Partial Substitution of Hydroxyl by Azide: An Unprecedented 2D Azido–Copper–Hydroxyl Compound with a [Cu$_{24}$] Macrocycle in the Presence of [Cu(H$_2$O)$_6$]$^{2+}$

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The investigation of magnetic materials with fascinating structures and unusual magnetic behavior has witnessed flourishing development.[1,2] Transition-metal hydroxides are of particular significance because of their potential application in magnetic devices (as substitutes for traditional ferrite or nanometric magnetic memory units), and have been extensively explored.[3] Even so, it is still a tremendous challenge for researchers to rationally design, precisely control, artfully modulate, and effectively re-assemble new transition-metal/hydroxide species (hydroxide-bridged clusters, chains, and layers).[3c,4] In the hydroxyl inorganic layers (such as Cu(OH)$_2$, FeO(OH), Mg(OH)$_2$, etc.), the hydroxide groups are present in μ_2 and μ_3 modes. To replace some of the hydroxide ligands with other bridging groups in order to alter the magnetic properties is still a challenge to chemists today. As we know, azide is one of the most studied ligands in magnetochemistry,[5] and its complexes display exciting magnetic properties ranging from long-range ordering to SMM (single-molecule magnet) and SCM (single-chain magnet) behavior.[6] Additionally, the magnetic interaction through an azide bridge can be easily predicted based on its bridging mode and the M-N-M angles. The most typical bridging modes are end-to-end (EE, μ_2-1,3) and end-on (EO, μ_2-1,1), usually resulting in antiferromagnetic and ferromagnetic coupling, respectively, but this greatly depends on the Cu-N-Cu angle for end-on azides.[7,8] Azides can also bridge more than two ions in their EO mode; for instance, it can bridge three metal ions in a pyramidal fashion analogous to that of a μ_3-OH group. In view of azides being able to take both μ_2-1,1 and μ_3-1,1,1 bridging modes, it may replace some OH positions in the 2D inorganic layer, which could lead to different magnetic behavior.[9] To avoid the inorganic layer collapsing or aggregating into a 3D solid, a second ligand is usually introduced into the system. Herein, phthalic acid (H$_2$-pta) is our second ligand of choice. A Cu^{II}/N$_3^-$/OH$^-$/pta^{2-} network could have a high negative charge and counterion will then be needed. Herein we report the synthesis of an unusual 2D N$_3$-Cu^{II}-OH complex, [Cu(H$_2$O)$_6$][{Cu$_2$(N$_3$)$_{4/3}$-(OH)(pta)}$_6$] (**1**). Indeed, our results show that the [Cu(H$_2$O)$_6$]$^{2+}$ complex ion from the Cu(NO$_3$)$_2$ aqueous solution may serve as a template for the [Cu$_{24}$] macrocycles.

The crystal structure of complex **1**[10] (Figure 1) consists of a new anionic 2D layer network containing two Cu^{II} ions, one phthalic anion (in μ_4-O,O',O'',O''' bridging mode), one μ_3 hydroxyl anion, and $^4/_3$ azide anions, which take μ_2-1,1 and μ_3-1,1,1 bridging modes (Figure S1). As can be seen in Figure 1 (top), Cu1 is five-coordinate with a distorted square-based pyramid CuN$_2$O$_3$ geometry formed by the coordination of two nitrogen atoms, from the μ_2-1,1- and μ_3-1,1,1-azide anions (apical position) (Cu1$-$N1=2.000(5), Cu1$-$N4=2.287(3) Å), and three oxygen atoms, one from the μ_3 hydroxyl anion and two from phthalic anions (Cu1$-$O5=1.969(4), Cu1$-$O1=1.983(4), Cu1$-$O4=2.018(4) Å). The square-based pyramidal coordination sphere of Cu2 is CuNO$_4$, in which the N atom is from a μ_2-1,1 azide anion (Cu2$-$N1A=1.972(5) Å), and the four oxygen atoms are from two μ_3 hydroxyl anions and two phthalic anions (one occupied the apical position) (Cu2$-$O5=1.954(4), Cu2$-$O5A=1.979(4), Cu2$-$O2=2.646, Cu2$-$O3=1.934(4) Å). Two hydroxyl anions in the μ_3 mode (Cu1-O5-Cu2=100.74, Cu1-O5-Cu2A=118.24, Cu2-O5-Cu2A=100.30°) bridge

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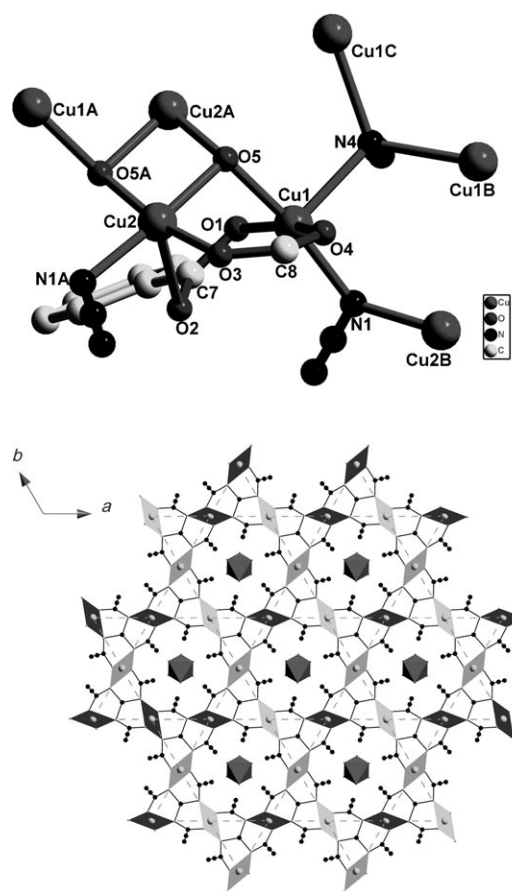Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200800068.

Figure 1. Top: The coordination environment of Cu^{II} ions in **1**. Bottom: The *kagóme* topology for the inorganic anionic sheet of **1**. Each [Cu$_4$] unit is treated as a four-connected node (dashed lines drawn for illustration).

Figure 2. Top: The 24-membered copper macrocycle was constructed from six [Cu$_4$] units in **1**. Bottom: [Cu(H$_2$O)$_6$]$^{2+}$ serves as counterion and template in **1**. Hydrogen bonds between [Cu(H$_2$O)$_6$]$^{2+}$ and the inorganic sheet are shown as dashed lines.

Cu1/Cu2/Cu2A and Cu1A/Cu2/Cu2A, respectively, holding together the tetranuclear [Cu$_4$] entity formed by the two trinuclear units sharing a Cu2-Cu2A edge. Each [Cu$_4$] unit is connected in turn to four neighboring [Cu$_4$] units by four μ_2-1,1 (Cu1-N1-Cu2B = 126.64°) and two μ_3-1,1,1 azide groups (Cu1-N4-Cu1B = 113.05, Cu1-N4-Cu1B = 113.04, Cu1-N4-Cu1B = 113.00°) to give an unprecedented inorganic 2D layer. If we treated the [Cu$_4$] unit as four-connected node, a 2D anion *kagóme* sheet would be obtained (Figure 1, bottom). Phthalic groups in the μ_4 binding mode are located alternately at both sides of the sheet and link to two [Cu$_4$] units. They help to reinforce the 2D network and isolate each layer, avoiding the formation of a 3D network.

Six [Cu$_4$] units construct a [Cu$_{24}$] macrocycle through μ_2-1,1 and μ_3-1,1,1 bridging azide groups (Figure 2, top). To the best of our knowledge, this copper macrocycle is the largest macrocycle in the azido–copper system reported to date. Because the phthalate aromatic groups are distributed up and down the layer, the huge cavity enclosed by the [Cu$_{24}$] macrocycle is not open for exchange. In fact, these cavities are not empty; they contain the [Cu(H$_2$O)$_6$]$^{2+}$ counterions. (Figure S2). The water molecules coordinated to the Cu^{II} ion form hydrogen bonds with the oxygen atoms of the phthalic
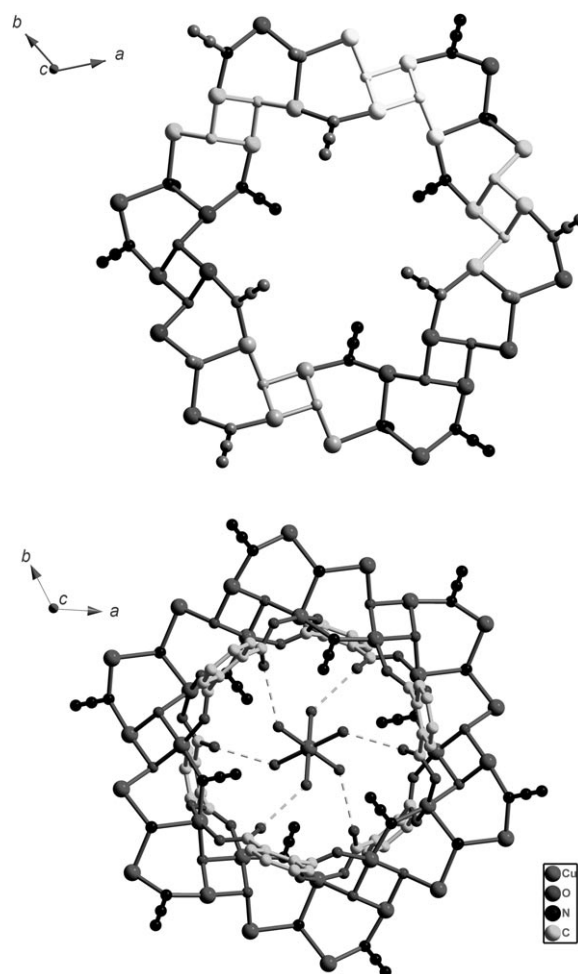
groups (O1W···O2 = 2.826 Å). Thus, it is reasonable for us to believe that [Cu(H$_2$O)$_6$]$^{2+}$ acts as a template in the assembly process of the 2D network (Figure 2, bottom). The ability of [Cu(H$_2$O)$_6$]$^{2+}$ to act as a counterion in coordination chemistry has been reported,[11] but examples of it acting as a template in the cavity of 2D network are still rare.

The magnetic properties of **1** were studied as a function of field and temperature. At 300 K the χT product has a value of 4.90 cm^3 K mol^{-1}, in good agreement with the expected χT product for 13 non-interacting Cu^{II} ions (4.875 cm^3 K mol^{-1} with $S = 1/2$ and $g = 2.0$). As the temperature goes down to 2 K, the χT product drops continuously to a value of zero, indicating that the overall magnetic interactions in **1** are antiferromagnetic (Figure 3, middle). The Curie law for a single Cu^{II} ion, corresponding to the [Cu(H$_2$O)$_6$]$^{2+}$ ion, was subtracted from the susceptibility of **1** (triangles in Figure 3, middle) resulting in the susceptibility for the anionic network (squares in Figure 3, middle), which shows clear average antiferromagnetic interactions leading to an $S = 0$ ground state. The susceptibility was measured at
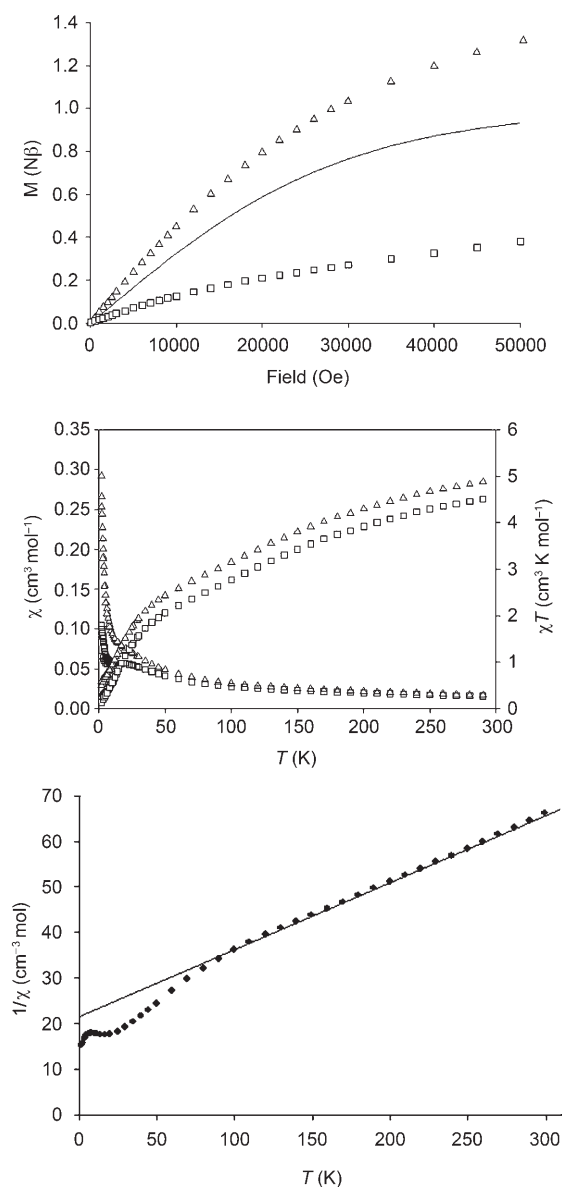
Figure 3. Top: Field dependence of the magnetization for **1** (triangles); Brilluoin function for one Cu^{II} ion with $S=1/2$ and $g=2.0$; magnetization for the anionic network $[\{Cu_2(N_3)_{4/3}(OH)(pta)\}_6]^{2-}$ (squares). Middle: Temperature dependence of the susceptibility of **1** (triangles); temperature dependence of the susceptibility of the anionic network $[\{Cu_2(N_3)_{4/3}(OH)(pta)\}_6]^{2-}$ (squares). Bottom: Curie plot for **1**. The solid line is the calculated susceptibility using the Curie–Weiss law at temperatures above 100 K.

0.05 T in the 2 to 30 K range and at 1.0 T between 2 and 300 K (Figure 3, middle) and it is not field dependent, indicating the lack of long-range magnetic ordering in **1**. The high-temperature data (above 100 K) follows the Curie law with a Curie–Weiss constant of −154 K (Figure 3, bottom), in agreement with the overall antiferromagnetic coupling in the layered structure of **1**.

The magnetization of **1** was studied at 2 K at applied fields from 0 to 5 T (Figure 3, top). The calculated magnetization of a single Cu^{II} ion with $g=2.0$ was subtracted from the magnetization of **1** to obtain the magnetization of the anionic network. The g value was chosen based on the room-temperature susceptibility data, which indicated an average g value very close to 2.0 for the Cu^{II} ions in complex **1**. The resulting magnetization rises without reaching saturation, reaching 0.38 μ_B per $[\{Cu_2(N_3)_{4/3}(OH)(pta)\}_6]^{2+}$ unit of the anionic 2D network of **1** at 5 T. This very low magnetization value and the lack of saturation indicates an $S=0$ ground state with some accessible excited states of larger S values that are populated due to the Zeeman splitting at fields as large as 5.0 T.

Both the Cu1 and Cu2 atoms are in a pentacoordinate, square-pyramidal coordination environment; thus the magnetic orbital is d$_{x^2-y^2}$ and lies on the basal plane of the square pyramid. The axis of the square pyramid of Cu1 and Cu2 is clearly elongated. The Cu1−N4 bond length, lying on the apical axis, is 2.287 Å and is elongated relative to the average Cu−L basal distance of 1.993 Å. For Cu2, the apical Cu2−O2 distance is 2.646 Å, clearly elongated with respect to the average distance in the basal plane, of 1.959 Å. The possible exchange pathways will be analyzed separately. First of all, the carboxylate bridges in the sample are all in the typical *syn,syn*-bridging mode. The O1−O2 carboxylate group bridges orthogonal Cu1 and Cu2 orbitals: the d$_{z^2}$ orbital on Cu2 is bridged by this carboxylate to the d$_{x^2-y^2}$ orbital on Cu1, which leads to ferromagnetic coupling. The O3−O4 carboxylate bridges the magnetic orbitals of Cu1 and Cu2 in a *syn,syn*-fashion providing an efficient pathway for antiferromagnetic coupling. The hydroxide groups bridge three Cu ions: two symmetry related Cu2 ions and one Cu1 ion. As reported by Hatfield and Hogson,[13] the coupling is antiferromagnetic for Cu-O-Cu angles above 98°. The Cu2-O5-Cu2A angle is 100.30°, the Cu2-O5-Cu1 angles is 118.24°, and the Cu2A-O5-Cu1 angle is 100.74°, thus the hydroxide groups in **1** mediate antiferromagnetic coupling. Finally, there are two types of azide bridges, one that bridges Cu1 and Cu2, and one that bridges Cu1 to the two symmetry related ions, Cu1A and Cu1B. The two azides bind in an end-on fashion, with only one N atom involved in the coordination to the Cu^{II} ions. A priori, end-on azido bridges, as seen in this complex, should lead to ferromagnetic coupling. However, this is not always the case, as recent theoretical studies point out the exchange pathway can change from ferromagnetic to antiferromagnetic depending on the M-N$_3$-M angle; in fact, for Cu-N-Cu angles greater than 104° the coupling is antiferromagnetic.[12] The Cu1-N1-Cu2 angle is 126.64°, and the orbitals involved are the magnetic orbitals (d$_{x^2-y^2}$) on both Cu ions; thus the coupling is expected to be antiferromagnetic. The second type of azide ligand bridges three symmetry related Cu1 ions in an end-on fashion with Cu1-N4-Cu1 angles of 113°; however, the three Cu1 ions use the full d$_{z^2}$ orbital in the bonding with the N4 atom from the azide. Overall, the antiferromagnetic exchange pathways in **1** dominate over the ferromagnetic ones. At very low temperatures the interactions of opposed sign compete, as indicated by the lack of a clear maximum in the susceptibility versus temperature plot, but given the structural

complexity of **1**, values for the pairwise interactions between the Cu^{II} ions could not be calculated.

In summary, substitution of some positions of hydroxyl with azide has resulted in an unprecedented 2D inorganic azido–copper–hydroxyl compound. The [Cu$_{24}$] macrocycles that form the 2D layers of **1** are likely templated around [Cu(H$_2$O)$_6$]$^{2+}$ cations through strong hydrogen bond interactions.

Experimental Section

Synthesis of 1: Compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of Cu(NO$_3$)$_2$·6H$_2$O, NaN$_3$, phthalic acid, NaOH and H$_2$O at ration of 2.2:1.4:1:3:1000 was sealed in a Teflon-lined autoclave and heated to 120°C for 2 days. The pure green crystals were obtained in ca. 20% yield based on Cu^{II} salt. Element analysis was satisfactory. IR (KBr pellet): $\tilde{v} = 3058, 2093, 1579, 1550, 1419, 1068, 846, 707, 682$ cm^{-1}. **Caution!** Azide complexes are potentially explosive and should be handled carefully.

Acknowledgements

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[10] Crystallographic data of **1**: C$_{48}$H$_{54}$Cu$_{13}$N$_{24}$O$_{36}$, $M_r = 2369.18$, trigonal, $P\bar{3}$, $a = 13.8310(12)$ Å, $c = 11.996(2)$ Å, $V = 1987.4(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.969$ g cm^{-3}, $2\theta_{max} = 52.22$ ($-15 \leq h \leq 16$, $-15 \leq k \leq 16$, $-14 \leq l \leq 11$), $T = 294(2)$ K, 9944 measured reflections, $R_1 = 0.0372$, $wR_2 = 0.1116$ for 1702 reflections [$I > 2\sigma(I)$], and $R_1 = 0.0648$, $wR_2 = 0.1277$ for 2345 independent reflections (all data) and 183 parameters, GOF = 1.168. CCDC 651942 contains 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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