A New Octanuclear Copper(II)−Nucleoside Wheel

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Recently, considerable attention has been paid to novel cyclic polynuclear metal complexes,[1] often regarded as the metal analogues of the corresponding calixarene.[2] The interest in these systems is due to the combination of their aesthetically appealing structures and the host−guest chemistry that results from the inclusion of small molecules or ions into their central cavities.[3]

Nucleobases, nucleosides, and nucleotides contain a large number of oxygen and nitrogen donor sites of different basicity and, hence, of different donor properties. Many research efforts have been devoted to the rational design and elaboration of biomimetic systems based on the interaction of nucleobases and its derivatives with a wide range of metal ions.[4] It is well-known that the metal−nucleobase interactions play a crucial role in the resulting structure and function of nucleic acids.[5] It has been shown that nucleobases can be incorporated into nanoscale macrocycles, and that they can be used to build metallocycle supramolecular arrays.[1a,6] However, as far as we know, there are only two examples of cyclic complexes containing uridine[7] and adenosine[8] nucleosides as ligands.

Here we report the synthesis, X-ray structure, magnetic investigation, and EPR study of the first example of a polynuclear copper-(II)−cytidine complex of formula $[Cu(H_2O)_6][Cu_8(Hcyd)_8(CF_3SO_3)_4](CF_3SO_3)_6 \cdot 12H_2O$ (**1**) (H₂cyd = cytidine).

X-ray quality crystals of **1** were obtained by slow evaporation of an aqueous solution containing $Cu(CF_3SO_3)_2$ and cytidine in a 1:1 molar ratio, the initial value of pH being 5.0. Complex **1** exhibits a fascinating calixarene-like structure which is made up of octanuclear $[Cu_8(Hcyd)_8(CF_3SO_3)_4]^{4+}$ rings that include mononuclear $[Cu(H_2O)_6]^{2+}$ cations (Figure 1 and Figure S1). Uncoordinated triflate anions and crystallization water molecules are also present in **1**.

The ring is built up of four dicopper(II) subunits, each one having as bridges two cytidinate−alkoxo and one O−S−O suphonate group. Simultaneously, the monodeprotonated cytidinate links these structural units to each other. In fact, the cytidinate ligand is coordinated to three copper atoms through the pyrimidine nitrogen N(3) and the ribose oxygen O(3′) and O(2′) atoms [av. values of the Cu−N(3), Cu−(O3′), and Cu−(O2′) bonds are 1.99(1), 2.05-(1), and 1.98(1) Å, respectively], the latter one acting as a bridge between the copper atoms in each dinuclear subunit (Figure 2). The elongated distorted octahedral coordination around each copper atom in **1** is achieved through the coordination of one triflate oxygen atom and the exocyclic pyrimidine oxygen O(2) [Cu−O bonds varying in the range of 2.412(3)−2.554(4) and 2.512(4)−2.711(4) Å, respectively] in axial positions. The values of the Cu−N(3) and Cu−O(2) bonds agree with those of the two examples reported in the literature.[9]
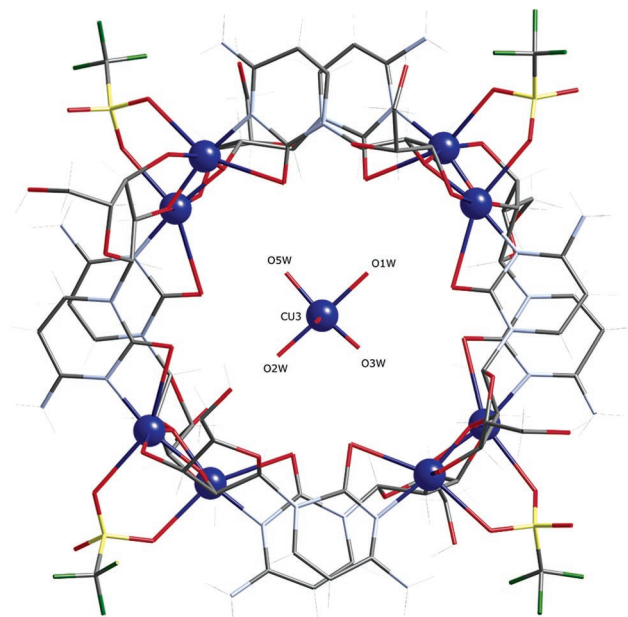

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Figure 1. View along the *y*-axis of the octanuclear $[Cu_8(Hcyd)_8(CF_3SO_3)_4]^{4+}$ host together with the mononuclear $[Cu(H_2O)_6]^{2+}$ guest.
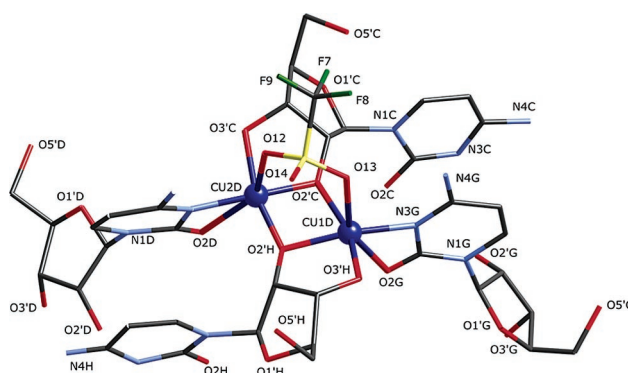

Figure 2. View of a fragment of **1** showing a dicopper(II) subunit.

The values of the copper−copper distance and those of the angle at the O(2′) bridge within the dicopper(II) subunits vary in the ranges of 2.972(3)−3.003(3) Å and 94.7(4)−100.8(4)°, respectively. The double ribose oxygen bridge of the cytidinate in **1** is unprecedented and in general very unusual for nucleosides. Such a coordination mode for the copper(II)−cytidine system was only suggested from an EPR study in dimethyl sulfoxide solutions.[10] Some examples in the solid state were reported elsewhere for adenosine,[11] guanosine,[12] and uridinate ions.[7]

In the case of uridinate, a complex of formula $Cu_8(urid)_8Na_8\cdot$ $5NaClO_4\cdot48H_2O$ (H_3urid = uridine) was reported which contains the octanuclear $[Cu_8(urid)_8]^{8-}$ anion and $[Na(H_2O)_6]^+$ cations, similarly to what is observed in **1**. Anyway, a careful comparison between the two structures reveals important differences. The uridinate ligand shows a three-coordination via N(3), O(3′), and O(2′), with the copper atoms adopting a square planar geometry. However, further coordination of the exocyclic oxygen atom and the triflate anions to copper in **1** leads to a 4 + 2 octahedral environment. Furthermore, the uridinate and the cytidinate exhibit different coordination modes (three- or four-coordination, respectively) and deprotonation degrees (three- and mono-deprotonated, respectively). This fact accounts for the different overall charge of the octanuclear $[Cu_8(Hcyd)_8(CF_3SO_3)_4]^{4+}$ (**1**) and $[Cu_8(urid)_8]^{8-}$ rings.

The eight copper atoms of the ring in **1** occupy the summits of a distorted square antiprism, the Cu···Cu separations across the cytidinate group varying in the range of 8.157(2)−8.488(2) Å. The ring shows receptor properties through multiple H-bonding interactions toward $[Cu(H_2O)_6]^{2+}$ cations which occupy the centers of the octanuclear motifs (Figure 1). They are linked to the wall of the toric-like anions by means of hydrogen bonds involving the O(2) atoms of the pyrimidine rings (that point toward the center of the cavities) and the four water molecules O1W, O2W, O3W, and O5W [OW···O distances varying in the range of 2.74(2)−3.27(1) Å]. The values of the Cu−O$_w$ bond distances lie in the range of 1.96-(2)−2.43(3) Å, and they are in agreement with those reported for similar complexes.[3a]

The structural analysis also revealed the occurrence of a large number of crystallization water molecules placed inside and outside of the rings that give rise to a extensive hydrogen-bond network involving the coordinated O(4W) and O(6W) water molecules and triflate anions. This leads to the formation of layers of octanuclear rings in the *ac* plane with a AB stacking sequence and channels running along the crystallographic *b*-axis (Figure S2). The resulting channel-like structure facilitates the adsorption/desorption of the solvent from the crystal, as shown by thermogravimetric analysis, with this process occurring with the loss of the crystallinity.

The magnetic properties of **1** under the form of $\chi_M T$ versus T plot [χ_M is the magnetic susceptibility per nine copper(II) ions] are shown in Figure S3. At room temperature, $\chi_M T$ is 3.07 cm^3 mol^{-1} K, a value which is significantly below that expected for nine magnetically isolated spin doublets ($\chi_M T = 3.72$ cm^3 mol^{-1} K with $g = 2.10$). When cooling, $\chi_M T$ continuously decreases to reach a plateau at $T \leq 80$ K with a value of 0.45 cm^3 mol^{-1} K. This curve is typical of a strong antiferromagnetic interaction, the Curie law at low temperature being due to a magnetically isolated spin doublet. The presence in **1** of four pairs of copper(II) ions, each pair being bridged by two ribose oxygen atoms with values at the bridging angle varying in the range of 94.7(4)−100.8(4)°, accounts for the strong antiferromagnetic coupling observed, in agreement with previous magneto-structural data for double alkoxo-bridged dinuclear copper(II) complexes.[13] The magnetic data of **1** were analyzed through a model of four identical copper(II) dimers with a strong intradimer antiferromagnetic interaction and a magnetically isolated spin doublet, the variable parameters being the average Landé factors for the dimer (g_d) and monomer (g_m) and the intradimer exchange coupling (J). Best-fit parameters are $J = -141$ cm^{-1}, $g_d = 2.08$, $g_m = 2.20$ with $R = 1.2 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calcd}(i)]^2/[(\chi_M T)_{obs}$

$(i)]$.[2] The value of J is consistent with the average value of the angle at the alkoxo bridge (θ) having in mind that the Cu_2O_2 core is not planar (a roof-shaped geometry with dihedral angles ranging from 20.6 to 25.9°).[13] The magnetization plot of **1** at 2.0 K (Figure S4) corresponds to the Brillouin function for an isolated spin doublet with $g = 2.20$, in full agreement with the interpretation given above.

The X-band EPR spectrum of **1** at $T \leq 80$ K is typical of a spin doublet of axial symmetry (see Figure S5) with g$_{||}$ (2.44) > $g_\perp$ (2.10) > 2.0 and hyperfine coupling ($A_{||} = 107$ G) on the parallel component [uniform signal splitting of the four peaks which arise from the hyperfine coupling with the copper nucleus ($I = 3/2$)]. This is consistent with the presence of the elongated tetragonal octahedron $[Cu(H_2O)_6]^{2+}$ having a $d(x^2 - y^2)$ ground state configuration.

In summary, a one-pot synthesis and characterizations of a very stable octanuclear $[Cu_8(H_2cyd)_8(CF_3SO_3)_4]^{4+}$ species which acts as a host toward the $[Cu(H_2O)_6]^{2+}$ cations has been reported, despite the high positive charge of eight copper(II) centers. This result opens new possibilities of recognition and complexation in the field of the host−guest chemistry, which might be combined with the intrinsic magnetic and structural properties of metal ions involved.

Supporting Information Available: X-ray crystallographic file in CIF format; view along the *c*-axis of the octanuclear entity and crystal packing of **1** (Figures S1 and S2); plots of $\chi_M T$ versus T (Figure S3), magnetization against H (Figure S4), and EPR spectra of **1** (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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