

Biphasic Solvothermal Synthesis: A New Approach for Hybrid Inorganic–Organic Materials

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Received October 28, 2001

Hybrid inorganic–organic materials, which may incorporate functionality from both their inorganic and organic components, have become a major research theme in materials science. Examples include surfactant micelles incorporated into mesoporous silicates,¹ organic template molecules in aluminosilicate zeolites² and open-framework metal phosphates,³ and surfactant monolayers used in the synthesis of nanoparticles⁴ and optical band-gap materials.⁵ We describe below a novel method for the synthesis of such materials, whereby reactions are carried out under biphasic solvothermal conditions. Our approach is illustrated with an application to an open-framework metal dicarboxylate, copper adipate: $\text{Cu}_3(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2(\text{C}_6\text{H}_{11}\text{OH})$.

The majority of the metal organic frameworks reported to date have been synthesized using solution methods under bench-top conditions (20–80 °C, 1 atm). Hydrothermal synthesis⁶ is less commonly used, but it has the attraction that it favors condensation of M–OH into M–O–M bonds,⁷ allowing the preparation of materials with multidimensional metal–oxygen frameworks. Recognizing that most metal salts are preferentially soluble in polar solvents, for example, water, and that the opposite is true for many organic reactants, we have utilized a higher temperature, biphasic solvothermal method that appears advantageous for synthesizing many classes of hybrid materials. Reaction at the interface of two immiscible solvents is a common technique for crystallizing compounds at low to moderate temperatures (<100 °C)⁸ and is commonly used to prepare hybrid inorganic–organic materials, in addition to other products. The use of biphasic solvothermal synthesis has a number of attractions that will be discussed below. To our knowledge, the only previous example of a related approach is the use of a biphasic solvothermal synthesis for SAPO-5, which used micelles to slow the hydrolysis of TEOS and control the rate of its crystallization.⁹

As an example of the biphasic synthesis approach, we have synthesized green single crystals of a remarkable copper adipate framework. Our preparation employs copper acetate dissolved in water as a mildly basic Cu^{2+} source, with adipic acid dissolved in an alcohol (typically 1-pentanol or cyclohexanol) layered above.¹⁰ These conditions, which are equivalent to approximately pH 4 in pure water, result in a mixture of two phases, one containing $\text{Cu}_3(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2(\text{C}_6\text{H}_{11}\text{OH})$ in green dendritic clusters plus an unidentified blue-green phase. After thorough inspection of several batches, we located a very small crystal for X-ray structural analysis.¹¹ Control reactions carried out in water and cyclohexanol, respectively, resulted in entirely different (and polycrystalline) products.

The structure of the green phase is based on a dimer unit first observed in the copper acetate structure¹² and common through copper carboxylate chemistry. The structure (Figure 1) contains two distinct motifs. In the first, each of the four dicarboxylates on the dimer bridge to a different dimer, resulting in a two-dimensional (2D) sheet, while in the second, pairs of dicarboxylate molecules bridge to adjacent dimers, resulting in a one-dimensional (1D) chain. In the three-dimensional structure, whose composition is $\text{Cu}_3(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2(\text{C}_6\text{H}_{11}\text{OH})$, 1D chains are stacked between 2D layers, with no connectivity except for van der Waals interactions (Figure 1b). To our knowledge, this is the first example of any compound where extended building units of different dimensionalities coexist in the same structure. Figure 2 illustrates the chains, where Cu(1) is separated from a crystallographically identical Cu(1) by 2.600(3) Å and one crystallographically independent adipate molecule bridges these dimers. The fifth ligand is an oxygen atom, and the proximity of a well-refined carbon atom at 1.467 Å indicates that a cyclohexanol molecule is coordinated to this site. The cyclohexanol molecule is heavily disordered, and the disordered carbon atoms have been omitted from the figures for clarity. The 2D sheets (Figure 3) are based on one independent dimer in which Cu[2] and Cu[3] are separated by 2.610(4) Å.

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(10) In a typical synthesis, 0.295 g of $\text{Cu}(\text{ac})_2 \cdot \text{H}_2\text{O}$ (Aldrich) was dissolved in 5.0 mL of H_2O in a Teflon liner; 0.250 g of adipic acid (Aldrich) was dissolved in 4.0 g of cyclohexanol (Aldrich) and carefully layered above the aqueous solution. The liner was sealed in a Parr autoclave and heated to 120 °C for 2 days and then cooled in air and the product was separated by filtration.

(11) Crystal data, $\text{Cu}_3(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2(\text{C}_6\text{H}_{11}\text{OH})$, crystal size, approximately $60 \times 40 \times 40 \mu\text{m}$; space group $P2_1/c$, $a = 8.792(2)$ Å, $b = 24.576(6)$ Å, $c = 13.768(3)$ Å, $\beta = 92.078(5)^\circ$, $U = 2972.9(1)$, $Z = 4$, $D_c = 1.790 \text{ Mg/m}^3$, $\text{GoF} = 0.779$, $wR2 = 0.1532$ for all data, $R1 = 0.0583$ for 1474 $F_o > 4\sigma(F_o)$ for 360 parameters. Because of the small crystal size, only 10 309 reflections above 1.0 Å resolution were used, of which 3106 were unique. Data collection was performed on a Siemens SMART CCD diffractometer with Mo K α radiation (0.71073 Å) at room temperature. Lorentz and polarization corrections were made, the structure was solved using direct methods, and the data were refined against $|F^2|$ using the SHELXTL suite. All non-hydrogen atoms were refined anisotropically except one carbon atom, which was refined isotropically. Hydrogen atoms were not refined because of the low number of reflections relative to parameters. 50% occupied C atoms were used to model the disordered cyclohexanol between the chains in the structure.

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(8) For a recent illustration, see Biradha, K.; Fujita, M. *J. Chem. Soc., Dalton Trans.* **2000**, 3805.

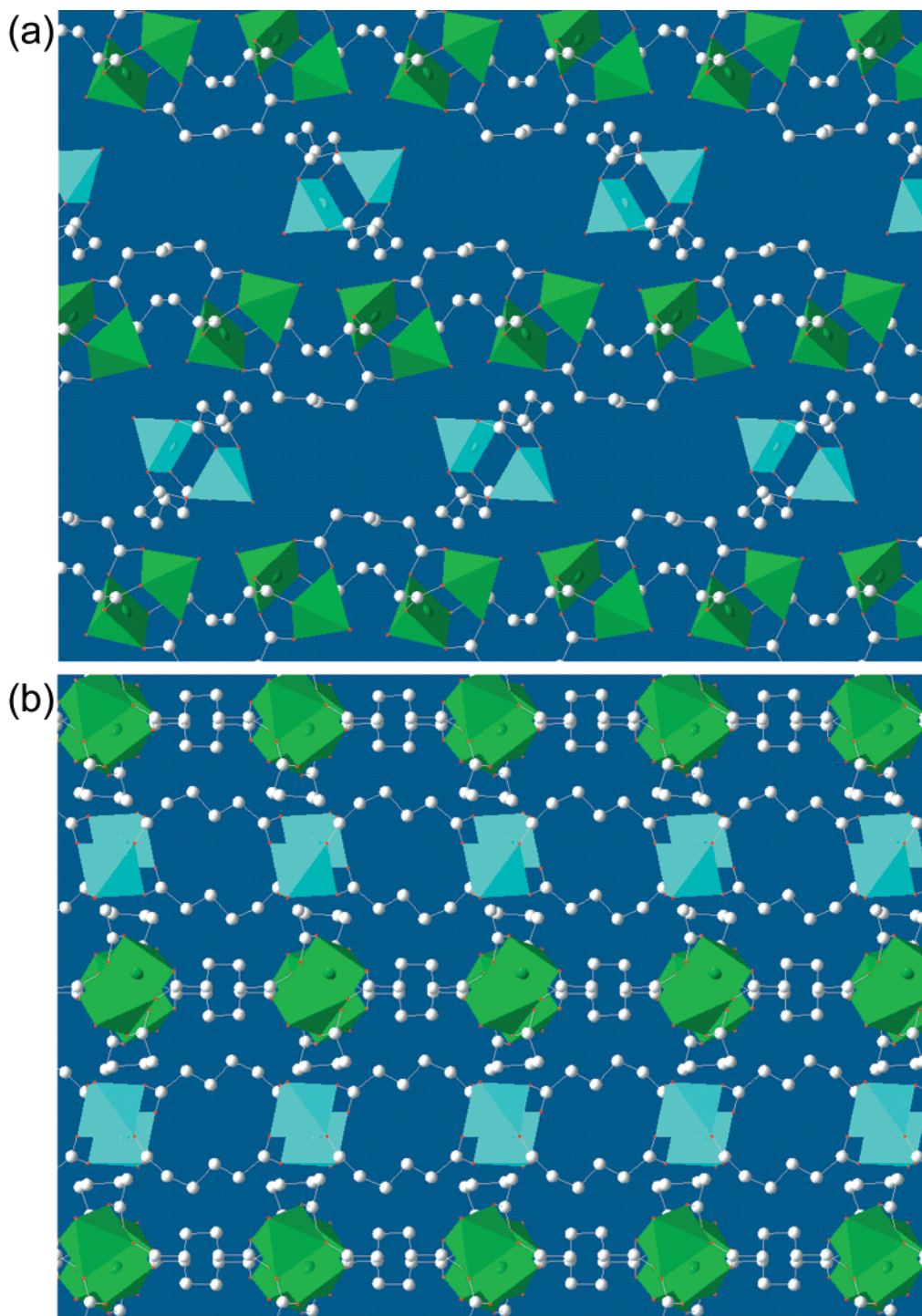


Figure 1. The structure of copper adipate, showing neutral chains (light green polyhedra) where two adipate units link adjacent dimers, and neutral sheets (dark green polyhedra) where each of the four adipate moieties link to separate dimers. Carbon atoms are shown in white. Figure 1a displays the structure along the *a* axis and 1b along the *c* axis.

Unlike the 1D chains, water is clearly the fifth ligand for these dimers. Two crystallographically distinct adipate molecules are involved in bridging the dimers. One is relatively flat and parallel to the sheet, while the second curves above (and below) the sheet, partially occupying space between the 1D chains (Figure 1b).

We have confirmed that the biphasic condition is sustained at high temperatures by viewing the reaction in a modified oven with a glass window in its door. The reaction was carried out, as described above, but in a glass vessel with Teflon screw tops, and visual observa-

tion of the reaction provides some insight into the course of the reaction. The green phase forms first at the interface between the two solvents; then, soon after, a blue-green product forms in the aqueous layer. Over time, the green phase disappears completely and is replaced by the blue-green phase. On the basis of this, we believe that the green product is a metastable phase that is later replaced by a more stable structure.

These visual observations, together with crystal structure, of the reaction suggest a unique mechanism of formation of the copper adipate. We hypothesize that

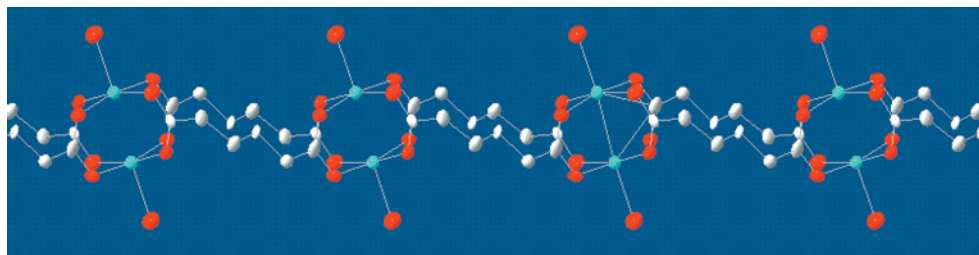


Figure 2. A single 1D chain, with Cu^{2+} in blue, carbon in white, and oxygen in red. The terminal oxygen ligand is an alcoholic oxygen from a disordered cyclohexanol molecule.

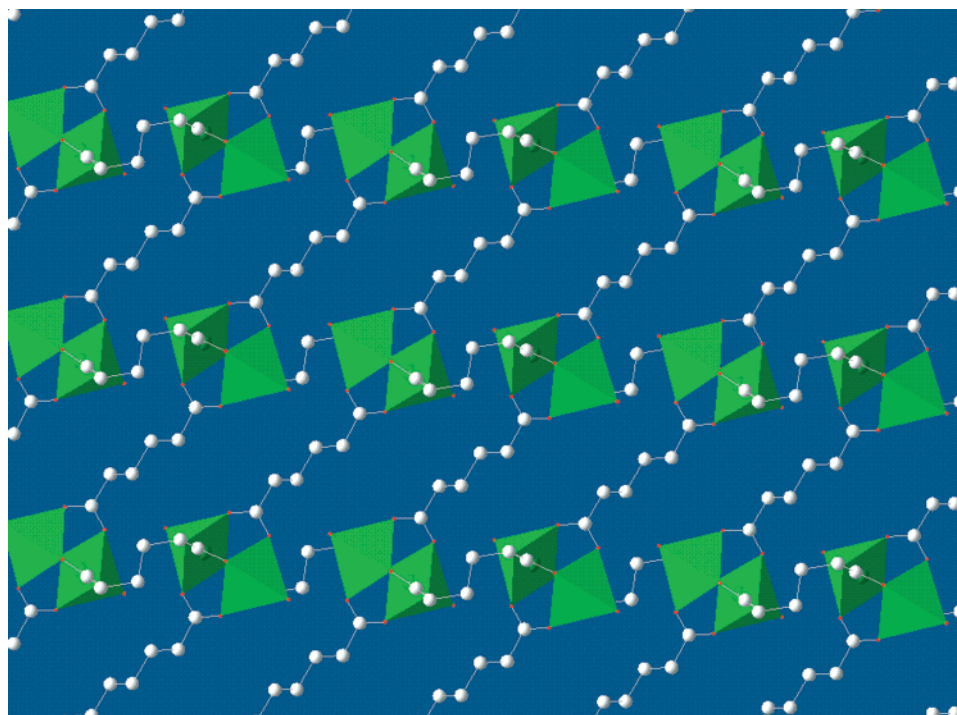


Figure 3. A plan view of the 2D sheet. Green polyhedra have been added around the Cu^{2+} centers for clarity.

1D chain molecules are present in the cyclohexanol phase, while molecular species resembling 2D sheets are present in the aqueous phase. This is supported by the presence of cyclohexanol bound to the 1D chains and water bound to the 2D sheets. The presence of both species at the interface allows nucleation of this phase. According to this hypothesis, the green compound can only form under biphasic conditions. The lack of any comparable compounds in the literature supports this conclusion.

Biphasic synthesis offers several advantages over conventional hydro-/solvothermal methods. In the case of the copper carboxylates, for example, we can avoid reduction of the copper by the carboxylic acid; this often results in the formation of copper metal or Cu_2O . Indeed, most Cu(II) -based organic polymers have been prepared at lower temperatures, but few hydrothermally.¹³ These are normally synthesized under basic conditions, and some reduction normally occurs. When biphasic synthesis is used, however, Cu(II) carboxylates form readily for most carboxylic acids,¹⁴ even under

acidic conditions, because the organic reactant is primarily in a different phase from the metal ions. We have also grown single crystals of several compounds where conventional methods yield only powders, including a novel phase of nickel succinate,¹⁵ as well as several related compounds.¹⁶ The nickel systems we have investigated are different in that the reactions only become thermodynamically favorable at elevated temperatures.¹⁷

In addition to the facile formation of single crystals and the ability to work with reducible cations, we believe that the method will also offer other advantages, such as the possibility of working with organic reactants that are unstable in hydrothermal conditions. We are also examining the generality of our approach by extending it to other systems. Natural extensions include metal amine coordination frameworks, metal organosulfur compounds, metal phosphonates and sul-

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(17) In the case of several nickel carboxylate compounds, we started from initially clear solutions and visually verified formation of product. Then, we observed complete dissolution of the product to yield a clear solution at room temperature over several weeks in the sealed reaction vessel. This observation proves the reaction is thermodynamically unfavorable at room temperature, rather than simply kinetically slow.

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(14) We encounter difficulty only for acids that are highly water soluble.

fonates, and more complex systems containing multiple metals or bridging molecules.

Acknowledgment. This work was supported by the MRSEC Program of the National Science Foundation under Award DMR00-80034. We also thank B. A. Adair,

T. Loiseau, X. Bu, R. Ahroon, M. C. Grossel, and P. Batail for valuable discussions and J. Doyle for modifications to a laboratory oven. P.M.F. gratefully acknowledges a fellowship from Rockwell.

CM010820Q