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Structures with Tunable Strong Ferromagnetic Coupling: from Unordered (1D) to Ordered (Discrete)

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Abstract: The X-ray crystal structures, magnetic susceptibilities from 2 to 300 K, and theoretical analyses of the magnetism for 1D and trinuclear azido Cu^{II} carboxylate complexes $[Cu_{1.5}(hnta)(N_3)_2(H_2O)]_n$ (**1**) and $[Cu_3(hnta)_4(N_3)_2(H_2O)_3]$ (**2**), respectively, where hnta is 6-hydroxynicotinate, are described. Although both exhibit strong ferromagnetic coupling, discrete complex **2** exhibits long-range ferromagnetic ordering, while the very similar 1D system **1** does not. Density functional calculations provided accurate J values and allowed rationalization of the ferromagnetic coupling in terms of the magnetic orbitals and spin densities.

Keywords: azides · carboxylate ligands · copper · density functional calculations · magnetic properties

Introduction

Molecule-based magnetic materials have been widely explored by theoretical chemists with the goal of accurately predicting the magnetic behavior of materials by understanding magnetostructural correlations, and by synthetic coordination chemists for preparing materials with desired magnetic properties.[1] To predict, design, control, and synthesize such materials, it is necessary to obtain insight into the relationship between structure and magnetic properties by combining synthetic chemistry with theoretical chemistry and solid-state physics.[2] Frequently, theoretical analyses or calculations are based on models, the relation between the structural parameters and magnetic characteristics are discussed, and perfect agreement between theory and experiment implies that these models can correctly give primary information about the magnetic coupling.[3] Furthermore, it has been demonstrated that various factors such as strict and accidental orthogonality of magnetic orbitals, spin polarization, and delocalization of unpaired electrons including charge transfer, have considerable influence in determining the nature of the magnetic coupling between spin centers.[4]

Moreover, the judicious selection of ligands to provide superexchange pathways for exchange coupling between metal spin centers is vital for synthetic chemists to synthesize magnetic materials.[5] Azido is a good bridging ligand and has been extensively explored by researchers,[6] probably because it can mediate ferromagnetic coupling in $\mu_{1,1}$ bridging mode (end-on, EO) and antiferromagnetic interactions in $\mu_{1,3}$ bridging mode (end-to-end, EE), in spite of several exceptions.[7] Carboxylate ligands are another hot topic in molecular magnetism, and exciting results such as single-chain and single-molecule magnets are gradually being reported,[8,9] especially after the emergence of Mn_{12}.[8a] To understand the magnetic exchange interaction mechanism of azide and carboxylate ligands, Ruiz and co-workers have established some models in which either of them acts as a bridging group between metal spin centers.[5,10] The synthetic chemistry of systems in which azide and carboxylate simultaneously act as bridging ligands has thrived in recent years,[11] but their structural models are scarcely developed, and theoretical studies are still in their infancy.[12]

Here, we report the syntheses, structures, and magnetic properties of $[Cu_{1.5}(hnta)(N_3)_2(H_2O)]_n$ (**1**) and $[Cu_3(hnta)_4(N_3)_2(H_2O)_3]$ (**2**), where hnta is 6-hydroxynicotinate, both of which show strong ferromagnetic coupling. As an

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important and surprising difference between them, discrete complex **2** exhibits long-range ferromagnetic ordering, while the very similar 1D system **1** does not. Moreover, we provide rationalization for the strong ferromagnetic coupling using DFT calculations, owing to the extreme uncertainty in calculating the *J* values from the experimental data. The calculated spin densities and the magnetic orbitals explain all these features well.

Results and Discussion

Syntheses: Although we have not experienced any problems in this work, azide and its complexes are potentially explosive. Only small amounts of the materials should be prepared and handled with care. All experiments were carried out in an isolated room, and all experimenters wore protective equipment. Both **1** and **2** can be synthesized in one pot at 140 °C over two days by mixing $Cu(NO_3)_2 \cdot 6H_2O$, NaN_3, 6-hydroxynicotinate, and H_2O in a ratio of 1:1:1:1000 without adjusting the pH value. To obtain pure products, the ratio of reagents and pH value were changed. By controlling the ratio and adjusting the pH value with triethylamine, black needlelike crystals of pure **1** and green block crystals of pure **2** were obtained.

Structures: Complex **1** is a unique alternating 1D Cu^{II} system (Figure 1), which differs from the azido–metal chains (EE, EO, EO/EE, EO/EO/EO/EO/EE, EO/EE/EE)[13] and N_3/M/RCOO chains reported before.[12,14] Cu1 has an elongated octahedral coordination environment (CuO_4N_2) and is located at the crystallographic inversion center, while Cu2 has a slightly distorted square-based pyramidal coordination environment (CuO_2N_3). The axial positions of Cu1 are occupied by two H_2O ligands (Cu2−O1W 2.504 Å), and the equatorial plane is formed by two oxygen atoms of carboxylates (Cu1−O1 1.950 Å) and two nitrogen atoms of two $\mu_{1,1}$ azide ligands (Cu1−N2 2.007 Å). The apical position of Cu2 is occupied by a bridging H_2O ligand (Cu2−O1W 2.414 Å), and the equatorial plane completed by a carboxlato oxygen atom (Cu2−O2 1.937 Å) and three nitrogen atoms from three $\mu_{1,1}$-azido ligands (Cu2−N2 1.973, Cu2−N5 1.977, Cu2−N5A 2.000 Å). In **1**, the Cu1-N2-Cu2 and Cu2-N5-Cu2 angles in the EO bridges are 103.21 and 99.17°, respectively. One *syn–syn* carboxylato and one $\mu_{1,1}$-azido ligand (the bridging H_2O ligand has a longer distance to Cu1) link two consecutive Cu^{II} centers to form trinuclear Cu^{II} entities (Cu2-Cu1-Cu2), which are connected into 1D chains by double $\mu_{1,1}$-azido bridges (Figure 1).

Compound **2** is an unusual trinuclear Cu^{II} complex (Figure 2). Cu1 has a distorted octahedral (CuO_4N_2) and Cu2 a distorted square-based pyramidal (CuO_4N) coordination geometry. The axial positions of Cu1 are occupied by two equivalent carboxylate oxygen atoms (Cu1−O2 1.933 Å), and the equatorial plane is formed by two equivalent terminal H_2O ligands (Cu1−O3W 2.543 Å) and two equivalent nitrogen atoms of two $\mu_{1,1}$-azido ligands (Cu1−N1 1.983 Å). The apical position of Cu2 is occupied by a terminal H_2O ligand (Cu2−O2W 2.249 Å), and the equatorial plane is completed by a terminal H_2O ligand (Cu2−O1W 2.087 Å), a nitrogen atom of a $\mu_{1,1}$-azido ligand (Cu2−N1 2.005 Å), and two oxygen atoms from two different carboxylato ligands (Cu2−O3 1.927, Cu2−O5 1.948 Å). The Cu1-N1-Cu2 angle in the EO bridges is 116.2°, which is larger than that of **1**. Notably, besides intermolecular hydrogen bonds and π–π interactions, intermolecular interactions occur between the terminal nitrogen atoms of the azido ligands of one entity and the nitrogen atoms of the pyridine ring of the neighboring entity (Figure 3).

Magnetic properties: For **1**, the $\chi_m T$ versus *T* curve for three Cu^{II} ions is shown in Figure 4. The $\chi_m T$ value at room temperature of 1.60 $cm^3 mol^{-1} K$, which is greater than that expected for three isolated Cu^{II} ions (ca. 1.20 $cm^3 mol^{-1} K$), in-

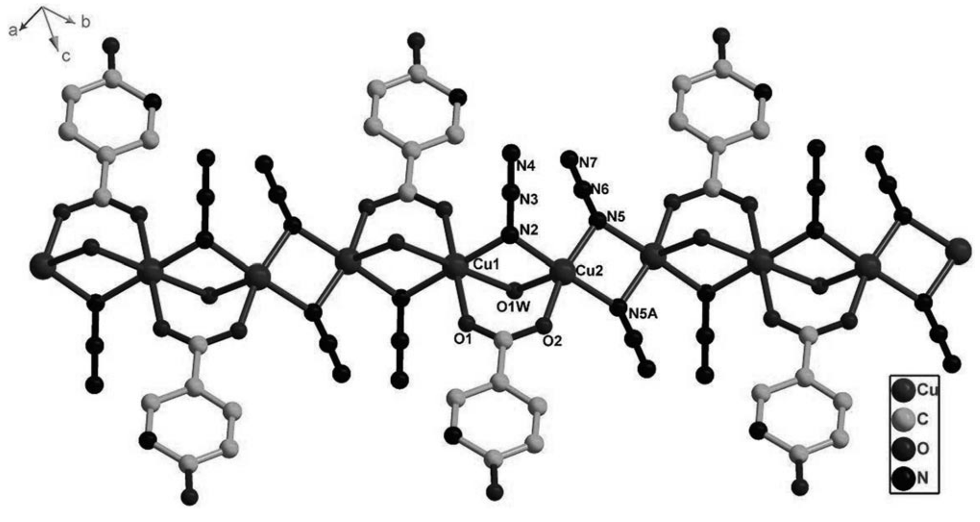

Figure 1. The unprecedented 1D alternating chain of **1**.

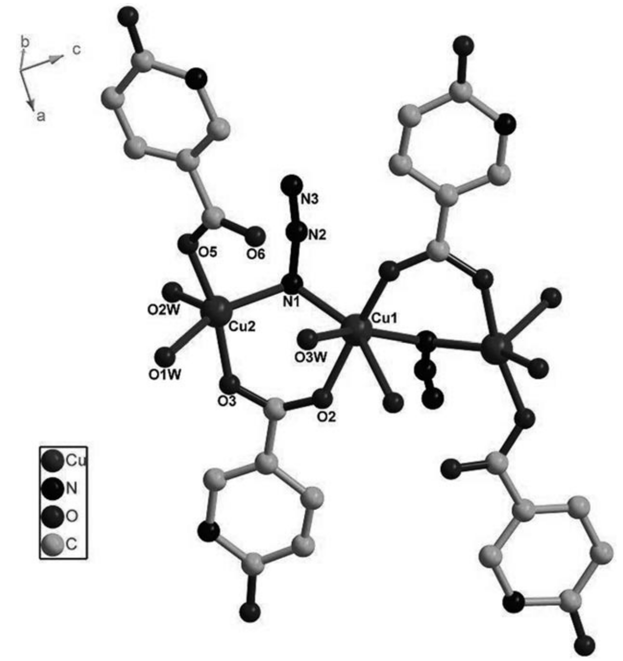

Figure 2. Isolated trinuclear unit of **2**.

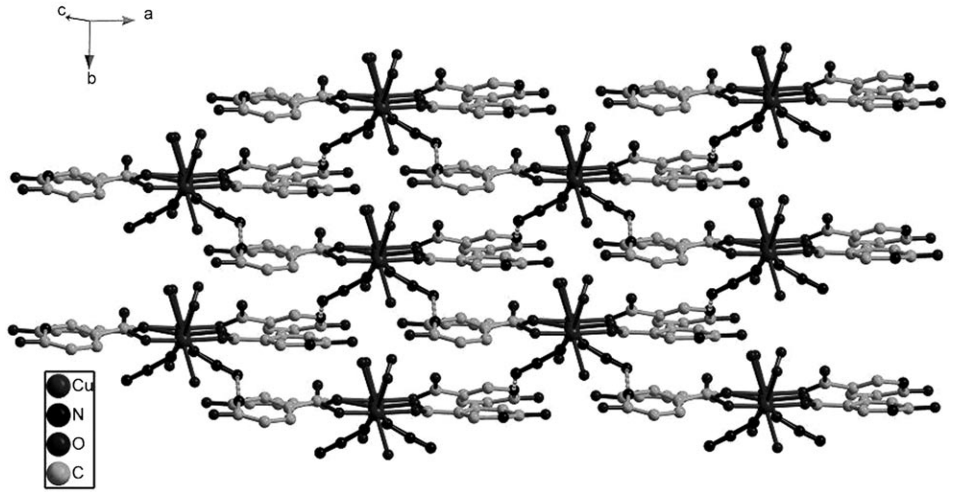

Figure 3. Packing of the trinuclear entities in **2**, showing the close proximity of the azido groups of one trinuclear unit to the pyridine ring of its neighbor.

creases to 14 $cm^3 mol^{-1} K$ at 4 K (short-order correlation in a ferromagnetic chain), and finally decreases between 4 and 2 K to 3 $cm^{-3} mol^{-1} K$. This kind of curve is a typical signature of a strongly coupled ferromagnetic system, with antiferromagnetic coupling between the chains, noticeable only at very low temperatures. In the literature there is no analytical formula for an alternating ferro–ferro 1D $S=1/2$ chain. In attempted fitting with the Clumag program,[15] the results dramatically depend on the cutoff temperature range (Clumag can treat only up to a ring of 12 Cu^{II} ions). The

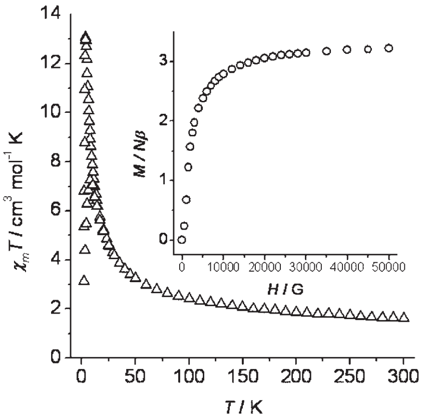

Figure 4. Plot of $\chi_m T$ versus T for **1**. Inset: Plot of reduced magnetization versus H at 2 K.

curve of the reduced magnetization (for three Cu^{II} ions) at 2 K tends to $3.2 N\beta$ at 5 T (Figure 4 inset), but the shape of the curve is far from the Brillouin function. Indeed, the rapid increase of the curve at low field indicates ferromagnetic ordering or very large J values.

To corroborate (or refute) the existence of ferromagnetic long-range ordering, measurements of the ac susceptibility and hysteresis loop were made, but with negative results. The shape of the $\chi_m T$ curve and the tendency to increase in a very pronounced form is thus due to intrachain ferromagnetic coupling. As indicated above, it is not possible to calculate the J values from experimental data. However, the slope of the curve indicates strong ferromagnetic coupling.

For **2**, the $\chi_m T$ versus T curve for three Cu^{II} ions is shown in Figure 5. The $\chi_m T$ value at room temperature of 1.60 $cm^3 mol^{-1} K$, which is greater than that expected for three isolated Cu^{II} ions (ca. 1.20 $cm^3 mol^{-1} K$), increases to 25 $cm^3 mol^{-1} K$ at 4 K, and decreases between 4 and 2 K to 3 $cm^3 mol^{-1} K$. Like **1**, this curve also implies a strongly coupled ferromagnetic system. Furthermore, the final $\chi_m T$ value (25 $cm^3 mol^{-1} K$) at 4 K is inappropriate for a trinuclear Cu^{II} complex unless it is ferromagnetically ordered in a 3D network. Indeed, the $\chi_m T$ value is field-dependent (Figure 5).

To corroborate this hypothesis, ac measurements were carried out and the hysteresis loop was determined. The hysteresis loop (Figure 6) does not give clear evidence for magnetic ordering. Although there is an abrupt increase in $N\beta$ at very low fields, the gap between the increasing and de-

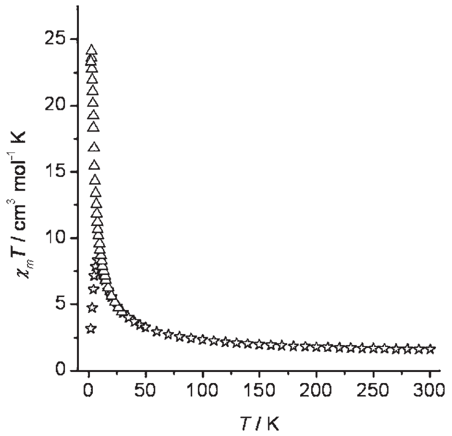

Figure 5. Plot of $\chi_m T$ versus T for **2** in external fields of 200 (triangles) and 2000 G (stars).

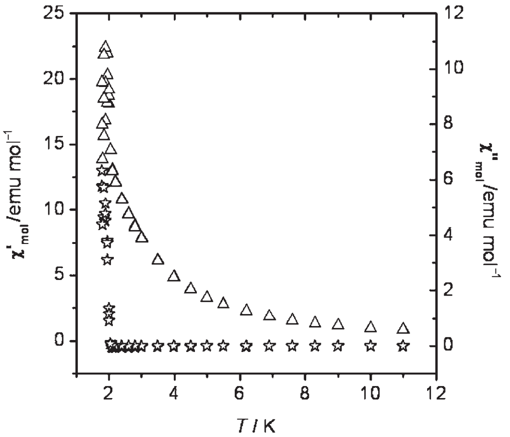

Figure 7. Alternating-current susceptibility measurements for **2** at low temperature. Triangles correspond to the in-phase signal and stars to the out-of-phase signal.

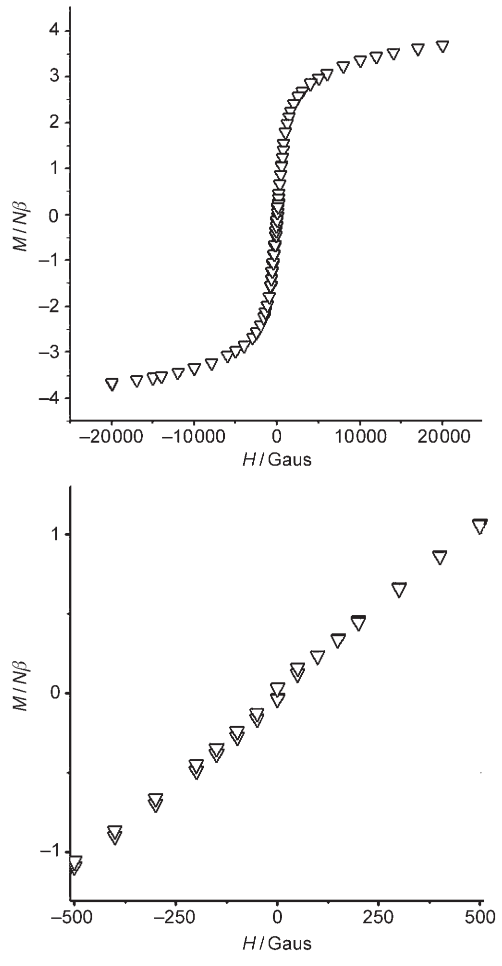

Figure 6. Hysteresis loop (top) and central part of the hysteresis loop (bottom) for **2**.

creasing values is only slightly noticeable at very low fields (Figure 6). However, the ac measurements (Figure 7) clearly indicate the existence of this magnetic ordering, although the T_c will be less than 2 K. Indeed, there is a strong out-of-phase signal, frequency-independent, without a maximum in the range of temperatures studied (<2 K; Figure 7).

DFT calculations: To understand the magnetic behavior and gain insight into the exchange mechanism in **1** and **2**, DFT calculations were performed with the Gaussian03 program,[16] using the B3LYP functional[17] and an Ahlrichs TZVP basis[18] for Cu^{II} ions, and an Ahlrichs SVP basis set for the remaining atoms.[19] For **1**, the J values were calculated for the two different Cu-bridge-Cu dimers that can be taken from the chain by using the Hamiltonian $H=-JS_1S_2$. The broken-symmetry procedure was used to evaluate the singlet-state energy. The J value was obtained from $[E(\mathrm{Tr})-E(\mathrm{BSS})]$ (Tr = triplet; BSS = broken-symmetry singlet). For the double azido moiety the calculated J values are $+199.1$ cm^{-1} and $+89.0$ cm^{-1} for the second moiety (azide + carboxylate). The J value of about 200 cm^{-1} is one of the largest found for this kind of systems, in agreement with the corresponding Cu-N-Cu angle (99.18°) which is one of the smallest reported to date.[10a] It seems logical that the two-azido moiety has a J value greater than that of the moiety with one azido and one carboxylato bridge, because the Cu-N-Cu angle is 103.21° (> 99.18°) and, furthermore, the carboxylato bridge in *syn–syn* coordination mode creates antiferromagnetic coupling.[10b] Thus the calculated J value in this case is the average between the two magnetic pathways. The spin-density analysis (Figure 8) reveals that these densities are very concentrated at the Cu^{II} ions and the two terminal nitrogen atoms of the azido group. One of these is the bridging N atom. This spin density is the origin of the strong ferromagnetic coupling. Since the magnetic orbitals are necessarily orthogonal, ferromagnetic coupling needs noticeable spin density on the bridge. Otherwise, the situation would result in paramagnetic behavior, but not ferromagnetic behavior.

The J value of **2** was obtained by applying calculations analogous to those for **1**, from $E(S{=}3/2,\alpha\alpha\alpha)-E(S{=}1/2,\alpha\beta\alpha)=2J$, thus taking into account that the energy of the

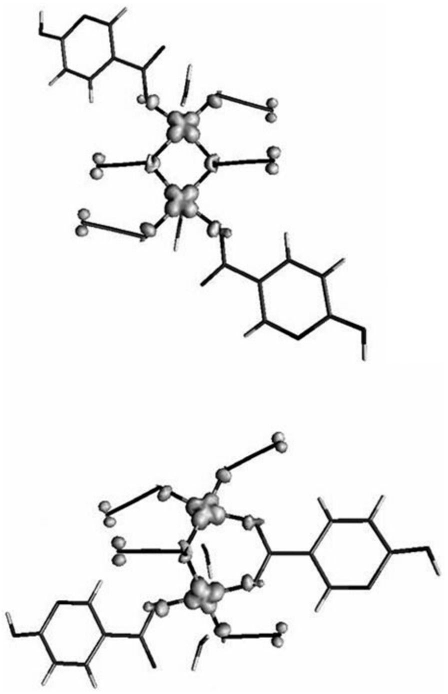

Figure 8. Plot of spin density of the two different moieties (two bridging azides, and one azide and one carboxylate) for **1**, from DFT calculations.

low-spin state is well described by means of the broken-symmetry DFT calculations.[20] The Hamiltonian employed was $H = -J(S_1S_2+S_2S_3)$. The two J values in the trinuclear system are identical due to the symmetry of the complex. The calculated J value was 69.7 cm^{-1} for the two symmetric moieties. This J value is similar in magnitude to that calculated (see above) for the azido carboxylato moiety in **1**. The Cu-N-Cu angle of 116.09° is the largest among the three analogous angles reported in this work. As a consequence, the ferromagnetic coupling would be the smallest.[10a] The spin-density analysis (Figure 9) reveals that these densities are very concentrated in the two terminal nitrogen atoms of the azido group, as in **1**, and this is corroboration for the strong ferromagnetic coupling.

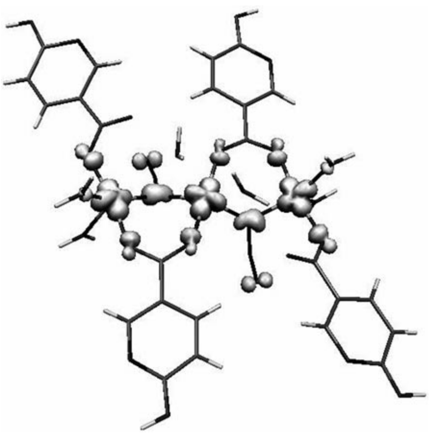

Figure 9. Plot of spin density for **2** from DFT calculations.

Finally, as a possible explanation for the difference between **1** (without magnetic ordering, 1D system) and **2** (with magnetic ordering, discrete system), it is important to study the network in **2** (Figure 3). The terminal nitrogen atom of the azido nitrogen atom of one entity is only 2.88 Å from the nitrogen atom of the pyridine ring of the neighboring entity. Given the above-mentioned high spin density on this terminal nitrogen atom, the ferromagnetic interactions through the network may be due to these intermolecular interactions. These short intermolecular interactions do not exist in the network formed by the 1D systems in **1**.

Conclusion

Two new azido–Cu^{II} complexes **1** and **2** have been synthesized under hydrothermal conditions, and both show strong ferromagnetic coupling. Density functional calculations indicated that both have large coupling constants, and their spin densities are highly concentrated on Cu^{II} and in the two terminal nitrogen atoms of the azido bridging groups. When the magnetic orbitals are orthogonal, strong spin density in the atoms of the bridge create the strong ferromagnetic coupling. Surprisingly, although the two complexes are very similar, only **2**, with discrete dimensionality, exhibits long-range ferromagnetic ordering, probably due to the short distance between the terminal nitrogen atom of the bridging azido ligand of one entity and the nitrogen atom of the pyridine ring of the neighboring entity. This short distance does not occur in the 1D system.

Experimental Section

Materials: All reagents were purchased from commercial sources and used without purification.

Physical measurements: IR spectra were measured on a Tensor 27 (Bruker) FTIR spectrometer with KBr pellets in the range 4000–400 cm^{-1}. Magnetic measurements were carried out in the Servei de Magnetoquímica (Universitat de Barcelona) on polycrystalline samples (30 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic field was 0.1 T. The diamagnetic corrections were evaluated from Pascal's constants.

Synthesis of $[Cu_{1.5}(hnta)(N_3)_2(H_2O)]_n$ (1): Compound **1** was synthesized hydrothermally under autogenous pressure. A mixture of $Cu(NO_3)_2{\cdot}6H_2O$ (0.75 mmol, 0.212 g), NaN_3 (1 mmol, 0.065 g), 6-hydroxynicotinate (0.5 mmol, 0.07 g), triethylamine (0.5 mmol, 0.096 g), and H_2O (500 mmol, 9 g) at ratio of 1.5:2:1:1:1000 was sealed in a Teflon-lined autoclave and heated to 140 °C for two days. After the autoclave was cooled to room temperature at 10 °C h^{-1}, black crystals were obtained in about 20 % yield based on the Cu^{II} salt. Elemental analysis was satisfactory. IR (KBr pellet): $\tilde{\nu}$ = 2101, 2064, 1644, 1607, 1571, 1542, 1500, 1416, 1278, 1209, 657 cm^{-1}.

Crystal data for 1: $C_{12}H_{12}Cu_3N_{14}O_8$, $M_r = 670.98$, triclinic, space group $P\bar{1}$, $a = 6.5782(18)$, $b = 8.855(2)$, $c = 10.700(3)$ Å, $\alpha = 68.458(4)$, $\beta = 83.528(4)$, $\gamma = 68.646(4)$°, $V = 539.8(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.064$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, GOF = 1.106, $R1$ ($wR2$) = 0.0350 (0.0935) [1988 observed ($I > 2\sigma(I)$)] for 2434 ($R_{int} = 0.0111$) independent reflections out of a total of 3308 reflections with 169 parameters.

Synthesis of $[Cu_3(hnta)_4(N_3)_2(H_2O)_3]$ (2). Compound **2** was synthesized hydrothermally under autogenous pressure. A mixture of Cu-

$(NO_3)_2{\cdot}6\,H_2O$ (0.75 mmol, 0.212 g), NaN_3 (1 mmol, 0.065 g), 6-hydroxynicotinate (1 mmol, 0.140 g), and H_2O (500 mmol, 9 g) in a ratio of 1.5:2:2:1000 was sealed in a Teflon-lined autoclave and heated to 140 °C for two days. After the autoclave was cooled to room temperature at 10 °C h^{-1}, green crystals were obtained in about 25 % yield based on the Cu^{II} salt. Elemental analysis was satisfactory. IR (KBr pellet): $\tilde{\nu}=2087$, 1645, 1624, 1603, 1564, 1541, 1410, 1337, 1216, 788, 658 cm^{-1}.

Crystal data for 2: $C_{24}H_{28}Cu_3N_{10}O_{18}$, $M_r=935.18$, monoclinic, space group $C2$, $a=19.828(14)$, $b=7.152(4)$, $c=11.752(7)$ Å, $\beta=96.802(17)°$, $V=1654.8(19)$ Å^3, $Z=2$, $\rho_{calcd}=1.877$ g cm$^{?3}$, $\lambda(Mo_{K\alpha})=0.71073$ Å, GOF = 1.078, $R1$ ($wR2$) = 0.1095 (0.2693) [1970 observed ($I>2\sigma(I)$] for 2356 ($R_{int}=0.0635$) independent reflections out of a total of 4035 reflections with 249 parameters.

Caution! Azide and its complexes are potentially explosive. Only small amounts of materials should be prepared and handled with care.

X-ray crystallography: The chosen crystals were mounted on a glass fiber. All diffraction data were collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) in ω scan mode. The program SAINT was used for integration of the diffraction profiles.[21] Structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied using SADABS program).[22] The positions of metal atoms were located from the direct-method E map; other non-hydrogen atoms were located in difference Fourier syntheses and least-squares refinement cycles, and finally refined anisotropically. The hydrogen atoms of the ligands were placed theoretically onto the specific atoms and refined isotropically as riding atoms.

CCDC-634508 (**1**) and CCDC-634509 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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