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Two New Copper Azido Polymorphs: Structures, Magnetic Properties, and Effects of “Noninnocent” Reagents in Hydrothermal Methods

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Two new 3D copper(II) azido isomers, $[Cu(N_3)(nic)]_\infty$ (**1** and **2**) (nic = nicotinate), have been synthesized and characterized. To the best of our knowledge, **1** is the first metal azido complex showing *rutile*-type topology, while **2** is a chiral compound obtained by spontaneous resolution upon crystallization.

The synthesis of coordination architectures with desired magnetic properties and unique structures has become one of the most interesting research topics in coordination chemistry and molecular magnetism.[1] The azido ligand is a very good choice for preparing such complexes because of its rich coordination modes and efficient pathways of magnetic exchange.[2] To date, there have been many reports concerning the versatility of azide complexes with diverse structures spanning from discrete molecules to 3D arrays with interesting magnetic properties.[3−5] Probably owing to the negative charge of azide, it was known that most of the coligands in metal azido complexes are neutral organic ligands, and negatively charged ligands are less common.[6]

The hydrothermal method is a good synthetic methodology for the synthesis of extended coordination networks and is a very powerful tool to obtain new materials, but because of the potential explosive character of azide, hydrothermal synthesis is not common in the metal azido field. If the safety problem can be well handled, the hydrothermal method is of great synthetic potential in the field of metal azido compounds. Because the hydrothermal reaction takes place in a sealed vessel in certain conditions, it is very difficult to assess the role of each of the reagents used. However, as is the case in the results reported here, some reagents may control the formation of the product in ways that are difficult to predict beforehand.

Herein, we describe two new 3D copper(II) azide complexes of formula $[Cu(N_3)(nic)]_\infty$ (nic = nicotinate) that display two completely different solid-state arrangements, synthesized by hydrothermal methods. The two compounds were obtained from $Cu(NO_3)_2{\cdot}6H_2O$, NaN_3, Hnic, MoO_3, and H_2O for **1** and $Cu(NO_3)_2{\cdot}6H_2O$, NaN_3, Hnic, $Gd(NO_3)_3{\cdot}6H_2O$, ethylenediamine (en), and H_2O for **2**.[7] Interestingly,

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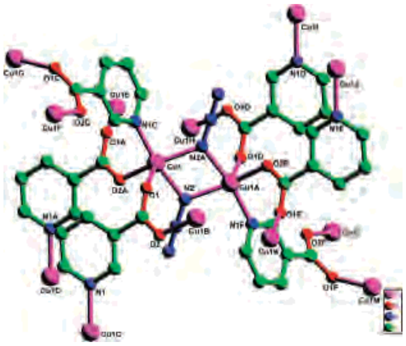

Figure 1. Linkage of the dinuclear Cu^{II} entity of **1**. H atoms are omitted for clarity.

MoO_3 plays a key role in the formation of **1**. We tried to obtain **1** without the presence of MoO_3 as reported in refs 6b and 6c, but all attempts were unsuccessful. The same phenomena occurred in the formation of **2** without $Gd(NO_3)_3 \cdot 6H_2O$ or en.[6d] The processes of hydrothermal reaction take place in a "dark room", and sometimes the results are not easily rationalized and are difficult to predict beforehand. So far, it is impossible for us to explain these peculiarities in the formation of **1** and **2**.

X-ray analysis[8] indicates that the asymmetric unit of **1** contains one Cu^{II} ion (Figure S1 in the Supporting Information), one azide anion, and one nic anion. Cu1 has a slightly distorted five-coordinated square-based pyramid (CuO_2N_3). The apical position of Cu1 is occupied by an O atom of the carboxylato [Cu1−O1 = 2.219(2) Å], and the equatorial plane is formed by an O atom of the carboxylato [Cu1−O2A = 1.962(2) Å], two equivalent N atoms of two $\mu_{1,1}$-bridging azides [Cu1−N2 = 2.001(2) Å; Cu1−N2A = 2.028(2) Å], and one N atom from a pyridine ring [Cu1−N1C = 1.991(2) Å]. First, double end-on (EO) azides link two Cu^{II} ions to form a dinuclear Cu^{II} entity (Figure 1), in which the Cu1−N2−Cu1A angle is 102.49(8)°. Second, these dinuclear entities form an 1D chain through an *anti*,*syn*-carboxylato bridging group of the nic ligand (Figure S2 in the Supporting Information). Finally, these chains are connected via the pyridine group of the nicotinate ligands (μ-N,O,O bridging mode) to build the 3D structure (Figure S3 in the Supporting Information). If the dinuclear Cu^{II} entity is treated as a 6-connected node and the nic ligand as a 3-connected node, the network of **1** can be described as a distorted infinite 3D (3,6)-connected rutile network (Figure 2).[9] To the best of our knowledge, **1** is the first metal azido complex with distorted *rutile* topology.

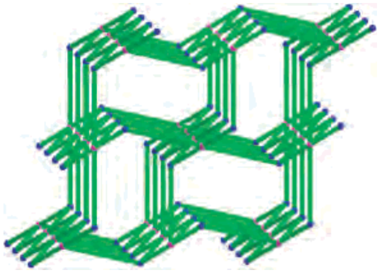

Figure 2. Rutile topology exhibited by **1**.

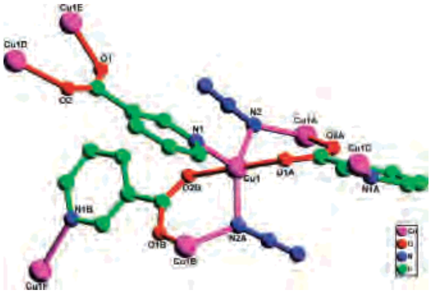

Figure 3. Linkage and coordination mode in complex **2**.

The asymmetric unit of **2** also contains one Cu^{II} ion, one azide ligand, and one nic anion (Figure S4 in the Supporting Information). The trigonal-bipyramidal Cu^{II} ions are coordinated by two O atoms [Cu1−O1A = 1.9571(16) Å; Cu1−O2B = 1.9806(15) Å], two N atoms of two azide ligands [Cu1−N2 = 1.994(2) Å; Cu1−N2C = 2.008(2) Å], and one N atom [Cu1−N1 = 2.225(2) Å] (Figure 3). The five-coordinated Cu^{II} ions are bridged into an 1D left-handed helical chain by nic with N and O atoms (Figure S5 in the Supporting Information). In this compound, all of the helical chains are left-handed and parallel and are joined by EO azide ligands to form a left-handed homochiral crystal, all of which is presented clearly in Figure 4. **2** is a good example of a chiral compound obtained by spontaneous resolution upon crystallization without a chiral auxiliary.

The magnetic properties of **1** [sample detected by X-ray powder diffraction (XRPD); see Figure S6 in the Supporting Information] as a $\chi_M T$ vs T plot (χ_M is the molar magnetic susceptibility for two Cu^{II} ions) and the reduced magnetization ($M/N\beta$ vs H) are shown in Figure 5. The value of $\chi_M T$ at 300 K is 0.95 $cm^3\ mol^{-1}$ K, which is higher than that expected for two magnetically quasi-isolated spin doublets ($g > 2.00$). Starting from room temperature, $\chi_M T$ values increase to 1.12 $cm^3\ mol^{-1}$ K at 60 K, and below 60 K, they decrease quickly to 0.86 $cm^3\ mol^{-1}$ K at 2 K. This feature is characteristic of a strong intradimer, [Cu_2], ferromagnetic

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(7) (a) Synthesis of **1**. **1** was hydrothermally synthesized under autogenous pressure. A mixture of $Cu(NO_3)_2 \cdot 6H_2O$, NaN_3, Hnic, MoO_3, and H_2O at a ratio of 1:1:1:1:2000 was sealed in a Teflon-lined autoclave, heated to 140 °C for 2 days, and cooled to room temperature at 10 °C h^{-1}. The black crystals of **1** were obtained in ca. 10% yield based on copper from an unknown powder and solution. Selected IR (KBr, cm^{-1}): 2085, 1603, 1550, 1407. Anal. Calcd for $C_6H_4N_4CuO_2$ (227.41): C, 31.7; H, 1.8; N, 24.6. Found: C, 31.3; H, 1.9; N, 24.1. (b) Synthesis of **2**. **2** was hydrothermally synthesized under autogenous pressure. A mixture of $Cu(NO_3)_2 \cdot 6H_2O$, NaN_3, Hnic, $Gd(NO_3)_3 \cdot 6H_2O$, en, and H_2O at a ratio of 1:1:1:1:1:2000 was sealed in a Teflon-lined autoclave, heated to 140 °C for 2 days, and cooled to room temperature at 10 °C h^{-1}. The black crystals of **2** were obtained in ca. 20% yield based on copper from the reaction solution. Anal. Calcd for $C_6H_4N_4CuO_2$ (227.41): C, 31.7; H, 1.8; N, 24.6. Found: C 31.2; H, 1.5; N, 24.3. ***Caution!*** *Azide complexes are potentially explosive. Only a small amount of the materials should be prepared and handled with care.*

(8) (a) Crystal data for **1**: $C_6H_4CuN_4O_2$, $M = 227.41$, monoclinic, $P21/c$, $a = 4.8720(14)$ Å, $b = 14.347(4)$ Å, $c = 11.655(3)$ Å, $\beta = 114.70(9)°$, $V = 740.1(4)$ Å^3, $Z = 4$, $D_c = 2.043$ Mg m^{-3}, $\mu = 2.916$ mm^{-1}, 1456 [R(int) = 0.0187] reflections, of which 118 were assumed as observed [$I > 2\sigma(I)$]. Final R1 = 0.0232, wR1 = 0.0612 [$I > 2\sigma(I)$]. CCDC 613080. (b) Crystal data for **2**: $C_6H_4CuN_4O_2$, $M = 227.67$, orthorhombic, $P2(1)2(1)2(1)$, $a = 6.4068(15)$ Å, $b = 9.701(2)$ Å, $c = 12.398(3)$ Å, $V = 770.5(3)$ Å^3, $Z = 4$, $D_c = 1.963$ Mg m^{-3}, $\mu = 2.801$ mm^{-1}, 4196 [R(int) = 0.0203] reflections, of which 1575 were assumed as observed [$I > 2\sigma(I)$]. Final R1 = 0.0194, wR1 = 0.0447 [$I > 2\sigma(I)$]. CCDC 635493.

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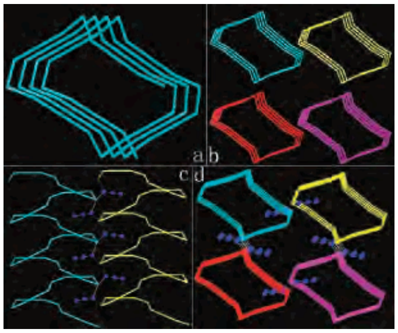

Figure 4. Formation scheme for complex **2**: (a) the left-handed chain; (b) the emergence of homochiral chains, (c) the two left-handed chains were joined by an EO azide; (d) homochiral chains constructed to 3D architecture by an EO azide.

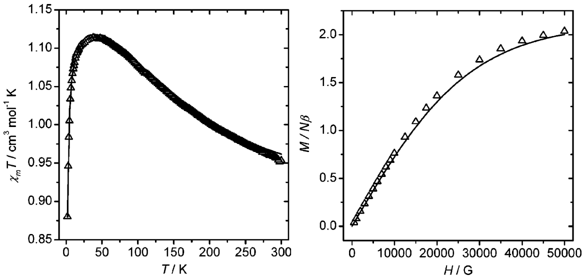

Figure 5. Left: plot of $\chi_M T$ vs T for **1** under an applied magnetic field of 0.1 T. The solid line indicates the best fit (see the text). Right: plot of the reduced magnetization ($M/N\beta$) at 2 K. The solid line represents the Brillouin function for two Cu ions assuming $g = 2.12$ (see the text).

coupling with weak interdimer and interchain antiferromagnetic interactions. The reduced molar magnetization at 2 K (Figure 5, right) corroborates the ferromagnetic coupling: the $M/N\beta$ value at 5 T is close to 2.1 $N\beta$, but the curve has a more pronounced slope than that of the Brillouin law (experimental points are above the theoretical curve for $g = 2.12$, as deduced from the susceptibility fit). **1** is, as commented in the previous part, a 3D Cu^{II} network. However, from a magnetic point of view, it may be considered as formed by dinuclear entities, linked among them through *syn*,*anti*-carboxylato at apical−equatorial positions (thus leading to very weak magnetic coupling) and through the pyridinecarboxylate ligand (which also mediates very weak coupling). The fit of the susceptibility data has been carried out by applying a modified Bleaney−Bowers formula, considering the mean-field approach for taking into account the interdimer interactions (J').[1b] The best-fit parameters obtained are $J = +132.3 \pm 2$ cm^{-1}, $J' = -0.60$ cm^{-1}, $g = 2.12 \pm 0.01$, and $R = 1.0 \times 10^{-5}$. The R factor is defined as $\sum_i[(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2/\sum_i[(\chi_m T)_{obs}]$.[10]

The strong ferromagnetic J value can be interpreted as a consequence of the existence of the two azido bridges in *EO* coordination mode, which gives ferromagnetic coupling. According to Ruiz et al.,[10] from density functional theory calculations there appears to be a clear correlation between the calculated J parameter and the Cu−N$_3$−Cu angle. From a theoretical point of view (omitting other factors), the J value decreases from a maximum at about $\theta = 90°$ with increasing θ, eventually reaching an antiferromagnetic regime for $\theta >$ 104−105°. The τ (distortion of the N$_3$ bridge with regard to the Cu$_2$N$_2$ plane) seems to have a negligible influence on the J value.[10] The Cu−N bond distances in **1** are in the range of the previously reported parameters. The J value of +132 cm^{-1} is in good agreement with other values already reported to date for similar Cu dimers with azido bridges; for further information, see Table S1 in the Supporting Information.

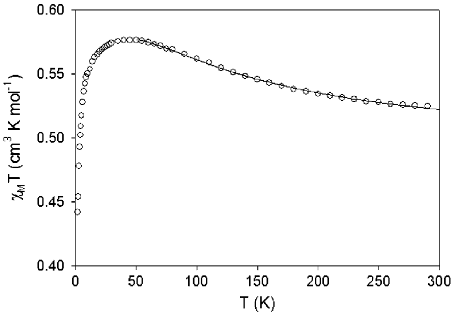

Figure 6. Plot of $\chi_M T$ vs T for **2** under an applied magnetic field of 0.1 T.

The magnetic properties of **2** (sample detected by XRPD; see Figure S7 in the Supporting Information) as a $\chi_M T$ vs T per Cu^{II} ion plot is shown in Figure 6. The high-temperature data (between 50 and 300 K) were fitted using a high-temperature series expansion derived for a ferromagnetically coupled chain of $S = {}^1/_2$ spins.[11] The best fit was obtained for $g = 2.29$, $J = 39.1$ cm^{-1}, and $\Theta = -33.0$ K, and it is shown as a solid line in the graph. There is an intrachain weak ferromagnetic coupling between the Cu^{II} ions, as is expected for the presence of EO azido bridges together with *syn*,*syn*-carboxylate bridges featured in the chain. The EO azido bridge will mediate a ferromagnetic exchange, while the *syn*,*syn*-carboxylate will provide a pathway of antiferromagnetic coupling between the Cu^{II} centers. As can be seen in the $\chi_M T$ vs T graph, the ferromagnetic exchange dominates but it is weak. The chains are not isolated, they are linked via the pyridine group of the nic ligand into a 3D network. A weak antiferromagetic coupling between the chains is observed, which in our model is reflected as a negative Curie−Weiss constant.

In summary, two new polymorphic coordination networks containing Cu^{II}, azido, and nic have been obtained. These two isomers are crystallized in very similar reaction conditions with the aid of a “noninnocent” reagent that does not exist in the final compound. The detailed role of these “noninnocent” reagents is not clear, but they are, nonetheless, necessary for obtaining the two different polymorphs **1** and **2**.

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Supporting Information Available: X-ray crystallographic data in CIF format, structures of **1** and **2**, XRPD patterns, and structural and magnetic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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