Solid state coordination chemistry of the copper cyanide–organoamine system: hydrothermal syntheses and structural characterization of [{$Cu_2(bpy)_2(CN)$}$Cu_5(CN)_6$] and [$Cu_4(CN)_4$(biquin)]

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The hydrothermal reactions of CuCN and $Cu(NO_3)_2 \cdot 2.5H_2O$ with the appropriate organonitrogen ligand in water yielded a one-dimensional chain, [$Cu_4(CN)_4$(biquin)] 1, and a material with a two-dimensional anionic honeycomb network and interpenetrating binuclear cations, [{$Cu_2(bpy)_2(CN)$}$Cu_5(CN)_6$] 2.

The contemporary interest in solid state inorganic materials reflects their properties, which endow these materials with applications ranging from heavy construction to microcircuitry.[1] A powerful synthetic approach for the manipulation of the microstructures of solid state inorganic materials exploits the incorporation of organic components, which contribute to the increased complexity as one constituent in a hierarchical structure exhibiting a synergistic interaction between the organic and inorganic substructures.[2,3] Organic materials have been demonstrated to play an important role in five subclasses of the oxide family of materials: zeolites,[4] mesoporous oxides of the MCM-41 type,[5] biomineralized materials,[6] microporous octahedral–tetrahedral framework transition metal phosphates[7] and organically templated molybdenum oxides.[8] We have recently extended this concept of templating anionic inorganic networks with organic constituents to the copper halide system, as represented by [{$Cu(en)_2$}$_2Cu_7Cl_{11}$].[9] The rich supramolecular chemistry of the metal derivatives of the pseudohalide cyanide[10] encouraged us to expand our investigations to the copper–cyanide–organoamine family of materials, exploiting the bridging cyano ligand as a rigid tether in the propagation of Cu^I geometry in solid state materials. These studies have resulted in a variety of one- and two-dimensional materials of which [$Cu_4(CN)_4$(biquin)] **1** and [{$Cu_2(bpy)_2(CN)$}$Cu_5(CN)_6$] **2** are representative (biquin = 2,2′-biquinoline; bpy = 2,2′-bipyridine).

Compound **1** was prepared as yellow–orange crystals in *ca.* 15–25% yield from the reaction of CuCN, $Cu(NO_3)_2 \cdot 2.5H_2O$, 2,2′-biquinoline and H_2O in the mole ratio 4.2 : 0.99 : 1.0 : 280 at 170 °C for 86.5 h. Compound **2** was prepared as light orange crystals in *ca.* 35% yield in a similar fashion from the reaction of CuCN, $Cu(NO_3)_2 \cdot 2.5H_2O$, 2,2′-bipyridine and water in the mole ratio 6.3 : 1.0 : 1.0 : 290. Compound **1** cocrystallized with a red phase, identified as [$Cu_2(CN)_2$(biquin)], while compound **2** cocrystallized with bright red crystals of [Cu(CN)(bpy)].[11] Curiously, the preparation of **1** and **2** in crystalline form and reasonable yields requires the presence of a Cu^{II} precursor. We have noted previously[12] that organoamines function as reducing agents in hydrothermal reactions, perhaps serving to generate a repository of reduced metal species for further aggregation. Optimization of yields may be accomplished by employing an excess of organonitrogen ligand to Cu^{II} precursor.

As shown in Fig. 1, the structure of **1**‡ exhibits a backbone constructed from a zigzag chain of two-coordinate {$Cu(CN)_2$} sites and three-coordinate {$Cu(CN)_3$} sites, with {Cu_2(CN)(biquin)} groups projecting from the chain. The Cu–CN backbone and its attendant side chains are nearly planar with the best plane parallel to the 101 crystallographic plane.

While Cu–CN chain structures have been reported,[13] the greater structural complexity of **1** derives from the presence of the biquinoline ligand, which may serve to passivate the copper chain with respect to extension in two or three dimensions.

The structure of **2**† consists of sheets of fused 36-membered puckered honeycomb rings interpenetrated by [$(bipyCu)_2CN$]$^+$ cations, shown in Fig. 2. The rings are composed of two nearly linear {$Cu(CN)_2$} sites, four ‘bent’ {$Cu(CN)_2$} moieties and six {$Cu(CN)_3$} distorted trigonal planar sites which serve as junctions between adjacent rings. As illustrated by the view of Fig. 3, each ring is interpenetrated by two space-filling and charge compensating [$Cu_2(bpy)_2(CN)$]$^+$ cations at an oblique angle to the {Cu(CN)Cu} axis of the cation with respect to the face of the ring. The honeycomb layers are offset along the stacking axis *b*, so as to generate channels of approximate dimensions 5.4 × 9.0 Å occupied by the cations (Fig. 4). Each cation interpenetrates rings from two adjacent layers, which are separated by 3.5 Å. While two-dimensional Cu–CN networks have been observed for [$Cu_3(en)_2(CN)_4$]$\cdot 6H_2O$[14] and K[$Cu_2(CN)_3$]$\cdot H_2O$,[15] the layers are constructed from significantly smaller 15 and 18 membered rings.

The structures of **1** and **2** demonstrate the power of hydrothermal synthesis in the preparation of organic–inorganic composite materials. Not only are differential solubility problems avoided, reducing the tendency to phase segregate, but structurally more complex metastable phases are favored.[16] The structural complexity, in general, reflects the versatility of the organonitrogen component which may function as counterion,

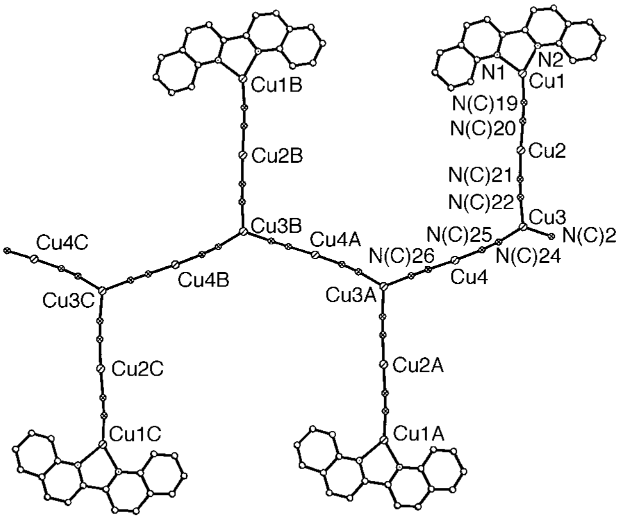

Fig. 1 A view of the structure of **1**. Selected bond lengths (Å) and angles (°): Cu1–N1 2.03(1), Cu1–N2 2.01(1), Cu1–N(C)19 1.84(2), Cu2–N(C)20 1.84(1), Cu2–N(C)21 1.85(2), Cu3–N(C)22 1.93(1), Cu3–N(C)23 1.91(2), Cu3–N(C)24 1.86(2), Cu4–N(C)25 1.84(2), Cu4–N(C)26 1.84(2), N1–Cu1–N2 81.3(5), N1–Cu1–N(C)19 130.6(7), N(2)–Cu1–N(C)19 147.5(7), N(C)20–Cu2–N(C)21 174.0(6), N(C)22–Cu3–N(C)24 118.4(6), N(C)22–Cu3–N(C)23 113.7(6), N(C)23–Cu3–N(C)24 128.0(6), N(C)25–Cu4–N(C)26 175.1(6).

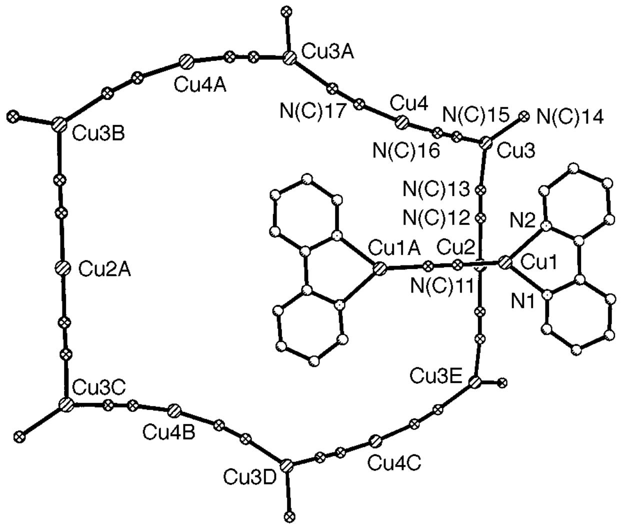

Fig. 2 A view of the honeycomb anionic network of **2** and of the location of the $[Cu_2(bipy)_2CN]^+$ cations. Selected bond lengths (Å) and angles (°): Cu1–N1 2.026(6), Cu1–N2 2.054(7), Cu1–N(C)11 1.846(7), Cu2–N(C)12 1.865(9), Cu3–N(C)13 1.994(8), Cu3–N(C)14 1.907(9), Cu(3)–N(C)15 1.924(8), Cu4–N(C)16 1.863(9), Cu4–N(C)17 1.843(7), N1–Cu1–N2 81.1(3), N1–Cu1–N(C)11 139.8(3), N2–Cu1–N(C)11 136.5(3), N(C)12–Cu2–N(C)12A 180.000(2), N(C)13–Cu3–N(C)14 116.6(3), N(C)13–Cu3–N(C)15 111.4(3), N(C)14–Cu3–N(C)15 130.1(4), N(C)16–Cu4–N(C)17 161.6(4).

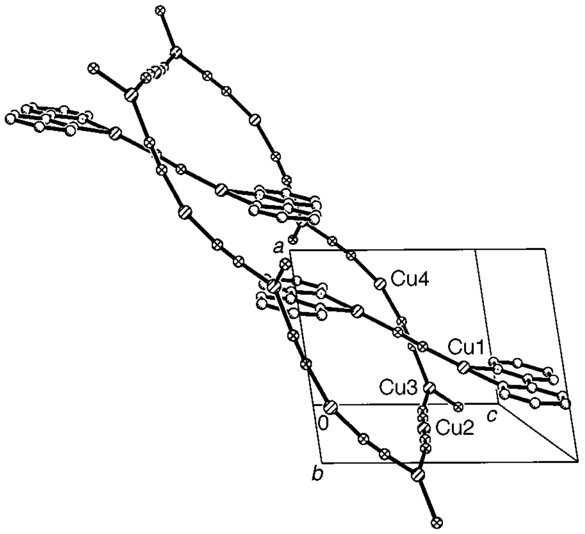

Fig. 3 A view of the interpenetration of a $\{Cu_{12}(CN)_{12}\}$ ring by two $[Cu_2(bipy)_2(CN)]^{1+}$ cations

ligand to the copper cyanide backbone or ligand in a coordination complex anion. In its role as ligand, the biquinoline in **1** serves to passivate the copper so as to prevent extension of the structure in more than one dimension. The increased hydrophobicity of biquinoline relative to bipyridine may result in the larger nonpolar domains localized in the interstrand regions. The role of the organic ligand as a component of a coordination complex cation, a recurring theme in metal oxide–organoamine chemistry,[17] appears to extend to the metal–halide and metal–psuedohalide phases. The large ring sizes of the copper cyanide networks of **2** are required to accommodate the large binuclear cations, suggesting that cation size in such structures may be a determinant not of interlamellar spacing but of ring topology and channel dimensions. We are investigating the roles of coordination complex cations of various sizes and shapes in defining the structures of metal halide and metal pseudohalide phases.

This work was supported by NSF Grant CHE9617232.

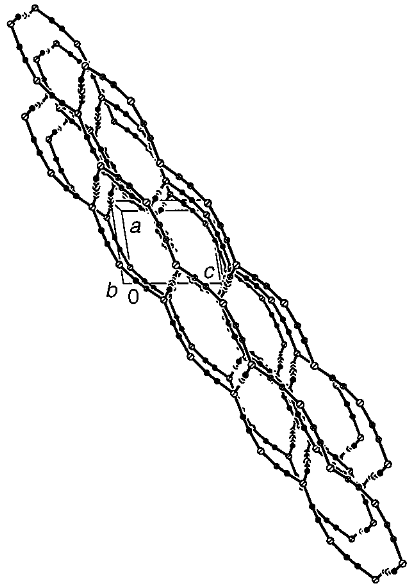

Fig. 4 A view down the crystallographic *b*-axis of the channels formed by offsetting of honeycomb layers in **2**

Notes and References

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‡ *Crystal data*: for **1**: $C_{22}H_{12}Cu_4N_6$, monoclinic, space group $P2_1/c$, a = 7.3947(7), b = 18.041(2), c = 16.002(1) Å, β = 98.550(2)°, V = 2111.1(3) Å^3, Z = 4, M_w = 614.54, D_c = 1.934 mg m^{-3}, T = 293(2) K, μ = 39.98 cm^{-1} (Mo-Kα, λ = 0.71073 Å), R_1 = 0.0866; wR_2 = 0.1770 (3626 reflections, all collected).

For **2**: $C_{27}H_{16}Cu_7N_{11}$, monoclinic, space group $P2_1/c$, a = 7.2422(2), b = 24.2930(2), c = 8.6645(2) Å, β = 98.742(1)°, V = 1506.68(6) Å^3, Z = 4, M_w = 939.28, D_c = 2.070 mg m^{-3}, T = 293(2) K, μ = 48.84 cm^{-1} (Mo-Kα, λ = 0.71073 Å), R_1 = 0.0590; wR_2 = 0.1223 (2653 reflections). CCDC 182/934.

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Received in Columbia, MO, USA, 7th April 1998; 8/02641F