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Synthesis of New Copper Cyanide complexes via the Transformation of Organonitrile to Inorganic Cyanide

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Hydrothermal reaction of diaminomaleonitrile and copper salts under different conditions resulted in copper cyanide coordination polymers $\{[Cu(H_2O)(NH_3)_4][Cu_3(CN)_5]\cdot H_2O\}_n$ (**1**), $\{(CH_3)_4N[Cu(H_2O)(NH_3)_4][Cu_4(CN)_7]\}_n$ (**2**), and $\{(CH_3OH_2)_2[Cu_2(CN)_3]\}_n$ (**3**). **1** and **2** are new mixed-valence Cu(I,II), two 3D organic−inorganic molecular framework complexes that exhibit ionic inclusion. **3** is an open copper cyanide framework hosting a guest molecule. Cyanides in **1**, **2**, and **3** are produced by in situ C−C bond cleavage of diaminomaleonitrile, and then the remaining product is oxidized to form an oxalate group. The potential porosity of the hydrated coordination polymer **3** was estimated using a computational method based on Connolly's algorithm.

Introduction

The cyanide group is the simplest species containing both carbon and nitrogen, which are both bioessential elements to form amino acids, proteins, nucleotides, and most other known biomolecules. Over the past decades, the synthesis of metal cyanide compounds has become a particularly important area of research and has attracted a growing interest because of potential applications as materials for catalysis, inorganic−organic zeolites, high-Tc molecular-based magnets, and high-temperature superconductors.[1–4] In particular, Cu(I)/Cu(II) cyanide complexes have received wide recognition for their unique physical and chemical properties including long-range magnetic order, luminescence, electron-transfer as well as bioinorganic chemistry relative to blue copper proteins and type I copper-containing enzymes.[5] Although some cyano-bridged mixed-valence

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Cu(I)/Cu(II) complexes have been reported, ionic inclusion complexes based on copper cyanides are still a rare observation. Williams et al. first reported an ionic inclusion complex with cationic $[Cu(en)_2(H_2O)]^{2+}$ guests encapsulated by a $[Cu_2(CN)_4]^{2-}$ network;[6] Kroeker et al. reported a mixed-valence Cu(I)/Cu(II)/Zn(II) heterometallic 2D puckered sheet, $[Zn(NC)_4(CuCN)_2]^{2-}$, with $[Cu(en)_2]^{2+}$ cations in the cavities;[7] Zubieta and colleagues reported a 2D $[Cu_5(CN)_7]^{2+}$ network encapsulating $[(bpy)_2Cu_2(CN)_2]^{2-}$ cations and crystal water molecules.[8] With only so few examples at hand, the need for a development of a convenient strategy for the synthesis of mixed-valence Cu(I)/(II) cyanide complexes is significant, especially because they are of such great biological importance and could also exhibit interesting electric properties.[9,10]

There is a great interest in developing Cu(I) and Cu(I,II) complexes under hydro(solvo) thermal conditions and in ascertaining that Cu(II) ions not only can be reduced to Cu(I) in the presence of nitrogen-containing ligands but also often play a catalytic role in hydro(solvo)thermal ligand reactions.[11] Acetonitrile in aqueous ammonia solution at high temperature can decompose to form cyanides.[12] This prompted us to select the dinitrile ligand (diaminomaleonitrile) as a potential source for cyanide and to use it together with different copper salts and solvents as well as reaction conditions to synthesize new cyanide compounds, preferentially in a single crystalline form. Fortunately, by trial and error we have isolated two new mixed-valence Cu(I,II) complexes, two 3D organic−inorganic molecular frameworks with ionic inclusion $\{[Cu(H_2O)(NH_3)_4][Cu_3(CN)_5]\cdot H_2O\}_n$ (**1**) and $\{(CH_3)_4N[Cu(H_2O)(NH_3)_4][Cu_4(CN)_7]\}_n$ (**2**), and one porous copper cyanide framework hosting a guest molecule $\{[(CH_3OH_2)][Cu_2(CN)_3]\}_n$ (**3**). All three compounds have 3D topologies containing $Cu_2(CN)_2$ secondary building units (SBUs).

Experimental Section

General Remarks. All materials and reagents were obtained commercially and were used without further purification. Elemental (carbon, hydrogen, and nitrogen) analyses were performed on a PerkinElmer 2400 element analyzer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400∼4000 cm^{-1} range using a Nicolet Avatar 360 FTIR spectrophotometer. All of the materials and reagents were obtained commercially and used without further purification. Elemental (carbon, hydrogen, and nitrogen) analyses were performed on a PerkinElmer 2400 element analyzer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400∼4000 cm^{-1} range using a Nicolet Avatar 360 FTIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was undertaken on an ESCA Laboratory MkII instrument with $Mg-K_a$ radiation as the excitation source. TGA experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C min^{-1}.

Preparation of 1. A mixture of $Cu(OH)_2CuCO_3$ (0.110 g, 0.5 mmol), diaminomaleonitrile (0.108 g, 1 mmol), $NH_3\cdot H_2O$ (2 mL, 25%), and methanol (3 mL) was sealed in a 15 mL Teflon-lined reactor, which was heated in an oven to 110 °C for 48 h and then cooled to room temperature at a rate of 5 °C h^{-1}. Blue-plate crystals were obtained in low yield. Elemental analysis (%) Calcd for 1 ($C_5H_{16}Cu_4N_9O_2$), C, 12.30; H, 3.30; N, 25.81; Found: C, 12.11; H, 3.42, N, 25.96; IR(KBr, cm^{-1}): 3340, 3260, 2168, 2113, 2070, 1603, 1313, 696.

Preparation of 2. A mixture of $Cu(OH)_2CuCO_3$ (0.110 g, 0.5 mmol), diaminomaleonitrile (0.108 g, 1 mmol), $N(CH_3)_4Cl$ (0.055 mg, 1mmol), $NH_3\cdot H_2O$ (2 mL, 25%), and methanol (3 mL) was sealed in a 15 mL Teflon-lined reactor, which was heated in an oven to 160 °C for 72 h and then cooled to room temperature at a rate of 5 °C h^{-1}. Blue-block crystals were obtained in low yield. Elemental analysis (%) Calcd for 2 ($C_{11}H_{14}Cu_5N_{12}O$), C, 20.39; H, 2.18; N, 25.94; Found: C, 20.29; H, 2.12, N, 25.86. IR(KBr, cm^{-1}): 3334, 3255, 2167, 2108, 2067, 1608, 1257, 1193, 1107, 690.

Preparation of 3. A mixture of $Cu(OH)_2CuCO_3$ (0.110 g; 0.5 mmol), diaminomaleonitrile (0.108 g; 1 mmol), $Eu(NO_3)_3.6H_2O$ (0.111 mg; 0.25 mmol), $NH_3\cdot H_2O$ (2 mL, 25%), and methanol (3 mL) was sealed in a 15 mL Teflon-lined reactor, which was heated in an oven to 120 °C for 72 h and then cooled to room temperature at a rate of 5 °C h^{-1}. Colorless plate crystals were obtained in low yield. IR(KBr, cm^{-1}): 3630, 3184, 2169, 2085, 1681, 1577, 1458, 1382, 1006, 817.

Crystal Structure Determination. Single crystal X-ray diffraction data collections of **1**−**6** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection and reduction were performed using the APEX II software.[13] Multiscan absorption corrections were applied for all the data sets using *APEX II*.[13] All six structures were solved by direct methods and refined by full-matrix least-squares on F^2 using *SHELXTL*.[13] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms on water molecules or amino groups were located from difference Fourier maps and were also refined using a riding model. Crystallographic data for **1**−**2** are listed in Table 1 and selected bond lengths and angles for all compounds are given in Table 2. More details on the crystallographic information, as well as

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Table 1. Some Crystal, Data Collection, and Structure Refinement Parameters

compound	**1**	**2**	**3**
empirical formula	$C_5H_{16}Cu_4N_9O_2$	$C_{11}H_{26}Cu_5N_{12}O$	$C_8H_{10}Cu_4N_6O_2$
fw	488.43	660.19	476.38
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	*Pnma*	*Pbcn*
a /Å	7.9109(1)	14.3384(4)	8.1953(1)
b /Å	10.4906(2)	13.3522(4)	7.5577(2)
c /Å	18.9281(3)	12.3444(4)	13.4593(2)
V /Å^3	1570.84(4)	2363.33(12)	833.64(3)
Z	4	4	2
D_{calcd} (g/cm^3)	2.065	1.855	1.898
μ (mm^{-1})	5.355	4.453	5.038
F (000)	964	1316	464
params	185	146	55
GOF	1.011	1.079	1.121
R1 [a]	0.0340, 0.0531	0.0707, 0.1221	0.0291, 0.0362
wR2 [b]	0.0636, 0.0696	0.1883, 0.2197	0.0735, 0.0775

[a] $R1 = \Sigma F_0$. [b] $wR2 = \{[w(F_0^2 - F_c^2)^2]/\Sigma\{(F_0^2)^2\}^{1/2}$.

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **1**−**2**

		1			
C1−Cu2	2.106(6)	C1−Cu1	2.200(6)	C2−Cu2	2.041(6)
C2−Cu1	2.245(6)	C3−Cu1	1.925(6)	C4−Cu1	1.906(6)
Cu1−Cu2	2.504(9)	Cu2−N2[a]	2.000(5)	Cu2−N5	2.022(5)
Cu3−C5[b]	1.936(5)	Cu3−N3[c]	2.011(6)	Cu3−N1	2.026(5)
Cu3−N4[e]	2.069(5)	Cu4−N7	2.027(5)	Cu4−N9	2.034(5)
Cu4−N8	2.044(5)	Cu4−N6	2.057(5)	Cu4−O2*w*	2.257(5)
C4−Cu1−C3	125.1(2)	C4−Cu1−C1	107.8(2)		
C3−Cu1−C1	106.1(2)	C4−Cu1−C2	113.5(2)		
N5−Cu2−C1	99.1(2)	C2−Cu2−C1	114.3(2)		
N1−Cu3−N4[d]	113.1(2)	N7−Cu4−N9	165.8(2)		
N7−Cu4−N6	88.7(2)	N9−Cu4−N6	88.2(2)		
N8−Cu4−N6	166.2(2)	N7−Cu4−O2*w*	98.6(2)		
		2			
C1−Cu1	2.19(1)	C1−Cu1[f]	>2.06(1)	C2−Cu1	1.937(9)
Cu1−Cu1[f]	>2.480(2)	Cu2−N2[g]	1.991(1)	Cu2−N1	2.024(8)
Cu3−N7	1.989(2)	Cu3−N6	>2.044(1)	Cu3−N8	2.060(2)
Cu3−O1	2.210(2)				
C2−Cu1−C1[f]	>111.5(4)	C2−Cu1−C1	105.2(4)		
N2[g]−Cu2−N1	113.5(4)	N6−Cu3−O1	91.8(3)		
N7−Cu3−N6	89.3(4)	N8−Cu3−O1	103.3(7)		
N7−Cu3−N8	152.5(9)	N6−Cu3−N8	89.9(4)		
N7−Cu3−O1	104.2(7)				

Symmetry code: [a] $-0.5 + x, 0.5 - y, 1 - z$. [b] $-0.5 + x, -0.5 - y, 1 - z$. [c] $-1 + x, y, z$. [d] $-x, -0.5 + y, 1.5 - z$. [e] $0.5 + x, 0.5 - y, 1 - z$. [f] $1 - x, 1 - y, -z$. [g] $0.5 - x, 1 - y, 0.5 + z$.

refinement data and anisotropic displacement parameters, are can be found in the Supporting Information.

Results and Discussion

Structures. The analysis of the crystallographic data revealed that **1** and **2** are based on a rare structural molecular motif,[6–8,14] accommodating ionic guest complexes in the structure, and **3** is a α-Po related porous organic−inorganic framework. For **1**, all of the channels of the anionic 3D host lattice, $\{[Cu_3(CN)_5]^{2-}\}_n$, are identical and contain cationic guest ions, $[Cu(H_2O)(NH_3)_4]^{2+}$, and crystallization water molecules. More interestingly, for **2**, there are two different cationic units, $[Cu(H_2O)(NH_3)_4]^{2+}$ and $[N(CH_3)_4]^+$, surrounded by the anionic 3D host lattice, $\{[Cu_4(CN)_7]^{3-}\}_n$. For **3**, an open α-Po type $[Cu_2(CN)_3]^-$ framework containing intercalated protonated solvent molecules is observed.

The asymmetric unit of **1** is shown in Figure 1. It crystallizes in the orthorhombic space group $P2_12_12_1$ and has three crystallographically independent Cu(I) centers, five cyanides, one $[Cu(H_2O)(NH_3)_4]^{2+}$ unit, and one water molecule per asymmetric unit. In the anionic network $\{[Cu_3(CN)_5]^{2-}\}_n$, the Cu1 and Cu2 ions are tetrahedral and thus monovalent. Their coordination polyhedrons are defined by one μ_3,η^2 bridging cyanide ligand (Cu−C/*N* = 2.041(3)−2.247(5) Å), leading to a Cu···Cu distance of 2.504 Å. The other three coordinating sites are occupied by a μ_2,η^2 bridging cyanide (Cu−C/N = 1.906(3)−2.022(4) Å) ligands. Cu3 is also tetrahedral and monovalent. It is coordinated by four cyanide ligands (Cu3−C/N = 1.936(4)−2.069(5) Å). The C1/N1 and the C2/N2 ligands are each bound to Cu3 and Cu2, respectively, via a monodentate C/N atom, and the other

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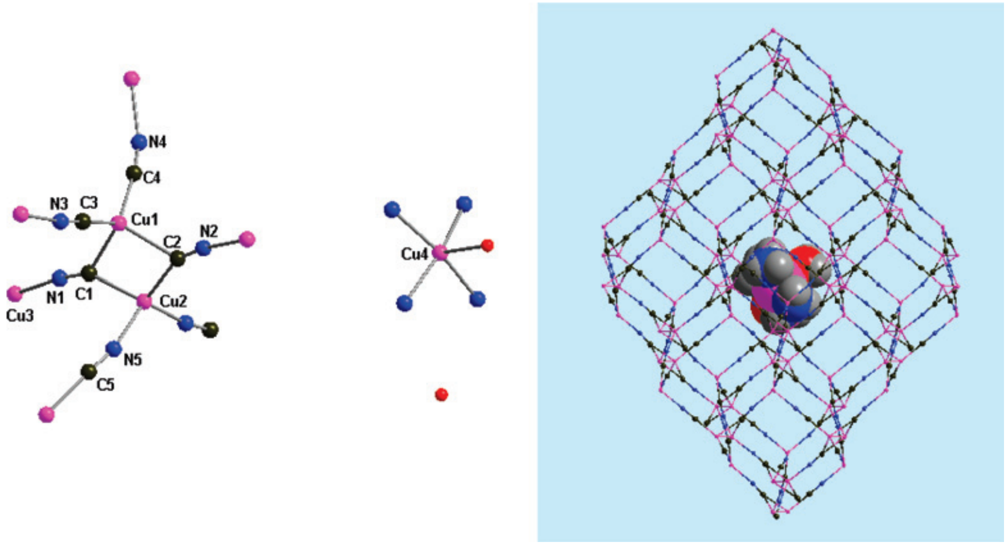

Figure 1. The asymmetrical unit of **1** is on the left. The right diagram shows the channels of the anionic network $\{[Cu_3(CN)_5]^{2-}\}_n$, with a trapped $[Cu(H_2O)(NH_3)_4]^{2+}$ complex cation and one water molecule.

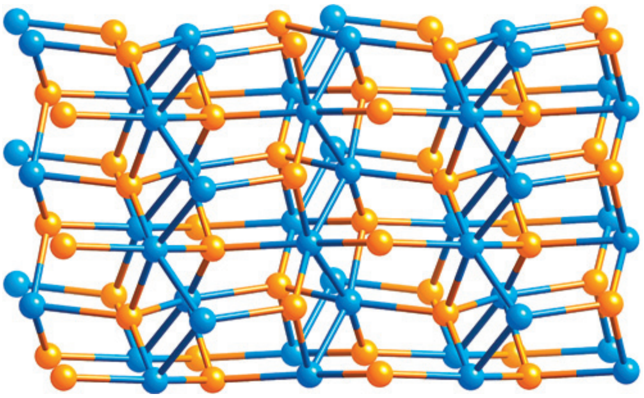

Figure 2. Schematic representation of the underlying 4,6-connected network topology in **1**. Blue spheres represent the $Cu_2(CN)_2$ SBUs, and orange spheres represent the Cu3 atoms.

C/N atom of these ligands functions as a bidentate μ-C/N bridge to Cu1 and Cu2. The other cyanide ligands (C3/N3, C4/N4, and C5/N5) are linearly bridging Cu1, Cu2, and Cu3 atoms with each other. In the ionic inclusion complex, the Cu4 atom has a pyramidal geometry, and it can thus be assumed to be divalent. It is coordinated by four ammonia molecules (Cu−N = 2.029(6)−2.058(6) Å) and one water molecule. The mixed-valence character of **1** is also demonstrated by XPS spectra (Figure S2 in the Supporting Information). The Cu−O2*w* bond distance of 2.261(4) Å is longer than other Cu−N bond distances.

The cyanide anions bridge the Cu1, Cu2, and Cu3 atoms into a 3D network. The net contains $Cu_2(CN)_2$ square motifs, a feature common to all of the structures described in this article, and thus in simplifying the network topology we will consider this as an SBU. In this structure, the $Cu1Cu2(CN)_2$ SBU acts as a 6-connecting node, whereas the Cu3 atom acts as a tetrahedral 4-connecting node. This gives an unusual overall 4,6-connected net with $(4^3.5^3)(4^5.5^6.6^3.7)$ topology (Figure 2). The network structure has voids that contain the ionic complex and water molecules. The shape of these voids is irregular, with approximate dimensions of 12 × 8 × 9.5 Å^3 and is constructed by 16 copper and 18 cyanide linkages (Figure 1).

The asymmetric unit of **2** is shown in Figure 3. It crystallizes the orthorhombic space group *Pnma* and consists of two crystallographically independent Cu(I) centers, three and a half cyanides, one $[Cu(H_2O)(NH_3)_4]^{2+}$ unit, and one $[N(CH_3)_4]^+$ unit per asymmetric unit. In the anionic molecular network $\{[Cu_4(CN)_7]^{3-}\}_n$, the Cu1 and Cu2 atoms are tetrahedral and thus monovalent. Each of them is coordinated by four cyanide ligands (Cu1−C/N = 1.941(2)−2.192(2) Å, Cu2−C/N = 1.964(4)−2.026(2) Å). The C1/N1 cyanide ligand is coordinated to a pair of symmetry-related Cu1 atoms at a distance of 2.480 Å on one side. On the other side it is coordinated to a Cu2 atom. The other C2/N2, CN3, CN4, and CN5 ligands linearily bridge Cu1 and Cu2 (for CN3, CN4, and CN5 cyanide ligands, each cyanide atom position was refined as being disordered equally between carbon and nitrogen, with equivalent thermal parameters). Of the two ionic inclusion cations, one is the same as **1** (with Cu−N = 1.991(2)−2.051(1) Å, Cu−O = 2.195(2)) and the other is a tetramethylammonium ion $[N(CH_3)_4]^+$ and is also disordered. To the best of our knowledge, no similar mixed-valence Cu(I,II) structure containing two different ionic units has been reported so far. Thus, the two different cationic units $[Cu(H_2O)(NH_3)_4]^{2+}$ and $[N(CH_3)_4]^+$ are surrounded by an anionic 3D host lattice, $\{[Cu_4(CN)_7]^{3-}\}_n$, to form an attractive network architecture (Figure 3). As before, the network consists of 6-connecting $Cu1_2(CN)_2$ nodes and 4-connecting Cu2 nodes, to give another unusual 4,6-connected net, this time with $(4^2.5^3.6)_2(4^4.5^4.6^4.8^3)$ topology (Figure 4).

A polymeric segment of **3** is shown in Figure 5. It can be described as an open framework hosting protonated methanol molecules, in which each corner is constituted by a dicopper unit. It crystallizes in the orthorhombic space group *Pbcn*, and in each asymmetric unit there is one crystallographically independent Cu(I) center, one and a half cyanides (the half-cyanide atom position was refined as being disordered

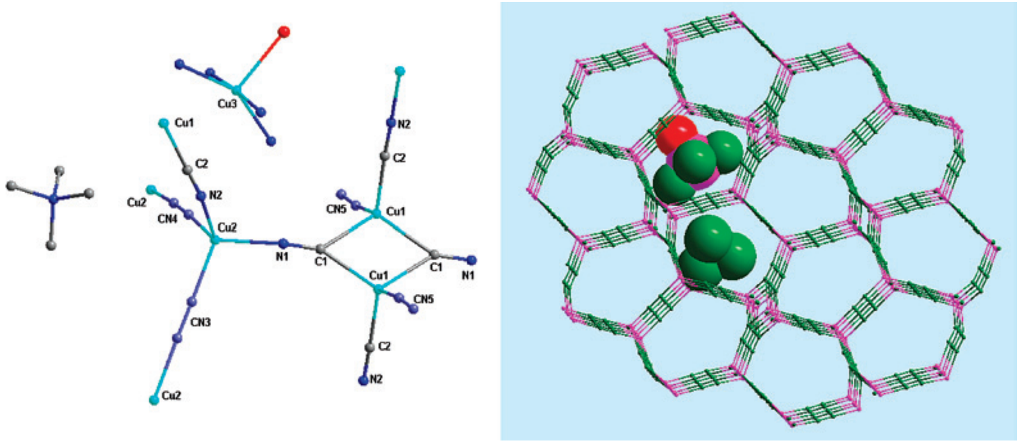

Figure 3. The asymmetrical unit of **2** is on the left. The right diagram shows the channels with two trapped $[Cu(H_2O)(NH_3)_4]^{2+}$ and $[N(CH_3)_4]^+$ complex cations by the anionic network $\{[Cu_4(CN)_7]^{3-}\}_n$.

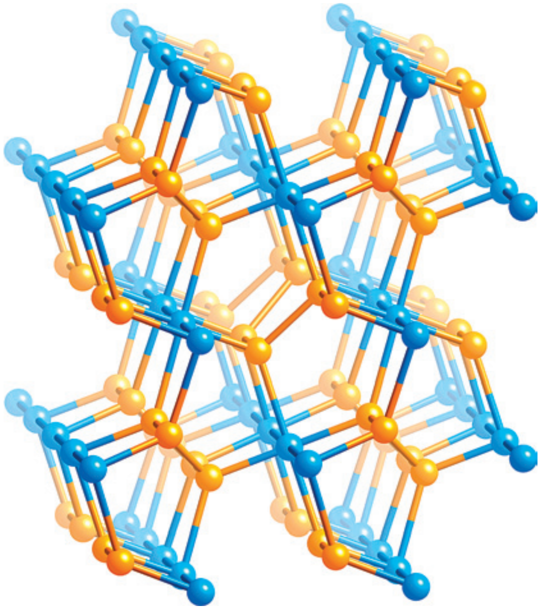

Figure 4. Schematic representation of the underlying 4,6-connected network topology in **2**. Blue spheres represent the $Cu_2(CN)_2$ SBUs, and orange spheres represent the Cu2 atoms.

equally between the carbon and nitrogen atoms, with equivalent thermal parameters) one protonated methanol molecule. A pair of tetrahedral Cu(I) atoms with a Cu···Cu separation of 2.473(2) Å is coordinated by two (μ_3,η^2) cyanide groups. The other coordinating positions are occupied by (μ_2,η^2) cyanide ligands, thus forming an interesting open molecular framework (Figure 5). Topologically, there are again 6-connecting $Cu_2(CN)_2$ nodes. However, in this case these are the only nodes present, and the underlying net is the commonly encountered α-Po net. The protonated methanol molecules in the cavities keep the charge balance, which was observed previously in other structures.[15] Investigation of other structures with the $[Cu_2(CN)_3]^-$ unit, such as $K[Cu_2(CN)_3]\cdot H_2O$,[16] $[Cu(H_2O)_4][Cu_4(CN)_6]$,[17] $H_3NCH_2CH_2NH_3$-$[Cu_4(CN)_6]\cdot 2H_2O$,[18] $NH_4[Cu_2(CN)_3]$ $\cdot H_2O_{19}$. and NEt_4-$[Cu_2(CN)_3]$,[20] showed all five related frameworks to have different motifs than that of **3**.

1 may also be obtained from different reagents or solvents (Supporting Information) such as the hydrothermal reaction of $Cu(OH)_2CuCO_3$, aqueous ammonia, and diaminomaleonitrile in methanol. Addition of $N(CH_3)_4Cl$ to the mixture gives rise to single crystals of **2**. When aqueous ammonia is not added, no crystals form. This indicates that aqueous ammonia is crucial for growing single crystals, particularly for obtaining cyanide groups from the decomposition of diaminomaleonitrile. The formation mechanism of the textual crystals is not very clear because as we have not been able to obtain any key intermediates. However, on the basis of the isolated ultimate products we have depicted a possible reaction mechanism as drawn in Scheme 1. The first step is probably a redox reaction involving Cu(II) and diaminomaleonitrile in the presence of aqueous ammonia, forming Cu(I), leading to the decomposing to form the cyanide groups. The second step is the assembly of Cu(I), the cyanide groups, and surplus Cu(II)−ammonia complex through a coordination interaction to generate **1** and **2**. We also have obtained related structures containing oxalate groups, **4**−**6**. On the basis of our results and according to the literature,[21] the main formation mechanism can be deduced as follows: the metal ions coordinate to the diaminomaleonitrile ligand, followed by C−C bond cleavage under ambient or high temperature to form cyanide, and then the remaining product is oxidized to form an oxalate group. Alternatively, the C═C double bond cleavage is followed by an oxidation to form the oxalate groups. For **4**, its structural unit consists of a

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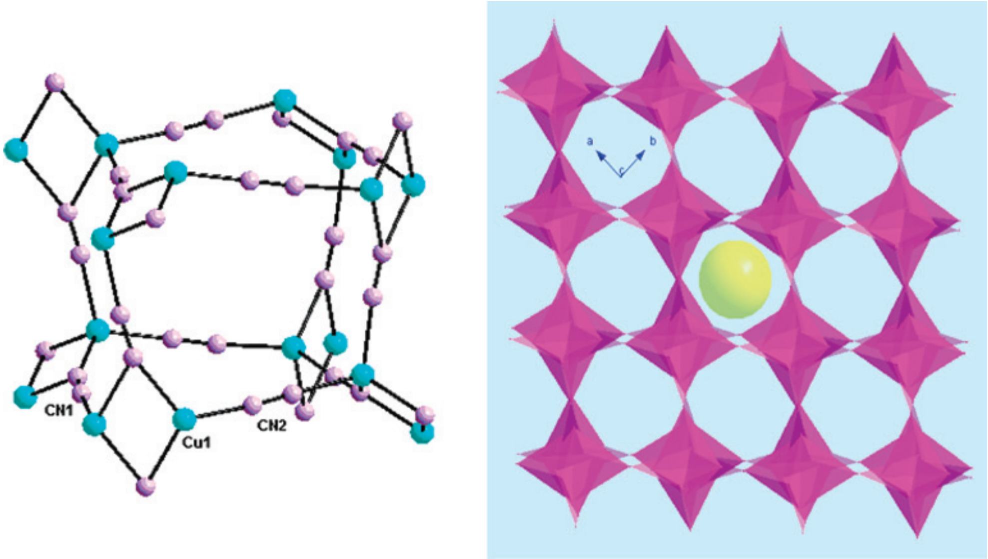
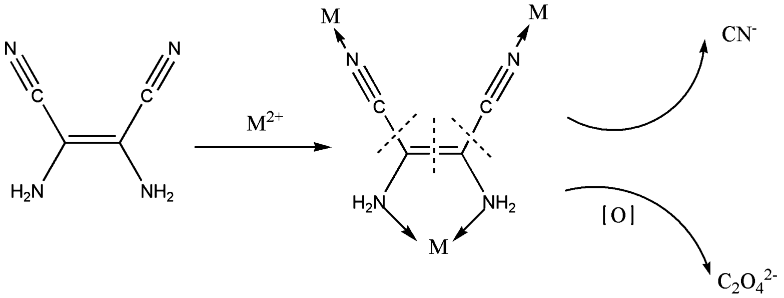


Figure 5. Portion of the 3D open framework of **3** with selected atom numbering on the left. The right diagram shows the open pseudocubical framework of compound **3**.

Scheme 1. The Possible Route to Form Cyanide and Oxalate Groups



$[Ni_2(NH_3)_8(C_2O_4)]^{2+}$ cationic unit and a $[Ni(CN)_4]^{2-}$ counterion. In the moiety of the cation unit, the Ni1 atom is coordinated by two oxygen atoms from one oxalate ligands and four ammonia molecules. The Ni2 atom lies on the center of symmetry and is defined by four cyanide groups (Figure S4 in the Supporting Information). Compounds **5**and **6** are isostructural and the metal center (Ni1 or Fe1) is coordinated by four oxygen atoms from two oxalate ligands and two ammonia molecules. The metal centers display a distorted octahedral coordination geometry (Figures S4 and S5 in the Supporting Information). Details are given in the Supporting Information.

Properties. A thermogravimetric analysis (TGA) trace of **1** (Figure S6 in the Supporting Information) performed in air atmosphere at a rate of 10 °C min^{-1} shows a first weight loss of about 14% in the range of 100−150 °C, indicating the removal of four ammonia molecules. The second step weight loss in the range of 150−480 °C can ascribe to the removal of a water molecules and cyanides. The weight increase was observed after 480 °C, thus indicating the oxidization of copper into CuO. The TGA trace of **3** (Figure S7 in the Supporting Information) performed in N_2 atmosphere at a rate of 10 °C min^{-1} shows a first weight loss of about 14% in the range of 150−220 °C, indicating the removal of methanol molecules. Afterward, the decomposition of cyanides occurred.

3 can be described as having a coordination network with rather high potential porosity. Gas adsorption is the usual way to characterize such a porosity. However, it is sometimes difficult to implement this method. This is especially the case for coordination polymers that often collapse or decompose during the preceding desorption step. Herein, we used instead a computational method to estimate the potential porosity of the hydrated coordination polymer.

Assuming that crystallization water molecules can be removed at low temperature without destroying the molecular network (by cold drying), we have formally removed and calculated the potential porosity of this dehydrated compound according to a computational method based on Connolly's algorithm[22] already described and successfully used elsewhere.[23] From these calculations, it appears that the compound presents two different types of channels (Figure 6). The smaller ones spread along the $\vec{c}$ axis and can only host−guest molecules with kinetic radii smaller than 1.50 Å (the kinetic diameter is the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy[24]). The bigger channels can host molecules

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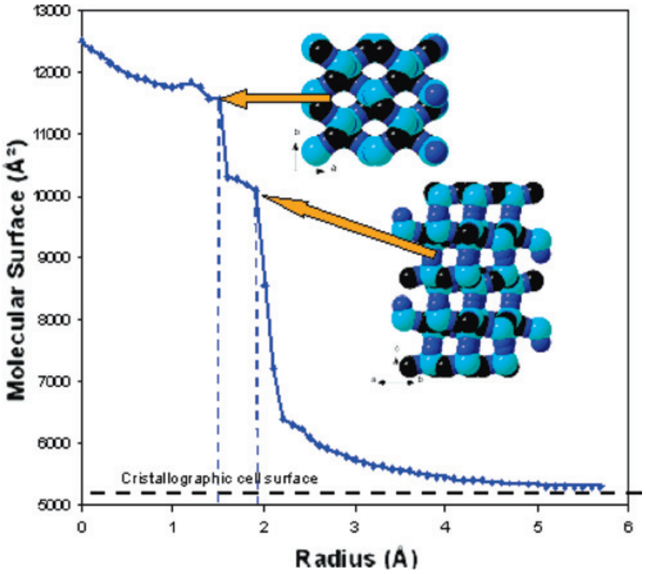

Figure 6. Porosity profile (molecular surface versus probe sphere radius) for **3**.

with kinetic radii smaller than 1.90 Å. Therefore, the potential porosity has been calculated for the largest kinetic radius a guest molecule can have and still be hosted by all the cavities, that is 1.45 Å (this value compares well with the usual kinetic radius of H_2[25]). With this probe sphere radius, the potential specific accessible surface of **3** is 390 m^2g^{-1}.

In summary, three novel 3D copper cyanide frameworks have been obtained by transforming organonitrile into inorganic cyanide. We believe that optimization of this method will open a new synthetic route for new cyanide-containing materials.

Supporting Information Available: X-ray crystallographic file (CIF) for **1**, **2**, and **3**, other structural CIFs, XPS spectra, TGA traces, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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