crystal data for **2**:  $\text{C}_{22}\text{H}_{14}\text{Cu}_2\text{N}_2\text{O}_6$  dark-blue block, size  $1.2 \times 1.0 \times 0.8\ \text{mm}^3$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.024(3)\ \text{\AA}$ ,  $b = 10.220(3)\ \text{\AA}$ ,  $c = 10.727(4)\ \text{\AA}$ ,  $\alpha = 74.42(3)^\circ$ ,  $\beta = 74.58(2)^\circ$ ,  $\gamma = 84.77(3)^\circ$ ,  $U = 1020.2(6)\ \text{\AA}^3$ ,  $2\theta_{\text{max}} = 55^\circ$ , Mo K $\alpha$  radiation ( $\lambda = 0.7107\ \text{\AA}$ )  $D_c = 1.72\ \text{g cm}^{-3}$  for  $Z = 2$ ;  $R = 0.041$ ,  $wR_2 = 0.103$  GOF = 1.05, for 4674 data collected with a Bruker-Axis P4-RA. Refinement using SHELX97 (Sheldrick, G. M., U. Göttingen, 1997). Anal. Calcd for  $\text{C}_{22}\text{H}_{14}\text{Cu}_2\text{N}_2\text{O}_6$  C, 49.91; H, 2.65; N, 5.29. Found C, 49.19; H, 2.65; N, 5.48%.

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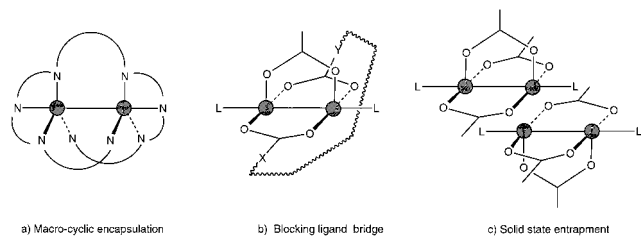
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**Figure 3.** Kinetic stabilization for mixed valence Cu(I)–Cu(II) dimers. (a)  $[\text{Cu}_2(\text{N}_8)]^{3+}$  refs 9 and 10, (b)  $[\text{Cu}_2(\text{O}_2\text{CR})_3\text{L}_2]$  ref 11, (c) compound **2**.

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  $\text{Cu}_A$  centers which are fully delocalized  $[\text{Cu}_2]^{3+}$  dimers (class III) bridged by cysteine units.<sup>14</sup> 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)<sup>9,10</sup> More recently, Lippard et al. have reported  $[\text{Cu}_2(\text{XDK})(\text{O}_2\text{CCF}_3)(\text{THF})_2]$  a complex with tri-carboxylate bridges, whereby one side of the dimer is sterically blocked from completing its coordination sphere (Figure 3b).<sup>11</sup> 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  $[\text{Cu}_2]^{3+}$  dimers,<sup>9–11</sup> 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.<sup>15</sup> 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  $1.73 \mu_B$  per  $[\text{Cu}_2]$  formula unit, consistent with one unpaired electron per dimer. The Weiss constant  $\Theta$  is close to zero and thus indicates little coupling between the  $S = 1/2$  spins through the 4,4′-bipyridine linkers.<sup>16</sup>

The formation of **2** has two key aspects, reduction of  $\text{Cu}^{2+}$  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  $\text{Cu}^{2+}$ , 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  $\text{Cu}^{2+}$  no bulk Cu was formed, presumably since reduced copper species become incorporated into crystals of **2**. Ethanol is thus an effective agent

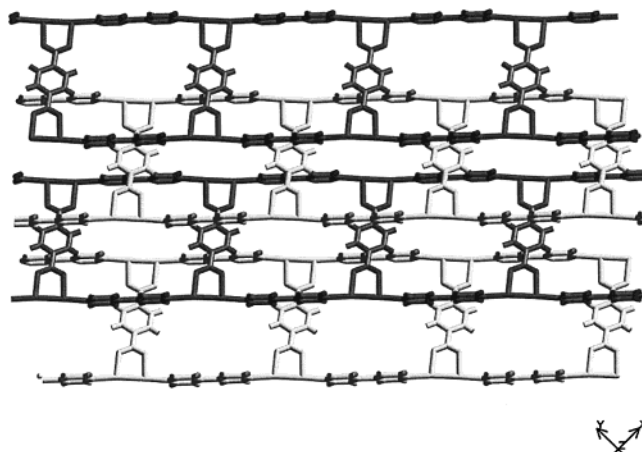
(12) EHM studies have been carried out on a model complex of **2**. These are in general agreement with those in refs 10a and 11.

(13) Using the program ValList, the Cu(I) and Cu(II) crystallographic sites give 46/54 and 49/51% compositions of Cu(I)/Cu(II), respectively. Wills, A. S.; Brown, I. D. *ValList*, Commissariat à l’Energie Atomique, France 1999. Program available from author at willsas@netscape.net.

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(15) Temperature-dependent magnetic susceptibilities were measured on a Quantum Design MPMS-5 SQUID magnetometer from 4 to 300 K at fields of 0.1 to 2.0 T.

(16) This contrasts with compound **1** which shows weak ferromagnetic interaction between its dimers: Zhang, X. X.; Chui, S. S.–Y.; Williams, I. D. *J. Appl. Phys.* **2000**, *87*, 6007–6009.



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

for the reduction of the Cu(II) though is not essential to the process. The quantitative formation of the polymer  $[\text{Cu}^{\text{I}}\text{Br}(4,4'\text{-bipy})]$  by Li and co-workers<sup>17</sup> 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).

Crystallization of **2** follows the formation of individual  $[\text{Cu}_2]^{3+}$  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  $[\text{Cu}_2]^{3+}$  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.<sup>18</sup> 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  $[\text{Cu}_2]$  dimers of neighboring chains are in van der Waals contact with each other ( $\text{Cu}(1) \cdots \text{Cu}(1') = 3.98 \text{ \AA}$ ), 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**.<sup>19</sup>

In this instance the entrapment of the  $[\text{Cu}_2]^{3+}$  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<sup>20</sup> 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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