Network Structures

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Interpenetrating Copper–Silver Cyanometallate Networks: Polymorphs and Topological Isomers[**]

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Transition-metal cyanides have a long and fascinating history and exhibit a diverse and interesting range of chemical and physical properties leading to technological applications.[1] Many complex cyanometallate can be viewed as supramolecular compounds[2,3] constructed from $M(CN)_x$ structural building blocks that have independent existence. These include simple ions, for example, square planar $[Ni(CN)_4]^{2-}$ and octahedral $[Fe(CN)_6]^{4-}$, but can also include larger

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fragments, for example, -{CuCN}- chains. Such units are relatively robust, have well-defined topology and geometry, and can be assembled in at least a semirational manner to form new solids by combining with themselves, other complex metal ions, or organic species such as amines to generate 1-, 2-, and 3-dimensional frameworks.[2,4,5]

We have been investigating the use of CuCN, both as a source of infinite -{CuCN}- chains and as a precursor to other Cu^I cyano species, for use as alternative structural building blocks in the construction of new cyanide complexes. We have found that monatomic species, such as halide ions, are capable of producing new zeolitic and interpenetrating frameworks when alkali-metal halides and CuCN react under modest conditions.[6,7] Urban et al. recently achieved similar results using silver cyanide and cesium halides.[8] An extension of this approach is to replace the halides, which form bridges between copper–cyanide building units, with complex cyanide anions in the hope of producing framework materials with larger pore sizes. We selected $[Ag(CN)_2]^-$ as a bridging unit because it has been successfully used in the past to link other metal ions, for example, Mn^{II} and Cd^{II}, into 3D networks.[2,9,10] Employing $[Ag(CN)_2]^-$ has the additional attraction of providing a synthetic route to mixed Cu^I/Ag^I cyanides, which, despite the similarity in the chemistry of copper and silver in the +1 oxidation state, surprisingly remained unknown before this work. The Cu^I/Ag^I cyanide materials have the formula $A[Ag_2Cu(CN)_4]$ (A = K, Rb, Cs) and contain remarkable interpenetrating anionic networks assembled from $\{Cu(CN)_4\}^{3-}$ and $\{Ag(CN)_2\}^-$ units. These units are connected in different ways in the Rb and Cs compounds to produce two-dimensional (form I) and three-dimensional (form II) networks of the same formula. These materials challenge our views of what constitutes and distinguishes polymorphs and topological isomers.

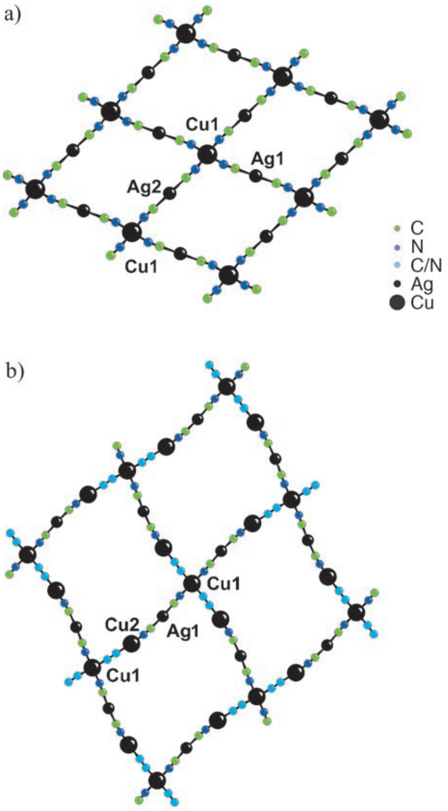

Figure 1. Portions of the sheets derived from a (4,4)-connected net for a) $A[Ag_2Cu(CN)_4]$ (form I, A = K, Rb, Cs) and b) $A[Ag_2Cu(CN)_4]$ (form II, A = Rb, Cs). The bridging cyanide groups bond through the carbon atom to silver, but are disordered when they bridge Cu(1) and Cu(2) atoms in (b).

Reaction of excess $K[Ag(CN)_2]$ with CuCN under hydrothermal conditions produced single crystals of $K[Ag_2Cu(CN)_4]$ (**1**, form I).[11] This material can also be made at room temperature by adding an aqueous solution of $K_3[Cu(CN)_4]$ to $AgNO_3$ in a 1:2 molar ratio. The Rb and Cs analogues $Rb[Ag_2Cu(CN)_4]$ (**2**, form I) and $Cs[Ag_2Cu(CN)_4]$ (**3**, form I) were also produced in hydrothermal reactions, but in each case, a second form, $Rb[Ag_2Cu(CN)_4]$ (**4**, form II) and $Cs[Ag_2Cu(CN)_4]$ (**5**, form II), predominated.[11]

Although form I of $A[Ag_2Cu(CN)_4]$ (**1**–**3**) has a two-dimensional network, and form II (**4**, **5**) a three-dimensional network, a good starting point for describing the structures is to view them both as derived from a (4,4)-connected net. Figure 1 shows the two different sheets found in these forms, both of which have this connectivity. Copper atoms are located at the 4-connected nodes in both forms.

In form I, all the copper atoms are identical and are linked by almost-linear bridging -{NC-Ag-CN}- units. In form II, there are two types of copper atoms: one type (Cu(1)) occurs at the nodes of the (4,4)-connected net and the second (Cu(2)) occurs within the -{NC-Cu(2)-NC-Ag(1)-CN}- unit that links the Cu(1) nodes. As a consequence of the tetrahedral coordination around the copper center, the sheets in both forms I and II are buckled. Neither of the resulting sheets fills the space very efficiently, and the structures formed from isolated sheets of these types, if they could be produced, would have very large free volumes. This situation is not the case in these materials. Instead, further copies of the sheets occupy the space (Figure 2). In form I, the structure consists of AAA-stacked layers of three identical interpenetrating sheets. In form II, four sheets can interpenetrate because the longer internode linkers (-{NC-Cu(2)-NC-Ag(1)-CN}- units) produce a larger mesh size than that found in form I. Figure 3 shows two layers formed from these interpenetrating sheets and clearly shows the buckling of the layers for each compound. In form I, the layers are sufficiently close together that the potassium ions within the layers also interact with cyanide groups in neighboring layers. The layers in form II, which stack in an ABAB pattern, are well separated, but, in contrast to form I, there are coordinatively unsaturated copper atoms on the outside of the layers. These Cu(2) atoms complete their tetrahedral coordination by forming bonds to two -{NC-Ag(2)-CN-Ag(3)-CN}- units external to the sheet. These units link sheets in adjacent layers to form a three-dimensional framework consisting of four identical interpenetrating networks. As in form I, the alkali-metal cations lie within the layers of buckled sheets.

Threefold parallel interpenetration of (4,4)-connected nets to form layers, as observed in form I, is very rare for coordinatively bonded networks[16,17] and this is the first

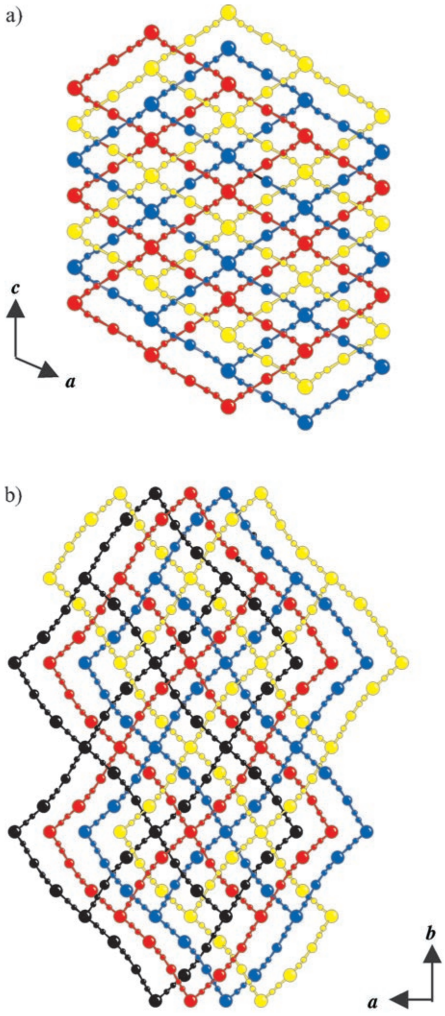

Figure 2. Layers derived from parallel interpenetration of a) three of the sheets shown in Figure 1 a) for $A[Ag_2Cu(CN)_4]$ (form I) and b) four of the sheets shown in Figure 1 b) for $A[Ag_2Cu(CN)_4]$ (form II). The different independent networks are shown in black, red, blue, and yellow.

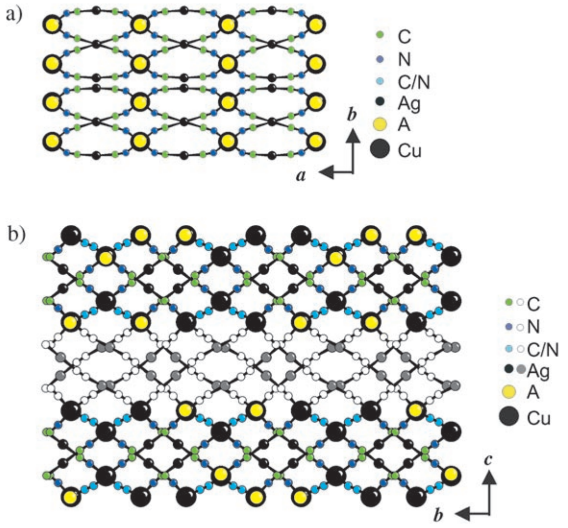

Figure 3. Side view showing the buckled sheets in a) $A[Ag_2Cu(CN)_4]$ (form I) forming a layered structure and b) $A[Ag_2Cu(CN)_4]$ (form II) forming a three-dimensional structure. The open and gray circles in (b) correspond to -{NC-Ag(2)-CN-Ag(3)-CN}- units that interlink the layers shown in Figure 2 b) to form the 3D structure containing four independent networks.

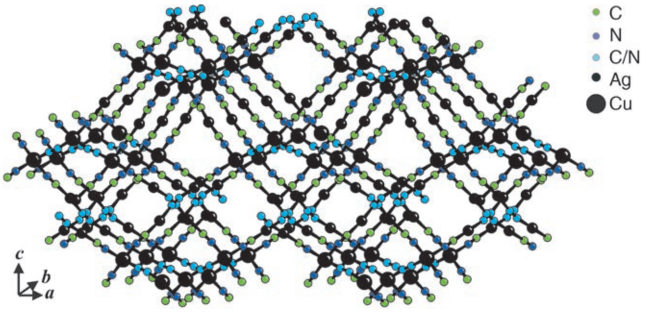

Figure 4. View of a single network found in $A[Ag_2Cu(CN)_4]$ (form II) showing self interpenetration.

totally inorganic example. Previous examples all have organic spacers between the metal centers at the nodes.[18–20] Form II, according to the recent classification of interpenetrating 3D networks by Blatov and co-workers,[21,22] belongs to Class Ia, which means that the four identical three-dimensional networks are related by simple translations ([1/2, 1/2, 1/2] (19.26 Å) and the symmetry-related operations). The 3D network found in form II[23] is, to the best of our knowledge, of a previously unknown type.[17,24,25] Moreover, this new network is self-penetrating (Figure 4) as rings containing six and eight copper atoms catenate within the structure. Interpenetration of self-penetrating networks is a rare combination[26] and, as is observed here, can lead to very complicated entangled structures.

It is remarkable that compounds of $A[Ag_2Cu(CN)_4]$ (A = Rb and Cs) form two distinct types of interpenetrating solid. These exceptional materials are true topological isomers because not only do they have frameworks of the same composition constructed from the same units, but their overall compositions are also identical. Most quoted examples of topological isomerism found in supramolecular chemistry involve the inclusion of different guest molecules, typically the solvent used in preparation,[27] and the overall compositions of the related compounds are therefore different. As the compositions of forms I and II are identical, and both are extended solids, they can also be classified as polymorphs according to the normal usage of that term.

Our experiments show that form II is the thermodynamically more stable phase of $Cs[Ag_2Cu(CN)_4]$ both under hydrothermal conditions and at atmospheric pressure at 300 K. Form I is the kinetically favored product, being formed immediately upon reaction between solutions containing A^+ (A = K and Cs), $Cu(CN)_4^{3-}$, and Ag^+, and also it appears as a minor phase in shorter hydrothermal reactions. It is interesting that $K[Ag_2Cu(CN)_4]$ has only been found in form I and does not convert to a form II analogue even on prolonged hydrothermal reaction. A further illustration of the thermodynamic stability of Cs[$Ag_2Cu(CN)_4$] (form II) is that it can be formed by stirring a polycrystalline sample of K[$Ag_2Cu(CN)_4$] in an aqueous solution of $CsNO_3$.

In summary, the first family of Cu^I/Ag^I cyanides has been prepared. The compounds of general formula A[$Ag_2Cu(CN)_4$] (A = K, Rb and Cs) form curious interpenetrating two- and three-dimensional networks, the latter of which is also self penetrating. The two forms of the Rb and Cs compounds are both topological isomers and polymorphs. Further work will include analysis of the correlation between the uniaxial negative thermal expansion and the contraction of this axis upon increasing radius of the alkali-metal cation in all these materials. We are also attempting the preparation of A[$M_2M'(CN)_4$] materials using other metals.

Experimental Section

K[$Ag_2Cu(CN)_4$] (**1**, form I): Colorless rectangular plates[11] (IR: $\tilde{\nu} = \nu$(CN) 2135(vs), 2120(vs) cm^{-1}) were obtained by heating CuCN (0.09 g, 1 mmol) with K[$Ag(CN)_2$] (1.39 g, 7 mmol) in H_2O (5 mL) in a teflon-lined autoclave at 453 K for 24 h and could be easily separated from a fernlike growth of metallic silver. A polycrystalline sample of **1** was prepared at 300 K by adding a solution of K_3[$Cu(CN)_4$] (1.42 g, 5 mmol) in H_2O (5 mL) to $AgNO_3$ (1.75 g, 10 mmol) dissolved in H_2O (5 mL). A dark-gray precipitate formed immediately. In contrast, addition of the $AgNO_3$ solution to the K_3[$Cu(CN)_4$] solution resulted in significant contamination by AgCN.

Rb[$Ag_2Cu(CN)_4$] (**2**, form I and **4**, form II): Hydrothermal reaction of CuCN (0.09 g, 1 mmol), NaCN (0.15 g, 3 mmol), $RbNO_3$ (0.44 g, 3 mmol), and $AgNO_3$ (0.34 g, 2 mmol) in H_2O (5 mL) at 413 K for 3 days produced a mixture of colorless crystals—a majority of rectangular needles (**4**) and a minority of rectangular blocks (**2**)—which were easily separated for diffraction studies.[11]

Polycrystalline **2** was prepared at 300 K by adding $RbNO_3$ (0.44 g, 3 mmol) to a solution of Na_3[$Cu(CN)_4$] (0.24 g, 1 mmol) in H_2O (2.5 mL). The resulting solution was then added to a solution of $AgNO_3$ (0.34 g, 2 mmol) in H_2O (2.5 mL) and a gray precipitate formed immediately. Compound **2** was the major component, together with a significant amount of AgCN. Allowing the precipitate to sit in the mother liquor at room temperature for 14 days led to the growth of single crystals of **2** (IR: $\tilde{\nu} = \nu$(CN) 2130(s), 2110(vs), 2089(s) cm^{-1}). Compound **4** was not produced in either room temperature reaction.

Cs[$Ag_2Cu(CN)_4$] (**3**, form I and **5**, form II): Hydrothermal reaction of CuCN (0.23 g, 2.5 mmol), KCN (0.49 g, 7.5 mmol) $CsNO_3$ (1.46 g, 7.5 mmol), and $AgNO_3$ (0.85 g, 5 mmol) in H_2O (10 mL) at 413 K for 3 days produced colorless needles of **5** (IR: $\tilde{\nu} = \nu$(CN) 2168(vs), 2139(vs), 2115(vs), 2094(vs) cm^{-1}) as the major phase, together with a small quantity of colorless rectangular blocks of **3** (IR: $\tilde{\nu} = \nu$(CN) 2136(vs), 2114(vs), 2091(s) cm^{-1}).[11] Heating an identical mixture for 8 days produced a pure sample of **5**. Polycrystalline **3** was prepared at 300 K by adding $CsNO_3$ (1.46 g, 7.5 mmol) to K_3[$Cu(CN)_4$] (1.42 g, 5 mmol) in H_2O (5 mL). The resulting solution was then added to $AgNO_3$ (0.85 g, 5 mmol) in H_2O (5 mL) and a gray precipitate formed immediately. Compound **3** was the major component, together with a small amount of AgCN. There was no evidence for the formation of **5** in this reaction.

Reactions of K[$Ag_2Cu(CN)_4$] (**1**, form I): Stirring **1** (0.30 g, 0.70 mmol) in a solution of $CsNO_3$ (0.68 g, 3.5 mmol) in H_2O (5 mL) for 9 days at 300 K produced a change in the [$Ag_2Cu(CN)_4$]$^-$ framework to give Cs[$Ag_2Cu(CN)_4$] (**5**, form II) as the major phase, together with small amounts of AgCN and Ag. The original [$Ag_2Cu(CN)_4$]$^-$ framework was, however, retained in a similar reaction in which $CsNO_3$ was replaced by KNO_3 (0.35 g, 3.5 mmol), although again some degradation to form AgCN occurred.

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