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# Self-Assembly of a Chiral Carbonate- and Cytidine-Containing Dodecanuclear Copper(II) Complex: a Multiarm-Supplied Globular Capsule

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A dodecanuclear copper(II) globular-shaped structure has been obtained with the cytidine nucleoside and the templating carbonate anion. It shows receptor properties through anion−cation and multiple anion−$\pi$ interactions toward $ClO_4^-$ as well as an overall antiferromagnetic coupling.

The design and synthesis of supramolecular metal-mediated assemblies of organic building blocks has been recognized as an excellent strategy to build well-defined nanosized molecules for potential application in molecular nanotechnology.[1] This method has great versatility because of the wide variety of transition-metal ions and multidentate ligands that allow control of the shape of these assemblies, regulation of their sizes, and functionalization of their structures.[2]

The constituents of the nucleic acids undoubtedly offer resourceful building blocks for complex formation with metal ions, as shown by the high ordered structures obtained;[3] however, quite surprisingly, a survey in the literature reveals that only a small number of X-ray structures including nucleosides has been published.[3d,e,4] In this respect, the first example of an octanuclear copper(II) cytidinate complex of formula $[Cu(H_2O)_6][Cu_8(Hcyd)_8(CF_3SO_3)_4](CF_3SO_3)_6\cdot 12H_2O$ (**3**; $H_2cyd$ = cytidine) exhibiting fascinating calixarene-like motifs was reported by some of us very recently.[3e]

Here we show how the cytidine can be a suitable candidate for the design of not only (supra)molecular metallocyclic arrays but also discrete macromolecules of nanoscopic dimensions with hollow structures, simply depending on the nature of the employed counterion. The chiral dodecanuclear copper(II) complex of formula $[Cu_{12}(Hcyd)_{12}(CO_3)_2](ClO_4)_8\cdot 11H_2O$ (**1**), which results from the spontaneous self-organization of cytidinate groups and $Cu^{II}$ ions upon atmospheric $CO_2$ uptake, opens this new research avenue.[5] Its preparation, X-ray structure, variable-temperature magnetic properties, and theoretical study by density functional theory (DFT)-type calculations (see the Supporting Information) are reported herein.

Initially, compound **1** was serendipitously isolated as a pale-green crystalline solid from the reaction of aqueous solutions of $Cu(ClO_4)_2\cdot 6H_2O$ and $H_2cyd$ in a 1:1 metal-to-ligand molar ratio, with the main product being X-ray-quality violet parallelepipeds of the mononuclear compound $[Cu(H_2cyd)_4](ClO_4)_2\cdot 5H_2O$ (**2**; see the Supporting Information). Once the structure of **1** was determined, it was prepared

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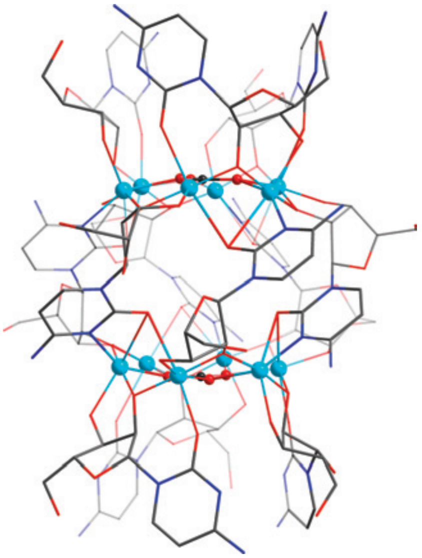

**Figure 1.** Side view of the globular-shaped dodecanuclear $[Cu_{12}(Hcyd)_{12}(CO_3)_2]^{8+}$ cation in **1**.

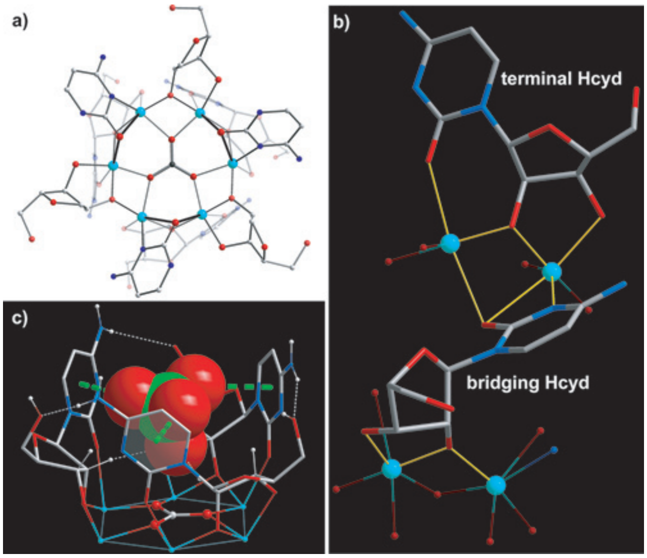

**Figure 2.** (a) Perspective view of the hexanuclear copper(II) motif in **1**, showing the centered $\mu_6$-carbonate ion [the values of the Cu−Cu distances vary in the range 3.027(2)−3.081(2) Å]. (b) View of a fragment of **1** showing the two different coordination modes of the Hcyd ligand. (c) View of the basketlike cavity in **1** with an encapsulated perchlorate anion.

as the unique product by slow diffusion of 2-propanol into an aqueous solution containing the reagents and whose pH was fixed at 7.0 with the careful addition of solid $Na_2CO_3$.

Compound **1** exhibits an aesthetic globular-shaped structure in which 12 $Cu^{II}$ ions are connected by 2 templating carbonate ions and 6 monodeprotonated cytidine molecules, to form an ellipsoidal capsule supplied by a further 6 hanging $Hcyd^-$ groups (Figure 1). Two *quasi*-planar hexagons of $Cu^{II}$ centers arise from the coordination of bridging carbonate ions in a $\mu_6$ fashion[5c,6] (Figure 2a), as is similarly observed in some $Ni^{II}$-, $Mo^V$-, and $V^{IV}CO_3^{2-}$-supported macrocyclic complexes.[5c,9] The overall structure can be viewed as an assembly of these two hexanuclear subunits, held together by six $Hcyd^-$ ligands coordinated via N(3)−O(2) and O(2′)−O(3′) as bidentate/unidentate bridges, so that the two carbonate ions are perfectly staggered (Figure S2 in the Supporting Information). These bridging $Hcyd^-$ ligands alternate in a head-to-tail fashion, so that in-set $\pi-\pi$ interactions take place between the heterocycles of neighboring $Hcyd^-$ with an interplanar distance of ca. 3.6 Å and about an 80% overlap. The orientation of the nucleobase rings is such to have the carbonyl pointing toward the inner part of the cavity, with O(2) simultaneously linked to two Cu atoms. In this way, each $Cu^{II}$ ion is six-coordinated in an elongated distorted octahedral environment (Figure S1 in the Supporting Information). The coordination mode of the $Hcyd^-$ ligand in **1** is related to that found in **3**, where a purely bidentate mode via N(3)−O(2) and an additional coordination via ribose O(3′) atoms and $\mu_2$-O(2′) were observed. Nevertheless, the bridging role of O(2) in **1** is unprecedented, and it could be invoked among the driving forces that allow the occurrence of this globular-shaped compound. The final dodecameric structure is completed by six terminal $Hcyd^-$ ligands, three for each $Cu_6$ moiety, coordinating through O(3′)−O(2′) and O(2)−O(3′) to two adjacent Cu atoms in the bidentate/monodentate coordination mode (Figure 2b). The exocyclic $NH_2$ groups and the ribose alcoholic termination strictly interact through intramolecular hydrogen bonds in such a way as to build a basketlike cavity (Figure 2c). Because of their nature, the two terminal cavities are good to encapsulate a perchlorate anion as a guest, which is anchored to the cytidinate arms by means of weak C−H(ribose)···O and anion−$\pi$-type interactions,[7] (Figures 2c and S3 in the Supporting Information), while two water molecules were found in the central hydrophilic hollow space.

A few points deserve to be discussed to close this structural description. There is no doubt that the substitution of the triflate counterion (**3**) by the perchlorate one (**1**) causes an expansion in the nuclearity of the resulting species. It is worth nothing that this is translated into not only a different topology net but also different receptor properties, with the octamer and dodecamer compounds having just one and two distinct cavities, respectively, capable of hosting cations (**3**) or anions (**1**) with the appropriate dimension and shape. At the same time, it is noticeable that **1** requires the assistance of a coordinated carbonate. However, no $CO_2$ fixation occurs in the presence of triflate, most likely because of the slowness of this process with respect to the direct coordination of the counterion to the $Cu^{II}$ ions, which definitively leads to the formation of **3**. The occurrence of the two types of $Hcyd^-$ ligands, one serving as a bridge and the other as a blocking group, is quite interesting from a coordination chemistry viewpoint.

It should be noted that not only do they exhibit two different coordination modes in **1** but also they do not match the observed one in **3**, with the bridging character of O(2) (bridging $Hcyd^-$) and the uncoordinated N(3) (terminal $Hcyd^-$) being unprecedented for a monodeprotonated cytidinate group, evidencing

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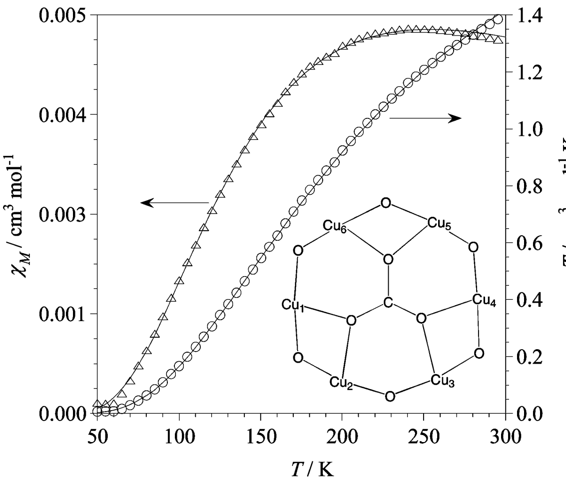

**Figure 3.** Temperature dependence of $\chi_M T$ and $\chi_M$ for **1**: (○ and △) experimental data; (—) best-fit curve (see text). The inset shows the magnetic coupling scheme within each hexanuclear ring.

its great versatility as a ligand. Finally, the occurrence in **1** as in **3** of coordination through O(2′) and O(3′), a very unusual feature for nucleosides, seems to validate the even partial (*in situ*) deprotonation of the neutral species as a good strategy to make the ribose O atoms competitive *versus* the N(3)−O(2) sites with respect to metal coordination.

The magnetic properties of **1** under the form of a $\chi_M T$ and $\chi_M$ *versus* $T$ plot ($\chi_M$ is the magnetic susceptibility per six Cu$^{II}$ ions) are shown in Figure 3. At room temperature, $\chi_M T$ is 1.32 cm$^3$ mol$^{-1}$ K, a value that is significantly below that expected for six magnetically isolated spin doublets ($\chi_M T$ = 2.25 cm$^3$ mol$^{-1}$ K with $g = 2.0$). When cooling, $\chi_M T$ continuously decreases to vanish at ca. 50 K. The magnetic susceptibility exhibits a broad maximum at ca. 230 K. These features are typical of an overall antiferromagnetic coupling, leading to a diamagnetic ground spin state.

The great intramolecular distance between the two hexameric rings in **1** allows us to consider it as two magnetically isolated hexacopper(II) rings. An inspection of the structure of each hexameric ring [Cu(1)−Cu(6)] shows the occurrence of several intraring exchange pathways involving the equatorial bonds at each Cu atom. This is why, in order to establish the best spin coupling model, we performed DFT-type calculations on the real hexameric unit.

These calculations (see Table S3 in the Supporting Information) show that the main exchange pathways and the calculated magnetic couplings across them are the following: (i) one ribose O atom and a carbonate O atom as two monatomic bridges ($J_{12} = J_{34} = J_{56} = J_I = -350$ cm$^{-1}$); (ii) one carbonate bridge in the *anti*−*anti* conformation ($J_{14} = J_{25} = J_{36} = J_{II} = -26$ cm$^{-1}$); (iii) one ribose O atom and a carbonate group in the *syn*−*syn* conformation as a bridge ($J_{16} = J_{23} = J_{45} = J_{III} = +37$ cm$^{-1}$); (iv) one carbonate bridge in the *anti*−*syn* conformation [$J_{13} = J_{35} = J_{15} = J_{24} = J_{46} = J_{26} = J_{IV} = -5.1$ cm$^{-1}$ (average value; see Table S3 in the Supporting Information)] (see inset of Figure 3).

Having this data in mind, the analysis of the magnetic data of **1** was carried out through the Hamiltonian $\hat{H} = -J_I(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_3\cdot\hat{S}_4 + \hat{S}_5\cdot\hat{S}_6) - J_{II}(\hat{S}_1\cdot\hat{S}_4 + \hat{S}_2\cdot\hat{S}_5 + \hat{S}_3\cdot\hat{S}_6) - J_{III}(\hat{S}_1\cdot\hat{S}_6 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_4\cdot\hat{S}_5) - J_{IV}(\hat{S}_1\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_5 + \hat{S}_1\cdot\hat{S}_5 + \hat{S}_2\cdot\hat{S}_4 + \hat{S}_4\cdot\hat{S}_6 + \hat{S}_2\cdot\hat{S}_6)$. The set of best-fit parameters were $J_I = -286$ cm$^{-1}$, $J_{II} = -41.8$ cm$^{-1}$, $J_{III} = +41.4$ cm$^{-1}$, and $J_{IV} = +3.3$ cm$^{-1}$ and $g = 2.06$. The calculated curve matches very well the magnetic data in the whole temperature range explored. It is quite satisfying to see that the values obtained through the fit agree in magnitude and sign with the calculated ones (except for $J_{IV}$, whose value is so small that the discrepancy observed is physically reasonable). The strongest magnetic coupling observed through the double monatomic bridges (I) is as expected,[8] and a survey of the available magnetostructural data of carbonate-bridged copper(II) complexes[9] shows that intermediate antiferromagnetic interactions are observed through the carbonate bridge in the *anti*−*anti* conformation (II), whereas they are weak, either ferro- or antiferromagnetic, across the *anti*−*syn* one (IV). Finally, the *a priori* surprising relatively large ferromagnetic coupling observed in III [a strong antiferromagnetic coupling is predicted in the copper(II) complexes when only one of the two bridges involving III occurs] is due to the countercomplementarity effect between the combined *syn*−*syn* carbonate and monatomic ribose O bridges, as known for dicopper(II) units with *syn*−*syn* carboxylate and either monatomic phenolate,[10a] alkoxo,[10b] hydroxo,[10c,d] or azido N (end-on coordination mode)[10e] atoms.

In summary, we report here the preparation and magnetostructural investigation of the second example of copper(II) cytidinate macromolecules exhibiting an overall antiferromagnetic behavior and a unprecedented multiarm-supplied globular shape, where two distinct cavities with different dimension/shape and receptor properties occur.

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**Supporting Information Available:** X-ray crystallographic files in CIF format, Figures S1−S3, details of the crystallography with selected bond distances for **1** and **2** (Tables S1 and S2), a view of the [Cu(H$_2$cyd)$_4$]$^{2+}$ cation in **2** (Figure S4) and its packing (Figure S5), synthesis of **1** and **2**, IR spectra (Figures S6 and S7), and a TGA curve for **1** (Figure S8), computational details and discussion on the calculated magnetic couplings, magnetic exchange couplings in **1** with an indication of the bridging ligands involved and selected structural parameters (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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