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Helices, Chirality and Interpenetration: the Versatility and Remarkable Interconversion of Silver−Copper Cyanide Frameworks

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Abstract: The structural transformations between cesium silver−copper cyanides under modest conditions, both in solution and in the solid state, are described. Three new cesium silver(I) copper(I) cyanides with three-dimensional (3-D) framework structures were prepared as single crystals from a one-pot reaction initially heated under hydrothermal conditions. The first product to appear, $Cs_3Ag_2Cu_3(CN)_8$ (**I**), when left in contact with the supernatant produced $CsAgCu(CN)_3$ (**II**) and $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**) over a few months *via* a series of thermodynamically controlled cascade reactions. Crystals of the hydrate (**III**) can be dehydrated to polycrystalline $CsAgCu(CN)_3$ (**II**) on heating at 100 °C in a remarkable solid-state transformation involving substantial breaking and reconnection of metal−cyanide linkages. Astonishingly, the conversion between the two known polymorphs of $CsAg_2Cu(CN)_4$, which also involves a major change in connectivity and topology, occurs at 180 °C as a single-crystal to single-crystal transformation. Structural features of note in these materials include the presence of helical copper−cyanide chains in (**I**) and (**II**), which in the latter compound produce a chiral material. In (**II**) and (**III**), the silver−copper cyanide networks are both self- and interpenetrating, features also seen in the known polymorphs of $CsAg_2Cu(CN)_4$.

Introduction

There has been a renaissance in the study of transition-metal−cyanide framework materials[1] many of which have potentially useful applications. These include oligonuclear compounds with interesting magnetic and redox behavior,[1a−d] and extended solids, including supramolecular compounds,[1c,e,f] which may exhibit porosity.[1g,h] All such materials can be viewed as constructed from $M(CN)_x^{n-}$ units. For example, the Prussian-Blue type materials, much studied because of their NTE behavior[2] and possible applications in gas storage,[3] are constructed from octahedral $M(CN)_6^{n-}$ units linked by corner sharing into expanded ReO_3 structures. Other possible primary $M(CN)_x^{n-}$ units available for framework construction include trigonal-planar $M(CN)_3^{n-}$ and square-planar $M(CN)_4^{n-}$ units which can fuse to form sheets, e.g. in $KCu_2(CN)_3 \cdot H_2O$[4,5] and $Ni(CN)_2 \cdot 3/2H_2O$,[6] respectively, and tetrahedral $M(CN)_4^{n-}$ units, which can produce three-dimensional (3-D) diamond-like structures, e.g., $Zn(CN)_2$[7] and $Cd(CN)_2$,[8] which contain two interpenetrating networks. Interestingly, a second, low-density polymorph of $Cd(CN)_2$ has recently been prepared consisting of a single diamondoid network.[9]

One unit that might initially appear unpromising as a precursor to 3-D structures is the infinite −{M−CN}− chain that is present in CuCN (LT-[10] and HT-[11]), AgCN[12] and AuCN.[13] However, these chains, which can be regarded as secondary building units, can be linked into frameworks using neutral bridging ligands, such as diamines, or anionic linkers,

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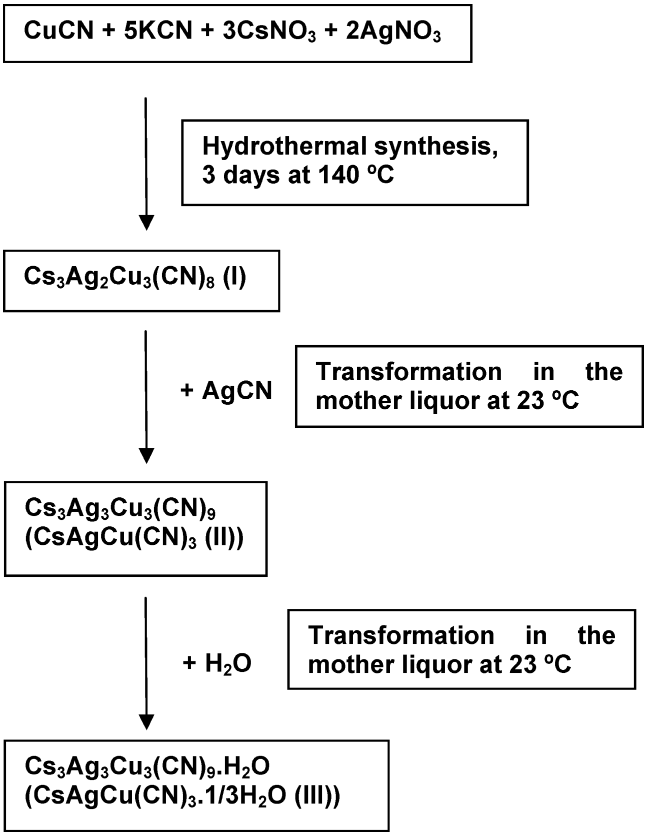
including halides or metal−cyanide groups, e.g., $[Ag(CN)_2]^-$.[1d,14] Another particularly attractive aspect of using chains as building blocks is that the attachment of ligands to the metal atoms in such chains causes the chains to bend and twist and, in certain cases, to form helices from initially achiral units. Isolated 2_1 helices are found in both the well-known compound, $KCu(CN)_2$,[15] and in the halogenocyanometallates, $(R_4N)(Cu(CN)X)$ (R = Et, X = Br,[16] I;[16] R = *n*-Bu, X = Br,[17] I[16,17]) where either terminal cyanide or halide ions attach to each copper in the infinite CuCN chains. In $KCu(CN)_2$[15] and $(Et_4N)(Cu(CN)X)$,[16] equal numbers of left- and right-handed helices occur in the crystals. In the $(Bu_4N)(Cu(CN)X)$ compounds, the bromide[17] and one of the two polymorphs of the iodide[16] spontaneously resolve. Linked helices have also been observed in $CsCu_3(CN)_3X$ (X = Cl, Br)[18] (3_1 helices) and $Cs_5Ag_9(CN)_8Cl_6$[19] (five-fold, 4_1 helices), but in each case, helices of both handedness are present in equal numbers, and the resulting frameworks are not chiral.

It is clear that not only are there many theoretical ways of linking together primary and secondary metal−cyanide units, but that a large number of these are practically attainable. It is interesting to speculate how the different materials may be related not only in structural, but also in thermodynamic and kinetic terms. To gain an insight into such relationships, we have been investigating cesium silver(I)−copper(I) cyanide frameworks and transformations between them. Previously, we have reported the structural characterization of two polymorphs of $CsAg_2Cu(CN)_4$.[20] The polymorphs are both assembled from primary $[Cu(CN)_4]^{3-}$ and $[Ag(CN)_2]^-$ units, but these are linked in different ways to produce three- and four-fold interpenetrating networks, denoted as forms 1 and 2, respectively. In the present work, we show that form 1 can be converted to form 2 on heating at 180 °C in a remarkable single-crystal to single-crystal transformation. In addition, we report the structure determination of three new Cs−Ag−CuCN phases, $Cs_3Ag_2Cu_3(CN)_8$ (**I**), $CsAgCu(CN)_3$ (**II**), and $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**), that appear sequentially from a one pot reaction initially heated under hydrothermal conditions (Scheme 1). Compounds (**I**) and (**II**) contain the same primary $[Cu(CN)_4]^{3-}$ units as found in $CsAg_2Cu(CN)_4$, but linked to form helical CuCN chains as secondary units. This produces, in the case of (**II**), a chiral compound. In $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**), which has the same framework stoichiometry as $CsAgCu(CN)_3$ (**II**), the CuCN chains have been broken and Cu is now found in both 3- and 4-coordination as $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$ units. We were surprised to find that on dehydration at 100 °C, crystals of (**III**) transform to polycrystalline (**II**). This solid-state transformation is amazing considering the large degree of structural reorganization, including bond-breaking and -making required for the interconversion.

Scheme 1. Formation Reactions of Cesium Silver−Copper Cyanides (**I**)−(**III**)



Experimental Section

Synthesis of Single Crystals. All reagents were supplied by Aldrich. Caution: Cyanide materials are toxic and must be handled with care. All syntheses were performed on millimolar scale, and samples were manipulated in a fume hood.

$Cs_3Ag_2Cu_3(CN)_8$ (I). Single crystals of $Cs_3Ag_2Cu_3(CN)_8$ (**I**) appeared when CuCN (0.0892 g, 1 mmol), KCN (0.3253 g, 5 mmol), $AgNO_3$ (0.3398 g, 2 mmol) and $CsNO_3$ (0.5858 g, 3 mmol) were heated in 5 mL of H_2O in an autoclave at 140 °C for 6 days. After this initial step, the product consisted of colorless needles of (**I**) as the major phase, together with a small quantity of unidentified fibrous white material in a colorless solution. A small number of crystals were removed from the autoclave for characterization, and the rest of the mixture was set aside. Infrared spectroscopy was carried out on a single crystal mounted on a KBr disk using an IRBruker Equinox FTIR coupled to a Bruker Scan2Scope microscope and showed ν(CN) 2112 cm^{-1}.

$CsAgCu(CN)_3$ (II). The above mixture was left at room temperature. Over a period of 2−3 months, colorless faceted blocks of (**II**), clearly of distinctly different morphology to that of (**I**), appeared in the mother liquor, and the number of crystals of (**I**) decreased. Single-crystal IR: ν(CN) 2093 cm^{-1}.

$CsAgCu(CN)_3 \cdot 1/3H_2O$ (III). After a further two months, colorless plates of (**III**) appeared in the mother liquor, which remained colorless. Crystals of (**III**) were not found until after the appearance of (**II**). The majority of these crystals were striated parallel to the long axis and clearly distinguishable from (**I**) and (**II**). Single-crystal IR: ν(OH) 3564(w), ν(CN) 2136(s); 2104(s); $\delta(OH_2)$ 1593(s) cm^{-1}.

$CsAg_2Cu(CN)_4$ (Forms 1 and 2). Both polymorphs of $CsAg_2Cu(CN)_4$ were prepared in a single reaction.[20] Hydrothermal

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Table 1. Crystallographic Data for Compounds (**I**), (**II**) and (**III**)

	$Cs_3Ag_2Cu_3(CN)_8$ (I)	$CsAgCu(CN)_3$ (II)	$CsAgCu(CN)_3 \cdot 1/3H_2O$ (III)
formula	$C_{24}Ag_6Cs_9Cu_9N_{24}$	$C_9Ag_3Cs_3Cu_3N_9$	$C_9Ag_3Cs_3Cu_3N_9OH_2$
M_r	3039.68	1147.17	1165.18
crystal habit	colorless needle	colorless block	colorless plate
crystal dimensions/mm^3	0.05 × 0.05 × 0.08	0.10 × 0.10 × 0.10	0.02 × 0.1 × 0.5
crystal system	tetragonal	hexagonal	triclinic
space group	$I4_1/a$ (No. 88)	$P6_122$ (No. 178)	$P\bar{1}$ (No. 2)
T/K	150(2)	150(2)	150(2)
a/Å	29.8146(5)	7.2298(3)	6.9760(1)
b/Å	29.8146(5)	7.2298(3)	10.8809(2)
c/Å	6.9588(1)	24.6254(8)	15.4101(3)
α/deg	90	90	80.1383(8)
β/deg	90	90	85.2979(8)
γ/deg	90	120	86.040(1)
V/Å^3	6185.75(17)	1114.72(7)	1146.74(3)
Z	4	2	2
λ/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	10.136	10.234	9.954
ρ_{calc}/Mg m^{-3}	3.264	3.417	3.374
$R(F)$, $_wR(F)$	0.0380, 0.0469	0.0215, 0.0248	0.0336, 0.0416

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 10 mL H_2O at 140 °C for 3 days produced colorless needles of form 2 (IR: ν(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 form 1 (IR: ν(CN) 2136(vs), 2114(vs), 2091(s) cm^{-1}).

Crystal Structure Determination. Details of the structure determination of $CsAg_2Cu(CN)_4$ (forms 1 and 2) have been reported elsewhere.[20] Crystals of compounds (**I**)−(**III**) were cooled under a stream of nitrogen from 293 to 150 K at a rate of 120 K h^{-1}. Single-crystal X-ray intensity data were collected using a Nonius KappaCCD diffractometer (graphite-monochromated Mo Kα radiation). Data sets were processed using *DENZO*[21] and *SCALEPACK*.[21] Full crystallographic details are given in Table 1. The structures of compounds (**I**)−(**III**) were solved by direct methods using the program *SIR92*[22] and all nonhydrogen atoms located. Subsequent difference Fourier calculations, which enabled the hydrogen atoms of the water molecule in (**III**) to be located, and least-squares refinements on F were carried out using the *CRYSTALS* suite of programs.[23] Compound (**II**) crystallizes in a chiral space group ($P6_122$). The Flack parameter[24] of 0.01(4) derived from the final refinement indicated that the assigned absolute structure was correct.

A frequently occurring problem for cyanide-containing compounds is the determination of the orientation of the C≡N group(s), for which 'head-to-tail' disorder commonly occurs. The problem is exacerbated by the similar X-ray form factors for C and N and the almost identical M−C and M−N bond lengths. In the initial stages of refinement, each C≡N group was modeled as $Z_x{\equiv}Z_y$ with starting values for the occupancies of both Z_x and Z_y set to (0.5C + 0.5N). The site occupancies were then refined subject to the constraints that the total occupancy for each site was 1.00 and the displacement parameters of C and N on the same site were equal. Inspection of the final models, in particular the anisotropic displacement parameters, showed that any difference between Cu−C and Cu−N bond lengths, where C and N partially occupy the same Z site, must be negligible.

All three compounds contain $[Ag(CN)_2]^-$ units linking Cu atoms. In these links, the C≡N groups were found to be fully ordered with carbon bonded to silver, as anticipated chemically. The occupancies of these groups were therefore fixed in subsequent refinements. In $Cs_3Ag_2Cu_3(CN)_8$ (**I**), there are three such ordered C≡N groups bridging Ag and Cu atoms. The occupancies of C and N in the six remaining $Z_x{\equiv}Z_y$ groups bridging Cu atoms were refined and show small but significant preferences for one of the two possible orientations of the C≡N group. In $CsAgCu(CN)_3$ (**II**), there are two distinct C≡N groups, one of which is fully ordered in the $[Ag(CN)_2]^-$ unit, and the other, between Cu atoms, has 0.5C/0.5N occupancy fixed by symmetry. In $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**), there are two silver-containing bridging units, $[Ag(CN)_2]^-$ and $[N{\equiv}C{-}Ag{-}Z{\equiv}Z{-}Ag{-}C{\equiv}N]^-$. In the second unit, the cyanide group which bridges two silver atoms is fully disordered by symmetry, as is one of the three C≡N groups bridging between Cu atoms. The occupancies of the two remaining $Z_x{\equiv}Z_y$ groups bridging Cu atoms refined to values not significantly different from 0.5C/0.5N.

Thermal Interconversions. Thermal interconversions between the cesium silver−copper cyanide phases are summarized in Scheme 2. Heating a sample of $Cs_3Ag_2Cu_3(CN)_8$ (**I**) under nitrogen at 180 °C produced a mixture of solids of which $CsAgCu(CN)_3$ (**II**) and CuCN were identified using powder X-ray diffraction. In the other cases, only a single solid was formed.

Dehydration of $CsAgCu(CN)_3 \cdot 1/3H_2O$ (III) to $CsAgCu(CN)_3$ (II). The formulae for $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**) and $CsAgCu(CN)_3$ (**II**) suggest, misleadingly, that (**III**) is simply the hydrated form of (**II**), whereas in reality they have very different structures with totally different connectivity of their metal−cyanide frameworks. We thought that dehydration of (**III**) might well produce a further form of $CsAgCu(CN)_3$ and first carried out a thermogravimetric experiment to explore this possibility.

Thermogravimetric analysis was performed using a TA Instruments Q50 thermogravimetric analyzer. Approximately 8 mg of hand picked crystals of $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**) were heated under a flow of dry nitrogen over the temperature range 25−200 °C at a heating rate of 5 °C min^{-1} (Figure S1). The observed weight loss of 1.53%, which was complete at 160 °C, is in excellent agreement with that calculated for loss of water (1.55%). A powder X-ray diffraction pattern of the off-white product showed that $CsAgCu(CN)_3$ (**II**) had been formed during the dehydration.

A single crystal of $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**) in the form of a flat plate was dehydrated by heating at 180 °C in air for 2 h. The product retained the morphology of the single crystal. However, an X-ray diffraction pattern, measured at room temperature using an Oxford Diffraction Gemini S Ultra single-crystal CCD diffractometer with a high-intensity Enhanced Ultra Cu Kα radiation source showed that the product was polycrystalline. The powder

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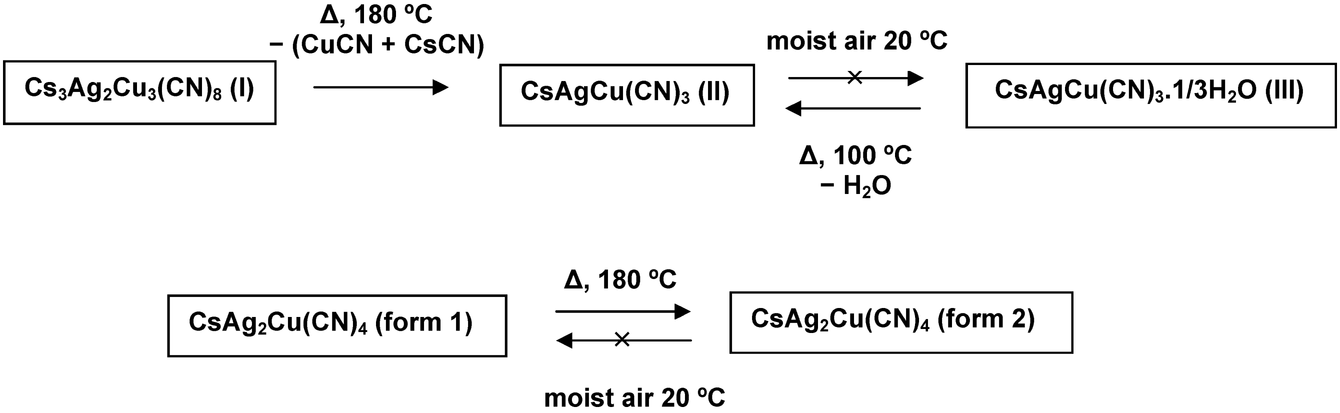

Scheme 2. Thermal Interconversions of (**I**)−(**III**) and $CsAg_2Cu(CN)_4$ (Forms 1 and 2) in the Solid State

diffraction pattern (Figure 1) confirmed that $CsAgCu(CN)_3$ (**II**) had been formed. A subsequent in situ dehydration experiment was performed by heating a crystal of (**III**) mounted on the diffractometer under flowing N_2, and the change in the diffraction pattern was followed as a function of temperature over the range 25−130 °C over a period of 6 h. This experiment showed that the conversion was complete at 130 °C. The sample remained crystalline throughout the reaction with no evidence for the formation of any amorphous or crystalline intermediate. At 110 °C, both the powder rings from $CsAgCu(CN)_3$ (**II**) and the diffraction spots from the $CsAgCu(CN)_3\cdot 1/3H_2O$ (**III**) single crystal coexisted. Ex situ dehydration of $CsAgCu(CN)_3\cdot 1/3H_2O$ (**III**) showed that heating in air at 100 °C for 12 h was sufficient to achieve the conversion. The samples of (**II**) did not rehydrate after leaving them in air at room temperature for more than 6 weeks.

Single Crystal X-ray Diffraction and DSC Studies of the Conversion of $CsAg_2Cu(CN)_4$ Polymorphs (Form 1 to Form 2). A single crystal of $CsAg_2Cu(CN)_4$ (form 1), heated in a stream of nitrogen on the Gemini diffractometer at 180 °C, converted to a single crystal of $CsAg_2Cu(CN)_4$ (form 2) after about 20 min. Similarly, raising $RbAg_2Cu(CN)_4$ (form 1) to 215 °C produced $RbAg_2Cu(CN)_4$ (form 2), but $KAg_2Cu(CN)_4$, for which no form 2 analogue is known,[20] remained unchanged up to 220 °C. Differential scanning calorimetry measurements were performed using a Mettler DSC823 instrument. An amount of 1.8 mg of polycrystalline $CsAg_2Cu(CN)_4$ (form 1) was heated under nitrogen over the temperature range 23−250 °C at a heating rate of 10 °C min^{-1} (Figure S2). An irreversible endothermic reaction was observed over the range 169−182 °C, in good agreement with the temperature of 180 °C measured for the conversion of form 1 to form 2 determined using X-ray diffraction. The corresponding enthalpy change for the conversion is 0.34 kJ mol^{-1}.

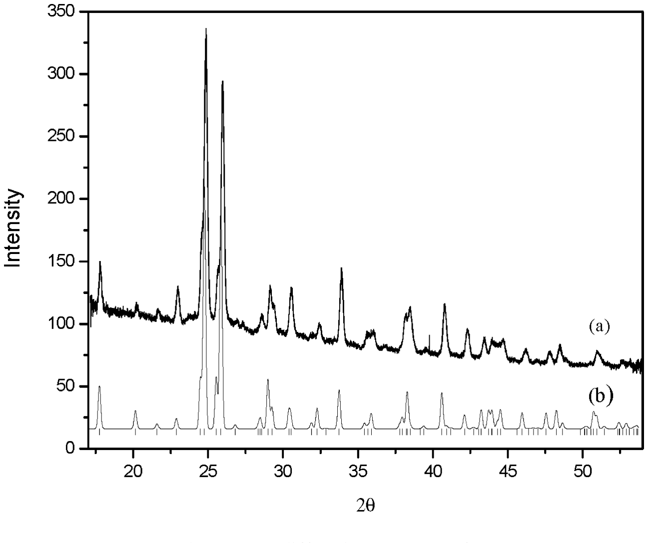

Figure 1. (a) Powder X-ray diffraction pattern of $CsAgCu(CN)_3$ (**II**) prepared by heating a crystal of $CsAgCu(CN)_3\cdot 1/3H_2O$ (**III**) in air at 180 °C which is in good agreement with pattern (b) simulated from single-crystal data for (**II**).

Structural Descriptions. $Cs_3Ag_2Cu_3(CN)_8$ (I) is assembled from Cu(2)CN chains which are twisted into 4_1 helices with a pitch of 6.96 Å. The helices run parallel to the *c* axis, and occur in equal numbers of left- and right-handed forms, alternating along the *a* and *b* directions, rendering the compound achiral (Figure 2). Adjacent helices are linked together *via* $[-N{\equiv}C-Ag(1)-C{\equiv}N-Cu(1)(CN)_2C{\equiv}N-]^{3-}$ units to form a 3-D framework structure. The remaining two cyanide groups on the bridging Cu(1) atom are linked by Ag(2) and Cu(3) atoms producing extra connectivity within the framework. Thus, in this material all the Cu atoms are in tetrahedral coordination, the deviation from regular geometry being greatest for Cu(2) (Table 2). Both Ag atoms are 2-coordinate, and the bond angle around Ag(2) is 180° by symmetry; but around Ag(1), the C−Ag(1)−C angle is reduced to 161.1(2)°, possibly as a result of a metallophilic interaction between Ag(1) and Cu(2). This interpretation is supported not only by the short Ag(1)···Cu(2) distance of 3.268(1) Å but also by the opening up of the Z(5)−Cu(2)−Z(7) angle to 122.1(2)°.

The anionic charge on the framework $[Ag_2Cu_3(CN)_8]^{3-}$ is balanced by Cs cations. A notable feature is that one of the three types of Cs cation, Cs(3), is disordered over four symmetry equivalent sites in the channels down the center of the Cu(2)-based helices. A similar situation has been observed previously in $Cs_5[Ag_4(CN)_4Cl]_2[AgCl_4]$,[19] where five helical AgCN chains are wound together to produce channels in which disordered Cs^+ ions reside. The remaining Cs cations, Cs(1) and Cs(2), are fully ordered in cavities bounded by Cu(1)Cu(2)Cu(3)Ag(1)- and Cu(1)Cu(2)-Ag(1)Ag(2)-containing chains.

$CsAgCu(CN)_3$ (II) is assembled from 6_1 helical Cu(1)CN chains of pitch 24.63 Å running parallel to the *c* axis (Figure 3a) linked by $[-N{\equiv}C-Ag(1)-C{\equiv}N-]^-$ units to form a 3-D anionic network of formula $[AgCu(CN)_3]^-$ in which the Cu(1) atoms are tetrahedrally coordinated. Three such networks of the same handedness interpenetrate (Figure 3b) to produce a chiral material (Figure 3c). In this compound the channels down the center of the helices are occupied by the $[Ag(CN)_2]^-$ bridging units from the other two networks.

The Cu atoms are in tetrahedral coordination, with only the Z(2)−Cu(1)−Z(2) angle of 130.4(2)° differing markedly from the tetrahedral angle (Table 3). This considerable opening of the tetrahedral angle within the chain is necessary to form a 6_1 helix. This geometrical constraint also causes the Cu(1)−Z(2)≡Z(2) angle of

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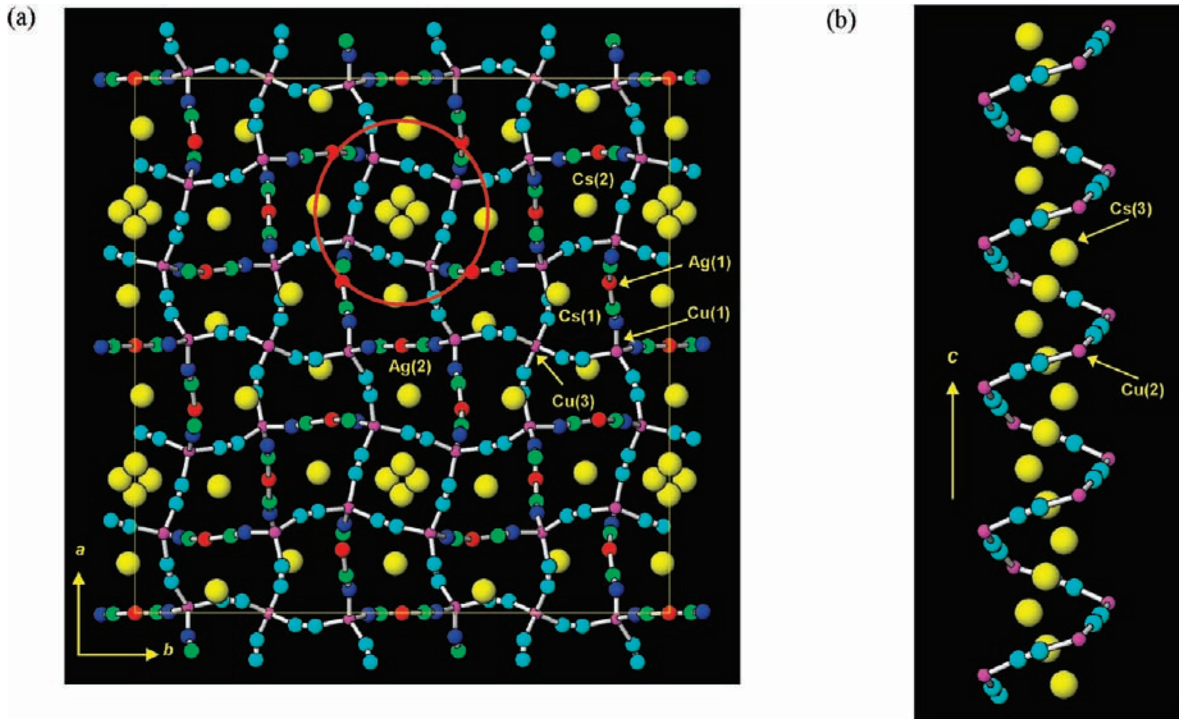

Figure 2. (a) $Cs_3Ag_2Cu_3(CN)_8$ (**I**) viewed down the *c* axis showing −(CuCN)− chains coiled into four-fold helices linked together through $[Cu(CN)_4]^{3-}$ and $[Ag(CN)_2]^-$ units to generate a 3-D framework. Adjacent helices have the opposite handedness. (b) View of four-fold helix, highlighted in the red circle in (a), showing how disordered Cs cations fill the channel running along the helix axis. Key: pink spheres, Cu; red, Ag; green, C; blue, N; cyan, disordered C/N; yellow, Cs. Drawing package: *ATOMS*.[25]

170.5(19)° to deviate significantly from linearity. Cs(1) cations balance the anionic charge on the $[AgCu(CN)_3]^-$ framework.

$CsAgCu(CN)_3 \cdot 1/3H_2O$ (III). In contrast to (**I**) and (**II**), compound (**III**) does not contain extended CuCN chains, but only chainlets containing four copper atoms constructed from two tetrahedral $[Cu(2)(CN)_4]^{3-}$ units terminated by $[Cu(1)(CN)_3]^{2-}$ units (Figure 4). The chainlets are linked together in several ways to form a 3-D network. The Cu(1) atoms are linked by $[Ag(1)_2(CN)_3]^-$ units and Cu(2) atoms linked *via* $[-N{\equiv}C-Ag(4)-C{\equiv}N-Cu(3)(CN)_2C{\equiv}N-]^{3-}$ units. Further cross-linking occurs between the Cu(3) atoms by two $[Ag(CN)_2]^-$ units containing Ag(2) and Ag(3) (Table 4). The structure can be described in terms of three such self-penetrating networks which in turn interpenetrate in parallel (Figure 4c). However, there are additional close contacts (Cu(1)···C(9) 2.412(7) Å) in which the 3-coordinate copper, $[Cu(1)(CN)_3]^{2-}$, interacts with the carbon of a bridging C(9)N(9) group in another network (Figure 4b). Such μ_2 interactions have been reported by others[26] who also note that, in contrast to carbonyls in cyanides, μ_2 interactions are very unsymmetrical with long and short M−C bonds. The anionic framework $[AgCu(CN)_3]^-$ has the same composition as that of (**II**), but a different structure and topology. The charge is again balanced by Cs cations but with water also contained in the cavities. The water molecules are located at 3.209(5) and 3.092(4) Å from Cs(2) and Cs(3), respectively, and are only weakly hydrogen bonded to the framework with four O(1)···N distances in the range 3.208(6)−3.383(6) Å.

Discussion of the Formation and Interconversion of Compounds (I), (II) and (III) and $CsAg_2Cu(CN)_4$ (Forms 1 and 2). Schemes 1 and 2 summarize the formation and thermal interconversion of the three new cesium silver−copper cyanides, respectively. The reactions are remarkable for a number of reasons, and the formation of three compounds with very different structures

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cs_3Ag_2Cu_3(CN)_8$ (**I**)[i]

Bond Distances			
Cu(1)−N(1)	2.029(5)	Ag(1)−C(1)	2.055(6)
Cu(1)−N(2)	1.982(5)	Ag(1)−C(3)	2.067(6)
Cu(1)−Z(4)	2.001(5)	Ag(2)−C(2)	2.071(5)
Cu(1)−Z(9)	1.954(6)	Ag(2)−C(2)[f]	2.071(5)
Cu(2)−N(3)[a]	2.064(5)		
Cu(2)−Z(5)	1.930(6)	C(1)−N(1)	1.141(8)
Cu(2)−Z(6)[b]	2.022(5)	C(2)−N(2)	1.146(8)
Cu(2)−Z(7)	1.947(6)	C(3)−N(3)	1.143(8)
Cu(3)−Z(8)	1.990(6)	Z(4)−Z(5)	1.149(7)
Cu(3)−Z(8)[c]	1.990(6)	Z(6)−Z(7)	1.156(8)
Cu(3)−Z(8)[d]	1.990(6)	Z(8)−Z(9)	1.146(8)
Cu(3)−Z(8)[e]	1.990(6)		
Angles			
N(1)−Cu(1)−N(2)	112.6(2)	Cu(1)−N(1)−C(1)	166.9(5)
N(1)−Cu(1)−Z(4)	105.4(2)	Cu(1)−N(2)−C(2)	173.8(5)
N(2)−Cu(1)−Z(4)	106.7(2)	Cu(2)[g]−N(3)−C(3)	178.0(6)
N(1)−Cu(1)−Z(9)	103.1(2)	Cu(1)−Z(4)−Z(5)	162.9(4)
N(2)−Cu(1)−Z(9)	116.7(2)	Cu(2)−Z(5)−Z(4)	173.4(5)
Z(4)−Cu(1)−Z(9)	111.9(2)	Cu(2)−Z(6)−Z(7)	173.4(5)
N(3)[a]−Cu(2)−Z(5)	105.4(2)	Cu(2)−Z(7)−Z(6)	174.0(5)
N(3)[a]−Cu(2)−Z(6)[b]	100.3(2)	Cu(3)−Z(8)−Z(9)	151.8(5)
Z(5)−Cu(2)−Z(6)[b]	113.6(2)	Cu(1)−Z(9)−Z(8)	164.3(6)
N(3)[a]−Cu(2)−Z(7)	106.2(2)	Ag(1)−C(1)−N(1)	175.9(5)
Z(5)−Cu(2)−Z(7)	122.1(2)	Ag(2)−C(2)−N(2)	178.8(5)
Z(6)[b]−Cu(2)−Z(7)	106.6(2)	Ag(1)−C(3)−N(3)	177.0(6)
Z(8)−Cu(3)−Z(8)[c]	108.96(16)	Cu(1)−Z(4)−Z(5)	162.9(4)
Z(8)−Cu(3)−Z(8)[d]	110.5(3)	Cu(2)−Z(5)−Z(4)	173.4(5)
Z(8)[c]−Cu(3)−Z(8)[d]	108.96(16)	Cu(2)[h]−Z(6)−Z(7)	173.4(5)
N(8)−Cu(3)−N(8)[e]	110.5(3)	Cu(2)[h]−Z(7)−Z(6)	174.0(5)
C(1)−Ag(1)−C(3)	161.1(2)	Cu(3)−Z(8)−Z(9)	151.8(5)
C(2)−Ag(2)−C(2)[f]	180	Cu(1)−Z(9)−Z(8)	164.3(6)

[a] Symmetry codes: 1/4 + *y*, 3/4 − *x*, −1/4 − *z*. [b] *y* − 1/4, 3/4 − *x*, *z* − 1/4. [c] 1/4 + *y*, 3/4 − *x*, 1/2, 7/4-*z*. [d] 1 − *x*, 1/2 − *y*, *z*. [e] 3/4 − *y*, *x* − 1/4, 7/4 − *z*. [f] 1/2 − *x*, 1/2 − *y*, 5/2 − *z*. [g] 3/4 − *y*, *x* − 1/4, −1/4 − *z*. [h] 3/4 − *y*, 1/4 + *x*, 1/4 + *z*. [i] Z = either C or N of disordered cyanide group.

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(26) (a) Zheng, J. M.; Batten, S. R.; Du, M. *Inorg. Chem.* **2005**, *44*, 3371. (b) Pretsch, T.; Brudgam, I.; Hartl, H. Z. *Anorg. Allg. Chem.* **2003**, *629*, 942. (c) Ouyang, L.; Aguiar, P. M.; Batchelor, R. J.; Kroeker, S.; Leznoff, D. B. *Chem. Commun.* **2006**, 744.

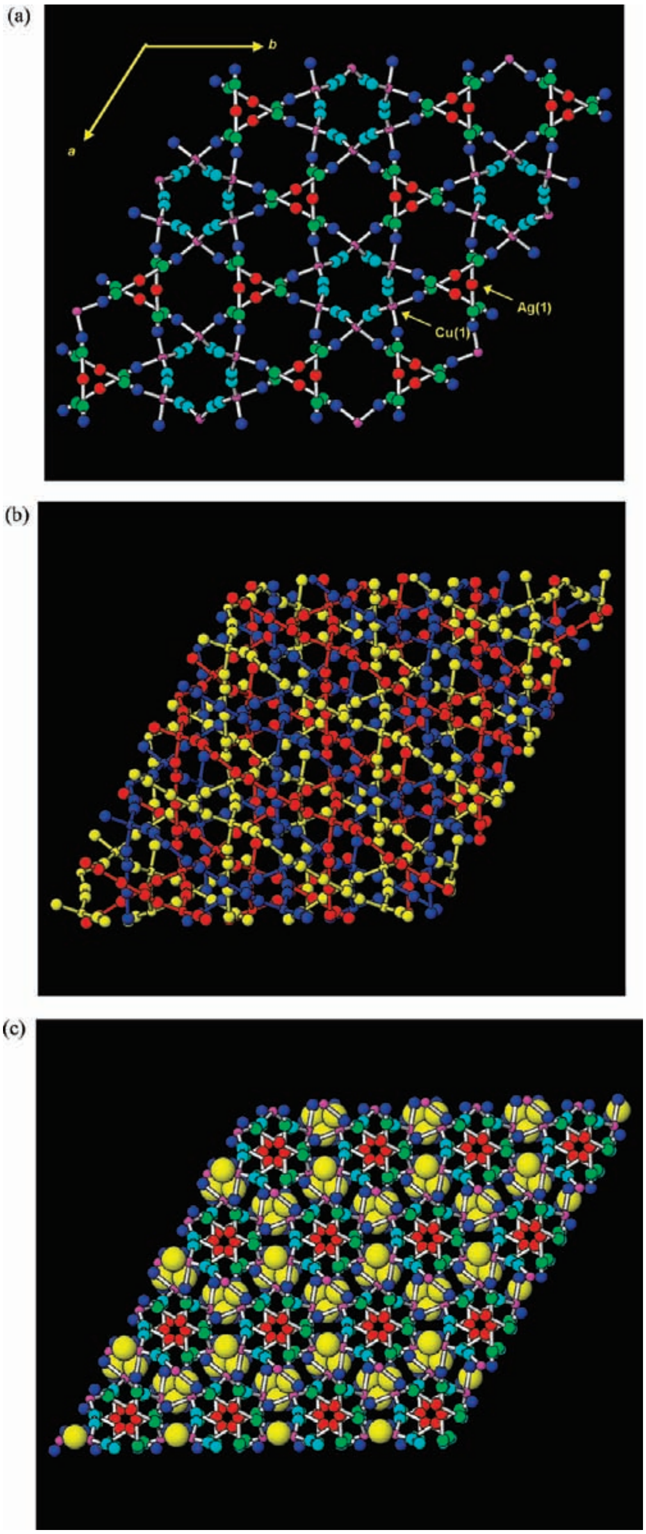

Figure 3. $CsAgCu(CN)_3$ (**II**) viewed along the *c* axis showing (a) one silver−copper−cyanide network consisting of −(CuCN)− chains coiled into six-fold helices linked together by $[NC-Ag-CN]^-$ units. Adjacent helices in the network have the same handedness. The network is 3-D and self-penetrating, (b) parallel interpenetration of three networks (in yellow, red and blue), and (c) the overall chiral structure showing the location of the Cs cations. Key as for Figure 2.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $CsAgCu(CN)_3$ (**II**)[d]

	Bond Distances		
Cu(1)−N(1)	2.048(4)	C(1)−N(1)	1.145(6)
Cu(1)−Z(2)	1.954(4)	Z(2)−Z(2)[c]	1.162(8)
Ag(1)−C(1)	2.066(5)		
	Angles		
N(1)−Cu(1)−N(1)[a]	107.1(3)	Z(2)−Cu(1)−Z(2)[a]	130.3(2)
N(1)−Cu(1)−Z(2)	104.17(16)	C(1)−Ag(1)−C(1)[b]	177.6(3)
N(1)[a]−Cu(1)−Z(2)	104.73(16)	Cu(1)−N(1)−C(1)	169.2(5)
N(1)−Cu(1)−Z(2)[a]	104.73(16)	Cu(1)−Z(2)−Z(2)[c]	170.85(19)
N(1)[a]−Cu(1)−Z(2)[a]	104.17(16)	Ag(1)−C(1)−N(1)	177.1(5)

[a] Symmetry codes: *x*, *x* − *y*, 1/6 − *z*. [b] 1 + *y*, *x* − 1, 1/3 − *z*. [c] *x* − *y*, −*y*, −*z*. [d] Z = either C or N of disordered cyanide group (occupancies of N(2) and C(2) are fixed at 0.5 by symmetry).

from a single-pot reaction is notable. The evolution of the products is of particular interest and contains a number of surprising features. For example, although the fact that the formation of a hydrate, $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**), as the final product in an aqueous environment is not unexpected, it is difficult to understand why the anhydrous compound $CsAgCu(CN)_3$ (**II**) is formed before the hydrated phase. The explanation is that the sequence of reactions is moving steadily downward in free energy. Indeed calculations of the packing densities of the materials show that all the conversions observed are to higher density forms (see Supporting Information). Therefore, kinetic factors must control which product is formed first. Kinetic factors might include the rates of formation and reaction of *specific* solution species, and as observed in the solvothermal syntheses of many zeolitic phases,[27] attempts to carry out the reactions stoichiometrically fail. Transforming $Cs_3Ag_2Cu_3(CN)_8$ (**I**) into 3 × $CsAgCu(CN)_3$ (**II**) requires the addition of AgCN to the framework, which is available from solution in the form of $[Ag(CN)_2]^-$ (Scheme 1). Converting $CsAgCu(CN)_3$ (**II**) to $CsAgCu(CN)_3 \cdot 1/3H_2O$ (**III**) requires a major rearrangement in connectivity between Cu− and Ag−cyanide units and a change in framework topology. Both these conversions probably proceed *via* dissolution and reprecipitation reactions. Remarkably, the second transformation can be reversed and (**III**) converts to (**II**) in the solid state at 100 °C. This reaction was totally unexpected since dehydrations at such moderate temperatures normally proceed with retention of network connectivity. In this conversion, significant bond-breaking and -making are taking place. The $[-NC-Ag-Z{\equiv}Z-Ag-CN-]^-$ units in (**III**) break, and CN^- is inserted leading to the formation of $[-NC-Ag-CN-]^-$ units, the only type of silver-containing unit found in (**II**). In addition, the short fragments of CuCN chains present in (**III**) recombine to form the extended chains found in (**II**). These changes are accompanied by large-scale atomic displacements, and there is no simple geometrical relationship between the structures of (**II**) and (**III**). Unsurprisingly, this dramatic rearrangement produces a polycrystalline product from a single crystal.

The observation that (**III**) converts to (**II**) in a solid-state reaction prompted us to investigate whether a similar conversion could be carried out between the $CsAg_2Cu(CN)_4$ phases (forms 1 and 2) we reported previously.[20] On heating a single crystal of $CsAg_2Cu(CN)_4$ (form 1), the metastable polymorph, it converted at 180 °C to $CsAg_2Cu(CN)_4$ (form 2), the higher density, thermodynamically stable polymorph.[20] In spite of the dramatic structural rearrangement, the transformation proceeded from single crystal to single crystal. Although both forms 1 and 2 are constructed from (4,4) connected nets, the mesh size is different in the two cases (Figure 5). In form 1, $[-NC-Ag-N-]^-$ units bridge copper nodes leading to alternation of Ag(I) and Cu(I) in the net, which has the formula $Ag_2Cu(CN)_4^-$. In form 2, however, the bridging unit between the Cu nodes is $[-NC-Ag-CN-Cu(CN)_2-CN-]^{3-}$ and the net has formula $Ag_2Cu_3(CN)_6^-$. In form 1, three nets interpenetrate to form a layered structure, whereas in form 2, four nets interpenetrate and are linked through $[-NC-Ag-Z{\equiv}Z-Ag-CN-]^-$ units to gener-

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(27) (a) Robson, H., Ed. *Verified Syntheses of Zeolitic Materials*, 2nd Revised Edition; Elsevier: Amsterdam, 2001. (b) Chippindale, A. M.; Cowley, A. R. *Microporous Mesoporous Mater.* **1998**, *21*, 271.

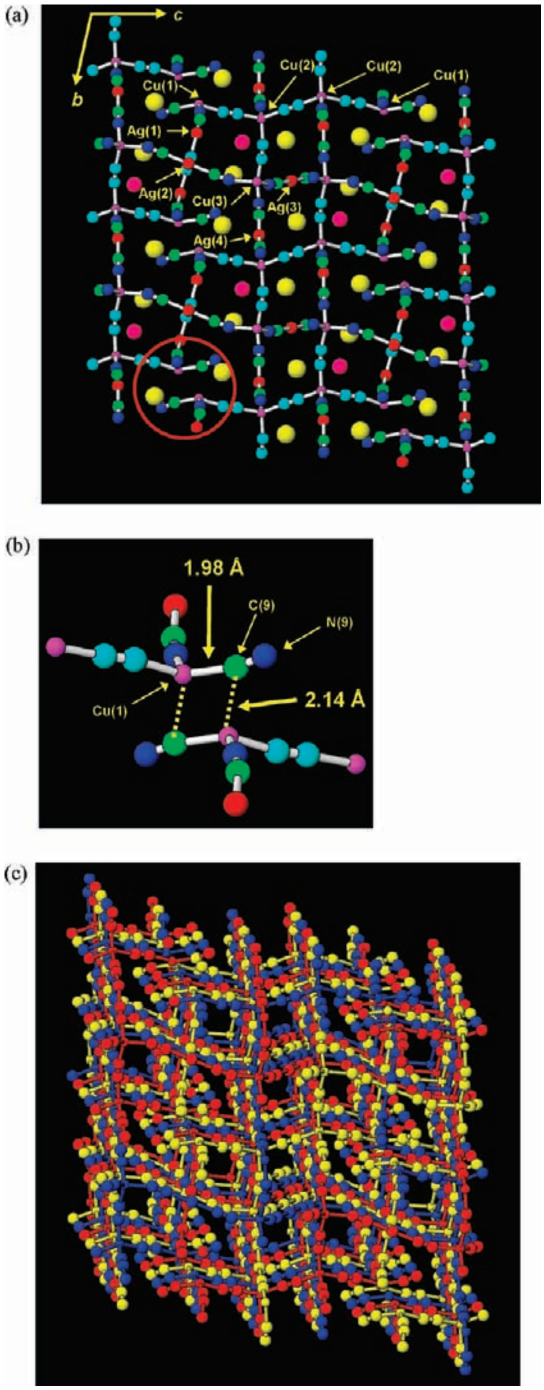

Figure 4. CsAgCu(CN)$_3$·1/3H$_2$O (**III**) (a) viewed along the *a* axis showing how fragments of −(CuCN)− chains are linked together *via* [Cu(CN)$_4$]$^{3-}$, [Ag(CN)$_2$]$^-$ and [Ag$_2$(CN)$_3$]$^-$ units to form a 3-D network which is self-penetrating. (b) View of the μ_2 cyanide interactions, highlighted in the red circle in (a), between two [Cu(CN)$_3$]$^{2-}$ groups at the ends of adjacent copper−cyanide chain fragments. (c) Offset view showing the three interpenetrating networks in yellow, red, and blue. Key as for Figure 2 with additional magenta spheres corresponding to H$_2$O.

Table 4. Selected Bond Distances (Å) and Angles (deg) for CsAgCu(CN)·1/3H$_2$O (**III**)[h]

Bond Distances			
Cu(1)−N(2)	2.054(5)	Ag(3)−C(4)	2.072(4)
Cu(1)−Z(7)	2.012(5)	Ag(3)−C(4)[c]	2.072(4)
Cu(1)−C(9)	1.983(6)	Ag(4)−C(5)[d]	2.076(5)
Cu(1)−C(9)[a]	2.412(7)	Ag(4)−C(6)	2.084(5)
Cu(2)−N(5)	2.082(4)	Z(1)−Z(1)[e]	1.16(1)
Cu(2)−Z(8)	1.962(5)	N(2)−C(2)	1.154(7)
Cu(2)−Z(10)	1.987(4)	N(3)−C(3)	1.148(6)
Cu(2)−Z(12)	1.967(5)	N(4)−C(4)	1.149(6)
Cu(3)−N(3)	2.090(4)	N(5)−C(5)	1.132(6)
Cu(3)−N(4)	1.965(4)	N(6)−C(6)	1.151(6)
Cu(3)−N(6)	1.968(4)	Z(7)−Z(8)	1.149(7)
Cu(3)−Z(11)	1.966(5)	N(9)−C(9)	1.136(8)
Ag(1)−Z(1)	2.131(5)	Z(10)−Z(11)	1.152(6)
Ag(1)−C(2)	2.101(5)	Z(12)−Z(12)[f]	1.153(9)
Ag(2)−C(3)	2.069(5)	O(1)−H(1)	0.85(5)
Ag(2)−C(3)[b]	2.069(5)	O(1)−H(2)	0.85(5)
Angles			
N(2)−Cu(1)−Z(7)	105.91(19)	C(3)−Ag(2)−C(3)[b]	180
N(2)−Cu(1)−C(9)	113.7(2)	C(4)−Ag(3)−C(4)[c]	180
Z(7)−Cu(1)−C(9)	125.4(2)	C(5)−Ag(4)−C(6)	158.32(19)
N(2)−Cu(1)−C(9)[a]	104.00(19)	Cu(1)−N(2)−C(2)	167.1(4)
Z(7)−Cu(1)−C(9)[a]	100.8(2)	Cu(1)−Z(7)−Z(8)	170.0(4)
C(9)−Cu(1)−C(9)[a]	104.33(19)	Cu(1)−C(9)−N(9)	166.6(6)
N(5)−Cu(2)−Z(8)	104.86(17)	Cu(1)[a]−C(9)−N(9)	117.7(6)
N(5)−Cu(2)−Z(10)	101.56(17)	Cu(2)−N(5)−C(5)	176.9(4)
Z(8)−Cu(2)−Z(10)	108.98(18)	Cu(2)−Z(8)−Z(7)	174.4(4)
N(5)−Cu(2)−Z(12)	102.71(17)	Cu(2)−Z(10)−Z(11)	168.4(4)
Z(8)−Cu(2)−Z(12)	123.86(18)	Cu(2)−Z(12)−Z(12)[f]	173.8(6)
Z(10)−Cu(2)−Z(12)	111.98(19)	Cu(3)−N(3)−C(3)	161.1(4)
Z(10)−Cu(2)−Z(8)	108.98(18)	Cu(3)−N(4)−C(4)	170.6(4)
Z(12)−Cu(2)−Z(8)	123.86(18)	Cu(3)−N(6)−C(6)	172.2(4)
N(3)−Cu(3)−N(4)	109.26(16)	Cu(3)−Z(11)−Z(10)	172.4(4)
N(3)−Cu(3)−N(6)	101.50(16)	Ag(1)−Z(1)−Z(1)[e]	172.6(6)
N(4)−Cu(3)−N(6)	113.29(16)	Ag(1)−C(2)−N(2)	173.9(4)
N(3)−Cu(3)−Z(11)	100.64(17)	Ag(2)−C(3)−N(3)	178.5(4)
N(4)−Cu(3)−Z(11)	115.27(17)	Ag(3)−C(4)−N(4)	178.0(4)
N(6)−Cu(3)−Z(11)	114.90(17)	Ag(4)[g]−C(5)−N(5)	178.5(4)
Z(1)−Ag(1)−C(2)	152.34(17)	Ag(4)−C(6)−N(6)	177.9(4)

[a] Symmetry codes: 2 − *x*, 2 − *y*, 1 − *z*. [b] 1 − *x*, 1 − *y*, 1 − *z*. [c] −*x*, 1 − *y*, −*z*. [d] 1 + *x*, *y* −1, *z*. [e] 4 − *x*, 1 − *y*, 1 − *z*. [f] 2 − *x*, 2 − *y*, −*z*. [g] *x* − 1, 1 + *y*, *z*. [h] Z = either C or N of disordered cyanide group.

ate a 3-D framework. The conversion of form 1 to form 2 thus involves bond-breaking and -making with significant changes in the connectivity. Figure 5 also shows the equation for the net to (net + bridge) conversion. Interestingly, the [Ag$_2$(CN)$_3$]$^-$ unit, which was converted into [Ag(CN)$_2$]$^-$ units in the (**III**) to (**II**) transformation, has been generated in this case.

Perhaps surprisingly, the conversion of form 1 to form 2 (the thermodynamically more stable form, at least between 20 and 230 °C) is endothermic as determined by DSC, although the enthalpy change is very small. This means that the entropy of form 2 must be higher than that of form 1. This is in line with the large degree of head-to-tail disorder in the C≡N groups found in form 2 and the complete absence of such disorder in form 1. Although form 2 has the higher packing density, its overall enthalpy of formation is slightly greater than that of form 1. This might arise in part because of the different energetic costs of forming Cu−CN−Cu and Ag−CN−Ag linkages in form 2 versus heterometallic Ag−CN−Cu linkages in form 1.

Single-crystal to single-crystal transformations in which covalent bonds are broken and made are rare and are normally only seen when relatively small changes in structure occur, e.g. on water loss[28] or the rearrangement of hydrogen bonds.[29] We note however that more substantial structural changes have been observed in a few single-crystal to single-crystal transformations. For example, in 1992, Abrahams et al. observed a conversion between two solvated forms of Cd(CN)$_2$.[30] Cd(CN)$_2$·2/3H$_2$O·Bu^{t}OH, with a honeycomb-like cadmium−cyanide framework, transformed to Cd(CN)$_2$·CHCl$_3$, with a single diamond framework. It was proposed that the transformation might occur *via* a shear mechanism in which blocks

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(29) May, L. J.; Shimizu, K. H. *Z. Krystallogr.* **2005**, *220*, 364.

(30) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Williams, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 10641.

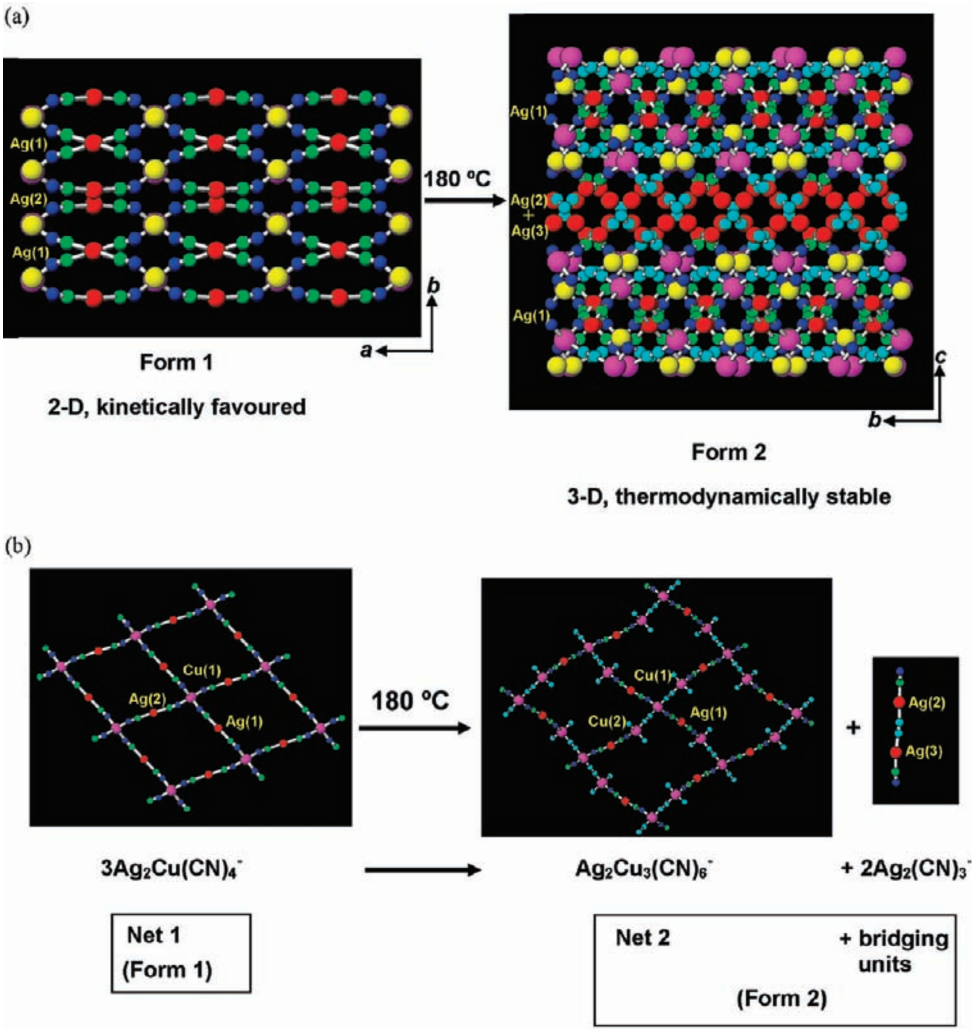

Figure 5. Conversion of the polymorphs of $CsAg_2Cu(CN)_4$ (forms 1 and 2) on heating at 180 °C. (a) Form 1 has a three-fold interpenetrating layered structure and Form 2, a four-fold interpenetrating 3-D structure.[20] Note that in this projection of form 1, the Cu atoms are directly behind the Cs atoms. (b) Detail of the different (4,4) connected nets present in form 1 and form 2 which have formula $Ag_2Cu(CN)_4^-$ and $Ag_2Cu_3(CN)_6^-$, respectively, together with the $[Ag_2(CN)_3]^-$ units which link the nets in form 2. The chemical equation describing this conversion is also shown. Key as for Figure 2.

of cadmium atoms move relative to each other. More recent examples include studies of MOFs by Bradshaw et al.[31] and Xue et al..[32] In both cases, two water molecules are lost from the coordination sphere of the metal ions, Co^{2+} and Cd^{2+}, respectively. In the former transformation, the water molecules are replaced by nitrogen of bipyridine and oxygen of methanol; in the latter oxygen atoms from the dicarboxylate ligands reestablish octahedral coordination around cadmium. In these cases, the authors were able to propose structural mechanisms to account for the transformations including which bonds were broken and made. In our example, it is difficult to see how simple combinations of atomic movements produce the overall structural change although it is possible to make some comments on the nature of the transformation.

Examination of the unit-cell metrics and volumes of the two forms of $CsAg_2Cu(CN)_4$ provides a partial explanation of the mechanism of the transformation of form 1 to form 2. Form 1 crystallizes in the monoclinic spacegroup *P*2/*c* with lattice parameters $a = 7.7266(3)$ Å, $b = 7.6129(3)$ Å, $c = 8.2541(3)$ Å, $\beta = 103.807(2)°$ and $V = 471.49(3)$ Å^3 at 150 K, whereas form 2 crystallizes in the orthorhombic spacegroup *Ibca* with lattice parameters $a = 8.5733(2)$ Å, $b = 20.6076(5)$ Å, $c = 31.5303(9)$ Å and $V = 5570.62(25)$ Å^3 at 150 K. The change in unit-cell volumes by a factor of ∼12 on going from form 1 to form 2 can be accounted for as the three-fold interpenetrating solid is being converted into the four-fold interpenetrating solid and 12 is the lowest common multiple. Although it is tempting to see the four-fold relationship between the *c* axes of the two forms as significant, examining the structures in projections which both contain the *c* axes is unprofitable. More promising, however, is the set of projections shown in Figure 5a where it can be envisaged that the silver atoms on the outside of the layers in form 1, Ag(2), together with one-third of those from the center of the layers, Ag(1), join to form the $[Ag_2(CN)_3]^-$ units (Ag(2) and Ag(3) in form 2) which bridge between the nets, forming the layers seen in form 2. Clearly, this must involve substantial movements, especially of the Ag(2) silver atoms in form 1, which are moving from the middle of the layers to the outside on transformation, a distance of about 5 Å.

Conclusions

Cesium silver(I)−copper(I) cyanides show a rich structural chemistry. Furthermore we have demonstrated that transformations can occur between such phases, both in contact with solutions and more interestingly in the solid state. These results suggest that metal−cyanide linkages are not as rigid as perhaps

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once assumed. This not only leads to the fascinating chemistry described above but also has implications for those applications of metal−cyanide-based materials in which such facile rearrangement of frameworks would be undesirable.

Acknowledgment. We thank Dr. D. J. Watkin, Chemical Crystallography Laboratory, Oxford, for use of X-ray facilities and the EPSRC for later provision of a single-crystal diffractometer in Reading (Grant No. EP/533526/1).

Supporting Information Available: X-ray crystallographic files in CIF format for compounds (**I**), (**II**) and (**III**); lattice parameters for (**I**), (**II**), (**III**) and forms 1 and 2 at 150 and 293 K; TG data for (**III**); DSC data for form 1, packing density information. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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