Hydrothermal Syntheses, Crystal Structures, and Properties of Two-Dimensional Homo- and Heterometallic Cyanide-Bridged Complexes: [Cu$_2$(CN)$_2$(bpym)] and [Fe(bipy)$_2$(CN)$_4$Cu$_2$] (bpym = 2,2'-Bipyrimidine, bipy = 2,2'-Bipyridine)

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The hydrothermal reaction of K$_3$[Fe(CN)$_6$], CuCl$_2$, and 2,2'-bipyridine (bipy) resulted in the formation of a 2D cyanide-bridged heterobimetallic Fe(II)–Cu(I) complex, [Fe(bipy)$_2$(CN)$_4$Cu$_2$], **1**. Working in the same conditions, but using 2,2'-bipyrimidine (bpym) instead of bipy and methanol as solvent, we obtained the homometallic Cu(I) complex [Cu$_2$(CN)$_2$(bpym)]$_2$, **2**. The structure of **1** consists of cyanide-bridged Fe(II)–Cu(I) layers, constructed from alternately fused 6 (Fe$_2$Cu$_4$) and 10 (Fe$_2$Cu$_8$) metal-membered centrosymmetric rings, in which copper(I) and iron(II) ions exhibit distorted trigonal planar and octahedral coooordination environments, respectively. The formation of **1** can be explained by assuming that, under high pressure and temperature, iron(III) and copper(II) ions are reduced with the simultaneous and/or subsequent substitution of four cyanide ligands by two bipy molecules in the ferricyanide anions. It is interesting to note that **1** is the first cyanide-bridged heterobimetallic complex prepared by solvothermal methods. The structure of **2** consists of neutral 2D honeycomb layers constructed from fused Cu$_6$(CN)$_4$(bpym)$_2$ rings, in which copper(I) atoms exhibit distorted tetrahedral geometry. The isolation of **1** and **2**, by using K$_3$[Fe(CN)$_6$] as starting material, demonstrates that hydrothermal chemistry can be used not only to prepare homometallic materials but also to prepare cyanide-bridged bimetallic materials. The temperature dependence of $\chi_M T$ and Mössbauer measurements for **1** reveal the existence of a high spin ↔ low spin equilibrium involving the Fe(II) ions.

Introduction

In the past few years, there has been considerable interest in the design and elaboration of multidimensional polymetallic coordination polymers.[1] This is not only due to their potential applications in electrical conductivity, molecule-based magnets, molecular absorption, ion-exchange, heterogeneous catalysis, etc., but also because of their intriguing structural diversity.[2] Among these materials, cyanide-bridged bimetallic systems, prepared by assembling cyanometalates and transition metal complex building blocks, have been shown to exhibit fascinating structures and interesting magnetic, electrochemical, magnetooptical, and zeolitic properties.[3] While a majority of synthetic procedures of these systems still follow conventional solution routes, increasing interest has been paid to the less conventional solvothermal

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techniques. In fact, Zubieta's group has recently reported a great variety of homometallic cyanide-bridged copper(I) extended systems, which were constructed through hydrothermal techniques by using CuCN and aromatic imine ligands as starting materials.[4,5] The topological characteristics of these systems strongly depend on the nature of both metal and organic ligands. In this paper, we report that, under hydrothermal conditions, reaction of $K_3[Fe(CN)_6]$, $CuCl_2$, and 2,2′-bipyridine (bipy) results in the formation of a 2D cyanide-bridged bimetallic Fe(II)−Cu(I) complex, $[Fe(bipy)_2(CN)_4Cu_2]$, **1**. As far as we know, this compound is the first cyanide-bridged bimetallic complex prepared by solvothermal techniques. It is of interest that working in the same conditions, but using bpym (2,2′-bipyrimidine) instead of bipy and methanol as solvent, the homometallic Cu(I) compound $[Cu_2(CN)_2(bpym)]$, **2**, was obtained.

Experimental Section

Preparation of the Complexes. [Fe(bipy)₂(CN)₄Cu₂], 1. A mixture of $CuCl_2$ (0.172 g, 1.28 mmol), 2,2′-bipyridine (0.199 g, 1.28 mmol), $K_3[Fe(CN)_6]$ (0.42 g, 1.28 mmol), and water (8 mL) was added to a Teflon-lined stainless steal Parr acid digestion vessel and heated at 170 °C for 3 days under autogenous pressure. After slow cooling to room temperature, dark red crystals of **1** were recovered as a pure phase. The yield was 45% based on 2,2′-

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Table 1. Crystallographic Data and Structural Refinement Details for Compounds

	1	**2**
empirical formula	$C_{24}H_{16}Cu_2FeN_8$	$C_{10}H_6Cu_2N_6$
fw	599.38	337.29
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	*P2₁/c*
a (Å)	17.076(3)	8.6661(5)
b (Å)	18.007(3)	8.7732(6)
c (Å)	15.895(3)	8.8312(7)
β (deg)	90	114.924(3)
V (Å³)	4887.5(15)	608.90(7)
Z	8	2
T (K)	193(2)	173(2)
λ (Å)	0.71069	0.71073
ρ (g cm⁻³)	1.629	1.840
μ (mm⁻¹)	2.339	3.480
GOF	1.040	1.114
R1[a] $[I > 2\sigma(I)]$	0.0540	0.0499
wR2[b] $[I > 2\sigma(I)]$	0.1193	0.0996

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

bipyridine. Anal. Calcd for $C_{24}H_{16}N_8FeCu_2$: C, 48.09; H, 2.69; N, 18.69. Found: C, 47.86; H, 2.87; N, 18.63. A Fe/Cu ratio of 0.51 was determined by SEM (scanning electron microscopy).

[Cu₂(CN)₂(bpym)], 2. Hydrothermal treatment of $CuCl_2$(0.043 g, 0.032 mmol), bipyrimidine (0.05, 0.32 mmol), $K_3[Fe(CN)_6]$ (0.105 g, 0.32 mmol), and methanol (8 mL) over 4 days at 180 °C gave, after slow cooling to room temperature, a brown powder and dark-red crystals of **2**. The yield was 25% based on bipyrimidine. Anal. Calcd for $C_{10}H_6N_6Cu_2$: C, 35.61; H,1.79; N, 24.92. Found: C, 35.22; H, 1.71; N, 24.48. It should be noted that when the same conditions as those employed for **1** were used, no crystals formed.

Physical Measurements. Elemental analyses were carried out at the Instrumentation Scientific Center of the University of Granada on a Fisons-Carlo Erba analyzer model EA 1108. IR spectra were recorded on a MIDAC progress-IR spectrometer using KBr pellets. Magnetization and variable-temperature (1.7−300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID operating at different magnetic fields. Experimental susceptibilities were corrected for diamagnetism and the magnetization of the sample holder.

X-ray Structure Determinations. Single-crystal data collection for **1** was performed at −80 °C on a Rigaku AFC7S diffractometer using graphite monochromatized Mo Kα radiation and the $\omega/2\theta$ scan mode ($2\theta_{max} = 50.5°$), while a crystal of **2** was measured on a Enraf Nonius KappaCCD diffactometer at −100 °C ($2\theta_{max} = 54.9°$). Totals of 4415 and 1365 unique reflections were collected for **1** and **2**, respectively. The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[6] For **1**, careful refinements indicated that all cyanide groups are ordered. For **2**, the bridging cyanide group is disordered with respect to the C and N termini, and refinement resulted in major occupancy of 0.781(12) for the Cu−N1a connectivity and minor occupancy of 0.219(12) for the Cu−C1b connectivity. The disordered CN atom positions of **2** are labeled in Table 3 and Figure 3 with X1 and X2. For both compounds, non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

The crystal data and details of refinement for the compounds are summarized in Table 1. Bond lengths and angles for the compounds are gathered in Tables 2 and 3.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Fe-C1	1.892(6)	Cu1−N4#2	1.919(5)
Fe−C2	1.895(6)	Cu2−N2	1.944(5)
Fe−N5	1.970(4)	Cu2−N3	1.952(5)
Fe−N16	1.996(4)	Cu2−C4	1.857(6)
Fe−N17	1.979(4)	N1−C1	1.158(7)
Fe−N28	1.994(4)	N2−C2	1.156(7)
Cu1−N1	1.950(5)	N3−C3	1.128(7)
Cu1−C3#1	1.875(5)	N4−C4	1.150(7)
C2−Fe−N16	173.83(19)	N3−C3−Cu1#1	171.5(5)
N5−Fe−N16	80.95(17)	C4−N4−Cu1#3	176.9(6)
N5−Fe−N17	178.10(19)	N4−C4−Cu2	175.2(5)
C1−Fe−N28	173.42(19)	C1−Fe−C2	92.6(2)
N17−Fe−N28	80.90(18)	C1−Fe−N5	88.9(2)
N4#2−Cu1−N1	105.8(2)	C2−Fe−N5	92.99(19)
C3#1−Cu1−N1	122.9(2)	C1−Fe−N17	92.6(2)
C3#1−Cu1−N4#2	131.3(2)	C2−Fe−N17	88.1(2)
C4−Cu2−N2	131.9(2)	C2−Fe−N28	88.3(2)
N2−Cu2−N3	102.33(19)	N5−Fe−N28	97.57(18)
C4−Cu2−N3	124.5(2)	N17−Fe−N28	80.90(18)
C1−N1−Cu1	161.5(5)	C1−Fe−N16	88.5(2)
N1−C1−Fe	175.2(5)	N17−Fe−N16	97.93(18)
C2−N2−Cu2	149.6(4)	N28−Fe−N16	91.30(18)
N2−C2−Fe	175.7(5)		
C3−N3−Cu2	164.0(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1, −x + 1, −y + 1, −z + 1; #2, −x + 1/2, y + 1/2, z; #3, −x + 1/2, y − 1/2, z.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Cu−X2#1	1.8992(16)
Cu−X1	1.9321(14)
Cu−N2	2.1235(15)
Cu−N6#2	2.1702(12)
X1−X2	1.152(2)
X2#1−Cu−X1	125.61(6)
X1−Cu−N2	112.91(6)
X2#1−Cu−N6#2	119.24(6)
X1−Cu−N6#2	97.90(5)
N2−Cu−N6#2	77.53(5)
X2−N1A-Cu	171.02(17)
X1−X2-Cu#3	173.44(16)

[a] Symmetry transformations used to generate equivalent atoms: #1, −x + 1, y + 1/2, −z + 3/2; #2, −x, −y, −z + 1; #3, −x + 1, y − 1/2, −z + 3/2.

Results and Discussion

It is well-known that hydrothermal methods allow the preparation of a rich variety of systems exhibiting intriguing architectures and new topologies.[7] Owing to the complexity of the solvothermal reactions, in principle, the control and prediction of crystal structures would not be possible. Nevertheless, it is clear from empirical observations that the architecture of the final product directly depends on the subtle interplay of the characteristics of metal ion (oxidation state, coordination preferences, plasticity of the coordination sphere, available coordination positions, redox capability, etc.) and ligand (type and number of donor groups, bridging capability, connectivity, steric constraints, etc.), as well as on the reaction conditions (temperature, heating time, solvent, etc.). For instance, the hydrothermal chemistry of CuCN with aromatic diimine ligands has been exploited to prepare a variety of homometallic 1D to 3D cyanide-bridged copper-(I) materials, for which subtle changes in some of the already mentioned factors often result in the formation of quite different structures.[4,5]

It should be pointed out that, as far as we know, no cyanide-bridged bimetallic complexes have been prepared by the solvothermal technique. In view of this and the great versatility of hydrothermal methods with regard to the almost limitless set of construction components that can be used, we decided to explore the possibility of preparing cyanide-bridged bimetallic assemblies from cyanometalate anions, metal cations, and aromatic nitrogen-containing ligands, these latter acting either as structure propagating or passivating agents about a metal site. Thus, hydrothermal reaction of $CuCl_2$, bipy, and $K_3[Fe(CN)_6]$ in water, using a 1:1:1 molar ratio, leads to the formation of the iron(II)−copper(I) heterometallic compound $[Fe(bipy)_2(CN)_4Cu_2]$, **1**. Under the reaction conditions, high pressure and temperature, iron(III) and copper(II) ions are reduced to iron(II) and copper(I) with the simultaneous and/or subsequent substitution in the ferricyanide anions of four cyanide ligands by two bipy molecules. Free cyanide from the dissociation of $[Fe(CN)_6]^{3-}$ probably functions as the main reducing agent yielding cyanogen $(CN)_2$ as oxidation product.

When, in the same hydrothermal conditions, bpym is used instead of bipy, no crystals formed. However, the use of methanol and a prolonged reaction time resulted in the formation of crystals of $[Cu_2(CN)_2(bpym)]$ (**2**) instead of the expected bimetallic complex. It should be noted that the use of KCN instead of $[Fe(CN)_6]^{3-}$ as source of cyanide anions did not yield **2** but the complex $[Cu_2(CN)_2(bpym)]\cdot H_2O$. X-ray powder diffraction studies have revealed that the structure of this compound is different from that of **2.** This result seems to indicate that the $Fe(CN)_6]^{3-}$ anion plays a role in the formation of **2**. The IR spectrum of **1** exhibits $\nu(CN)$ stretching bands at 2085, 2100, and 2121 cm^{-1}, pointing out the existence of different types of cyanide bridges in the structure. The IR spectrum of **2**, however, only exhibits one $\nu(CN)$ stretching band at 2120 cm^{-1}, which agrees well with the presence of only one type of cyanide bridge between copper(I) atoms.

X-ray Structures. The asymmetric unit of the structure of **1** together with the atomic labeling scheme is given in Figure 1. The structure consists of 2D layers, parallel to the *ab* plane, constructed from alternately fused 6 and 10 metal-membered centrosymmetric rings, in which metal centers are bridged by cyanide groups. The 6-metal rings (Fe_2Cu_4) exhibit a chair conformation and are defined by the sequence ($Fe^{II}−Cu^I−Cu^I−Fe^{II}−Cu^I−Cu^I$). Four adjacent rings of such kind form a larger 10 metal-membered ring (Fe_2Cu_8) defined by the sequence $\{(Cu^I)_4−Fe^{II}-(Cu^I)_4−Fe^{II}\}$. Each 10-metal ring shares 4 edges with 4 adjacent perpendicularly aligned 10-metal rings and 6 edges with 4 neighboring 6-metal rings, and each 6-metal ring shares all edges with 4 10-metal rings to form a unique 2D topology (Figure 2).

A similar 2D anionic structure has been recently reported for $[Ni(phen)_2V_4O_{11}]$.[8] Although this compound contains V_6 and V_{14} rings constructed from oxygen sharing VO_4 tetra-hedra, the orientation of these rings in the sheets is the same

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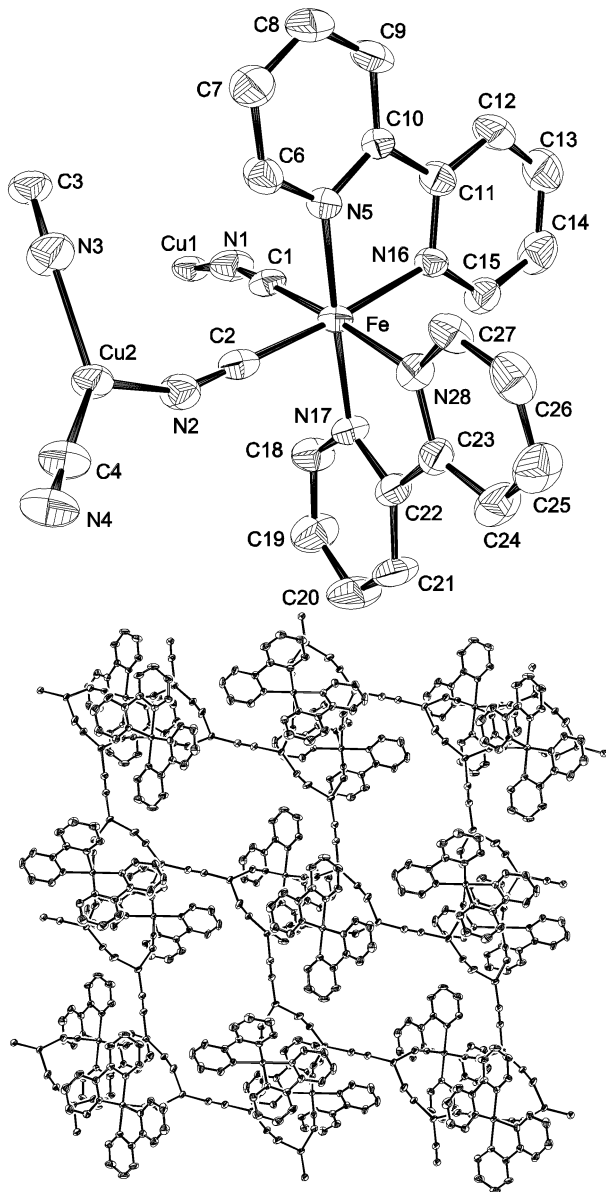
Figure 1. Perspective views of the asymmetric unit and network structure of **1**.
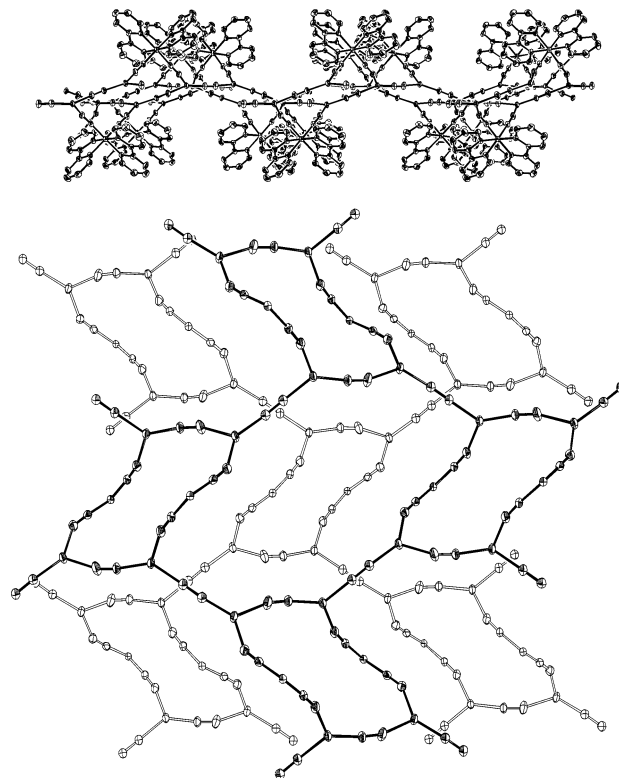

Figure 2. View down the *b* axis of a layer of **1** (top) and the stacking of two-dimensional sheets in **1** (bottom, bipyridine atoms are omitted for clarity).

as for **1**. As expected, the Fe_2Cu_8 rings are larger than the Fe_2Cu_4 rings, with approximate dimensions of 16×9.5 Å^2 and 10.5×6 Å^2, respectively. Within these rings, Fe^{II} atoms, which exhibit a distorted octahedral environment, are coordinated by four nitrogen atoms from two bidentate bipyridine ligands and two carbon atoms from two cyanide groups, these latter adopting a *cis* orientation and bridging each Fe^{II} atom to two Cu^I atoms. Although these cyanide bridges can adopt two orientations, Fe−CN−Cu and Fe−NC−Cu, a comparison of the C- and N-atom thermal parameters and overall residual factors in structural refinements performed on both orientations clearly points to the Fe−CN−Cu connectivity in the compound. Additional supporting evidence of the Fe−CN−Cu orientation includes short Fe−C distances and Fe−C−N angles closer to linearity than Cu−N−C angles as a consequence of the more covalent interaction with the Fe^{II} centers. Bond distances and angles around Fe^{II} atoms are comparable with those found for other cyanide-bridged

bimetallic complexes, prepared from the $[Fe(bipy)_2(CN)_2]$ building block.[9] For instance, in the molecular squares $[Fe_2-Cu_2(\mu\text{-}CN)_4(bipy)_6](PF_6)_4 \cdot 2H_2O \cdot 4CHCl_3$[9a] and $[Fe_2Co_2(\mu\text{-}CN)_4(bipy)_8](PF_6)_6 \cdot 2CHCl_3 \cdot 4CH_3NO_2$,[9b] both containing low spin $[Fe(bipy)_2(CN)_2]$ units like those of **1**, the Fe−C and C−N distances involving the cyanide groups were found in the ranges 1.878(7)−1.893(7) and 1.151(8)−1.161(8) Å, respectively. These distances, as it can be observed in Table 2, are very close to those found for **1**. Chiral Fe^{II} atoms, which are related by centers of symmetry located at the barycenter of the 6- and 10-membered rings, display opposite absolute configuration, and then, the crystal as a whole is racemic. There are two crystallographically independent Cu^I atoms in the structure, Cu1 and Cu2. Both sites assume a distorted trigonal-planar geometry through coordination to three cyanide groups, two bridging Cu^I atoms and the third one bridging Fe^{II} and Cu^I atoms. It should be noted that, according to calculations, none of the cyanide groups are disordered. The Fe···Cu1, Fe···Cu2, and Cu1···Cu2 distances across cyanide bridges are 4.916, 4.803, and 4.920 Å, respectively. A view down the *b* axis shows that Fe(bipy)$_2$ units are oriented in pairs above and below the mean plane of the sheet, giving rise to a sinuosidal wave motif (Figure 2). The space filling is achieved by appropriate stacking of layers, interdigitating bipy ligands in such a fashion as to align the bipy groups above and below one sheet with the

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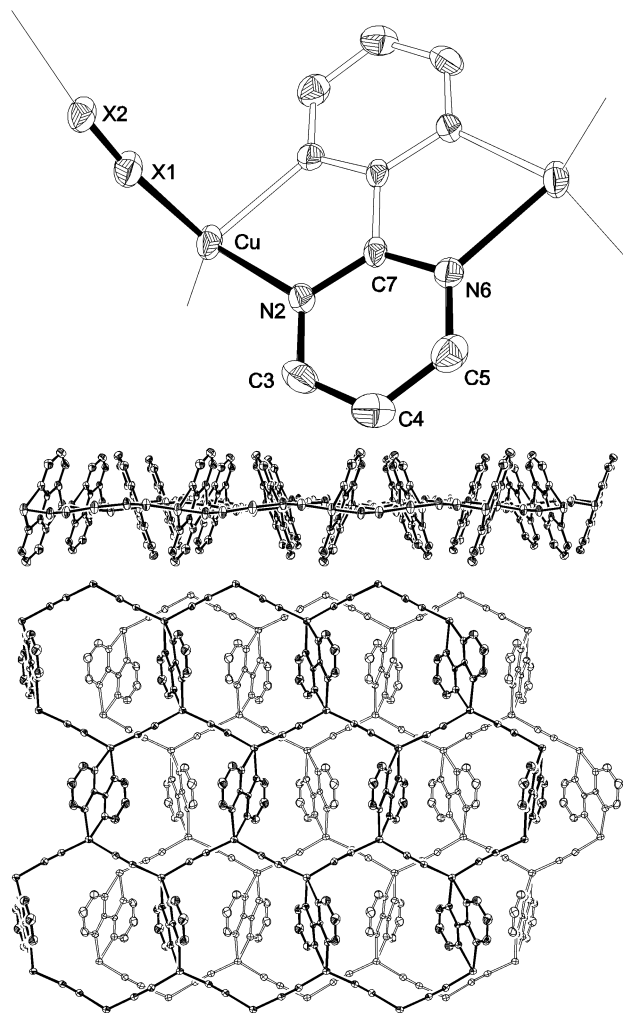
Figure 3. Asymmetric unit of **2** (top). Atoms from the disordered CN bridging groups are labeled as X. A view parallel to the plane of **2** (middle). The stacking of networks in **2** (bottom).

Figure 4. Thermal variation of $\chi_M T$ and Mössbauer spectra for **1**.

cavities in neighboring networks (Figure 2). This ultimately leads to an ABAB repeat pattern of layers, with a distance between mean-square planes through the atoms of the layers A and B of 7.94 Å.

It is noteworthy that **1** is the first example of a 2D layered cyano-bridged complex constructed of 6,10-net sheets and also the first example of a cyano-bridged bimetallic complex prepared by hydrothermal methods.

The structure of **2** is shown in Figure 3. A view down the *c* axis reveals that the crystal structure of **2** consists of neutral 2D (6,3) honeycomb layers constructed from fused $Cu_6(CN)_4$-$(bpym)_2$ rings. Alternatively, the structure may be described as constructed from puckered $\{Cu(CN)\}_\infty$ chains running along the *b* direction, linked by linear bis bidentate bridging bpym ligands to generate the (6,3) net topology. In this description, each Cu^I site, in a distorted tetrahedral coordination environment, is coordinated by two bridging cyano groups of the chain and one bridging bis bidentate bpym ligand. The distortion of Cu^I coordination polyhedron is mainly due to the small bite angle of the bpym leading to bond angles in the range 77.53−125.61°. The Cu···Cu distances across the bpym and cyanide ligands are 5.738 and
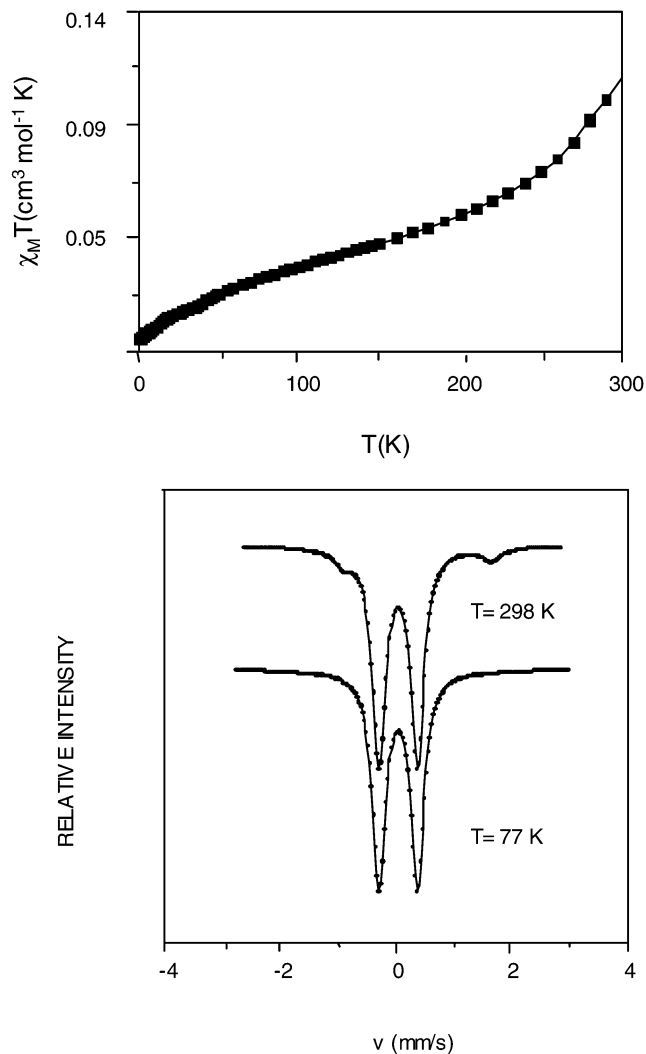
4.948 Å, respectively, whereas Cu···Cu distances across the ring range from 9.437 to 11.433 Å. The plane of the bpym is canted at 73° with respect to the layer plane. The bpym bridging ligands bonded to adjacent Cu atoms of the chain are tilted in opposite directions with respect to the normal to the network. The stacking of layers is in such a way that orients the sterically demanding bypm groups to project above and below the ring cavities of adjacent networks, giving rise to an ABAB repeat pattern of layers. The distance between mean-square planes through the atoms of the sheets A and B is 4.4 Å.

It should be noted that the network structure of **2** is topologically identical to those described for a series of systems prepared from hydrothermal chemistry of CuCN with linear dipodal ligands such as tetramethylpyrazine, quinoxaline, and phenazine.[4] In these materials, copper(I) atoms exhibit a trigonal-planar geometry as the linear bridging ligands are all bidentate, whereas for **2** the linear ligand is bis bidentate and, consequently, copper(I) atoms are four coordinated, adopting a tetrahedral geometry.

Magnetic Properties. The temperature dependence of $\chi_M T$ for **1** is given in Figure 4. The $\chi_M T$ value at 300 K of

0.125 cm^3 mol^{-1} K (1 μB) represents only about 4% of the expected value for an isolated high spin iron(II) ion ($S = 2$, $g = 2$). As the temperature decreases, the $\chi_M T$ value decreases markedly until ca. 150 K and then very slowly to a value of 0.052 cm^3 mol^{-1} K at 2 K. Even though the $\chi_M T$ values are very small, such magnetic behavior is consistent with that expected for a high spin $\leftrightarrow$ low spin equilibrium involving the Fe(II) atoms. The HS $\leftrightarrow$ LS equilibrium is corroborated by ^{57}Fe Mössbauer spectral measurements (Figure 4).

At room temperature, the spectrum of **1** shows features characteristic of both the high and low spin forms. Despite the very low population of the HS form, the high spin signal can be resolved from the spectrum background, with isomer shift (δ) and quadrupole splitting (ΔE_Q) values of 0.364 and 2.543 mm s^{-1}, respectively, whereas the LS signal, which is much more intense, has δ and ΔE_Q typical values of 0.038 and 0.661 mm s^{-1}, respectively. At 77 K, as the magnetic data reveal, all iron(II) atoms are in the low spin form, and consequently, the spectrum shows only the low spin signal with δ and ΔE_Q values of 0.113 and 0.702 mm s^{-1}, respectively. It is of interest that, recently, a series of cyanide-bridged Fe^{II}−M (M = Pd^{II}, Ni^{II}, Pt^{II}, Au^{I}, Ag^{I}) have been reported to exhibit thermal-, pressure-, and light-induced spin crossover transitions.[10]

In conclusion, the isolation of **1** and **2**, by using K$_3$[Fe(CN)$_6$] as starting material, demonstrates that hydrothermal chemistry is a flexible and effective synthetic tool to prepare not only homometallic but also cyano-bridged bimetallic materials. In view of this, solvothermal reactions involving different cyanometalate complexes and a wide variety of polydentate bridging ligands are currently under investigation with the aim of obtaining new cyanide-bridged materials exhibiting interesting structures and properties.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034155U

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