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Novel Hexanuclear Copper(II) Complex Built from a Simple Tetrachelating Triazole Ligand: Synthesis, Structure, and Magnetism

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Supporting Information

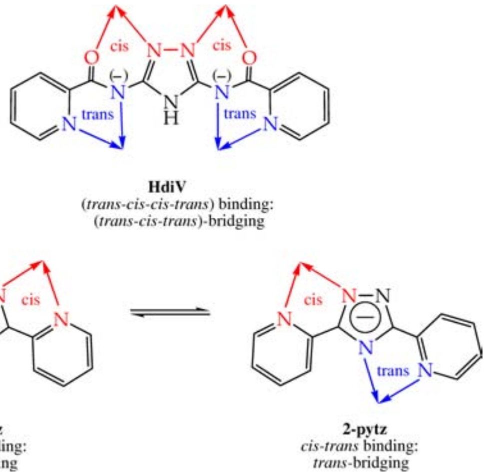
ABSTRACT: A new easy symmetric 3,5-disubstituted 1,2,4-triazole ligand (H_3diV) by reaction with an excess of copper(II) salt has afforded a novel hexanuclear compound (Cu/HdiV ratio of 6:2) through a bis(trans−cis−cis−trans) binding mode, exhibiting two types of Cu^{II} centers and two clearly distinguishable antiferromagnetic J_1 (-234 cm^{-1}) and J_2 (-35 cm^{-1}) coupling constants.

The versatility of triazoles to bridge metal centers in different ways is an area currently being explored to produce supramolecular structures with different potential functionalities, such as magnetic, optic, and electrochemical or simply as a starting point in crystal engineering.[1] On the other hand, the triazole systems afford discrete polymetallic complexes of interest to gain understanding on the mechanisms of biological systems and the nature of magnetic cooperativity.[1,2] The discrete polynuclear metal clusters are indeed ideal candidates for the investigation on the properties of molecule-based magnets.[1−3]

The 1,2,4-triazole-based ligands are commonly organized in three categories, namely, those containing a sole coordinative ring, those comprising two rings bridged by a spacer, and those having two or more functional groups. The last category is well represented by the 3,5-bis(pyridine-2-yl)-1,2,4-triazole ligand (known as Hpytz or Hbpt)[4] or its close derivatives.[1,2] Recently, Chen et al. have prepared, by hydrothermal synthesis, a series of polymeric structures based on the [Cu^I(2-pytz)] building block, which exhibited different conformations (i.e., molecular chairs, zippers, and zigzag and helical chains) as a result of the different binding modes of the ligand (Scheme 1, bottom).[5] From a different approach, Brooker et al. have reported triazole-based ligands containing pyridine pendant arms that showed enhanced denticity (i.e., bis-terdentate and bis-tetradentate binding), thus yielding unusual dinuclear and tetranuclear complexes.[2c] Brooker et al. have also shown that using bis-bidentate dipyridyl derivatives, under appropriate synthesis conditions (with selected coligands), trinuclear,[2d] tetranuclear, and even octanuclear[2e] systems can be isolated.

Our group has been developing 3-substituted or 3,5-disubstituted 1,2,4-triazole ligands with the aim of obtaining, by reaction with copper(II) salts, models of multicopper enzymes[6] or compounds with nuclease properties.[7] The first step in the DNA scission process is DNA binding, and the presence of multiple positively charged metallic centers has been proven to increase the affinity of the nuclease by the double helix, given the anionic nature of this biopolymer.[8] We have recently reported a tetranuclear and some binuclear triazole copper(II) complexes, which showed efficient DNA cleavage properties.[7]

Scheme 1. Bridging Mode of the Dideprotonated HdiV (this work) and the Monodeprotonated 2-pytz[5b] Ligands



In this context, a new potentially dinucleating ligand was designed and prepared: 3,5-bis(pyridine-2-yl-acetamido)-1,2,4-triazole = 3,5-bis(picolinamido)-1,2,4-triazole (hereafter shortened to H_3diV). The synthesis was performed by a one-pot reaction of guanazole with ethyl 2-picolinate in a glass oven.[9] The H_3diV ligand is similar to the Hpytz/Hbpt ligand. The difference between both compounds lies in the acetamido linker that connects the pyridine and triazole rings in H_3diV. Accordingly, this new derivative, through deprotonation at both acetamido groups (HdiV form), offers eight donor atoms and four chelating rings for metal coordination (Scheme 1, top).

The H_3diV ligand is insoluble in water and only moderately soluble in methanol. The addition of a copper perchlorate solution to a hot methanolic solution of the ligand in a 2:1 ratio yielded abundant pale-green precipitate. Instead, a high excess of copper salt (6:1) produced only some precipitate, which was removed by filtration. The resulting solution was allowed to evaporate. After a couple of months, from an almost dry solution, big sea-blue single crystals of compound **1** appeared.[10] Presumably, the high amount of perchlorate anions of the

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crystal structure is responsible for its water solubility. The X-ray diffraction study[11] revealed the hexameric nature of the copper(II) complex **1** (Figure 1 and S5, S7, and S8 in the Supporting Information, SI) of formula $[Cu_6(HdiV)_2(ClO_4)_6(H_2O)_{14}](ClO_4)_2\cdot 10H_2O$.

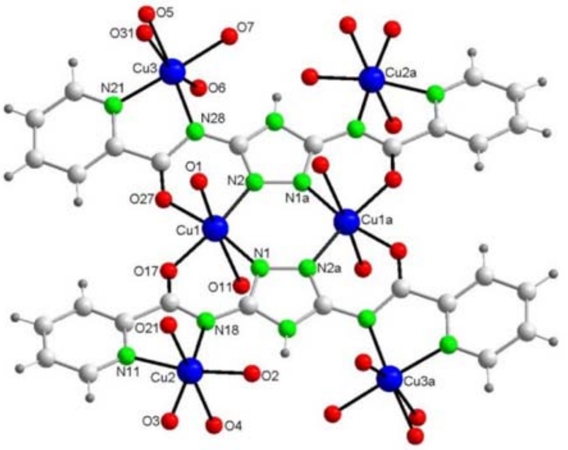

Figure 1. Structure of the cation of **1**. Selected distances (Å): Cu1−O17 1.923(5), Cu2−N18 2.028(5), Cu1−O27 1.954(5), Cu2−O3 1.995(6), Cu1−N2 1.957(6), Cu2−O21 2.519(7), Cu1−N1 1.963(6), Cu3−N21 1.978(6), Cu1−O1 2.428(8), Cu3−O5 1.989(6), Cu1−O11 2.809(9), Cu3−O7 1.991(5), Cu2−N11 1.985(7), Cu3−N28 2.035(6), Cu2−O2 1.984(6), Cu3−O6 2.269(7), Cu2−O4 2.332(8), Cu3−O31 2.577(7).

A literature revision among the highly nuclear 1,2,4-triazole compounds confirms the singularity of compound **1**.[1,12] To the best of our knowledge, such a hexanuclear "1 + 1 + 2 + 1 + 1" copper(II) cluster has never been reported. The only molecular complex with six metals found in the context of triazole and tetrazole ligands is the compound $[Cu_6(\mu_6\text{-}Cl)(\mu_3\text{-}OH)_2(\mu\text{-}L)_6Cl_9(H_2O)_3]\cdot 3H_2O$ [L = 4-(4-hydroxyphenyl)-1,2,4-triazole].[13] Its structure comprises two hydroxo-centered triangles. In general, the Cu_6 clusters are usually either of the cubane[14a]−cage[14b] type or of the steplike type.[3]

The structural unit cell of **1** contains a centrosymmetric cation $[Cu_6(HdiV)_2(ClO_4)_6(H_2O)_{14}]^{2+}$, 2 perchlorate anions, and 10 guest water molecules. The ligand H_3diV is doubly deprotonated at the two N18 and N28 acetamido positions and keeps the H atom of the triazole ring (then it is present as HdiV). The two central Cu^{II} ions are linked by a double $\mu_{1,2}$-triazole bridge. This binding mode is usual for 3,5-disubstituted triazole ligands (cis−cis binding or cis-bridging mode).[1−3] Four peripheral Cu^{II} ions, trans-chelated, are connected to the central Cu centers through a double NCN + NCO bridge, which involves the triazole ring and the substituent (trans−cis binding or trans-bridging mode; Scheme 1). Therefore, each HdiV ligand bridges four Cu ions in a trans−cis−trans mode.

A feature of this Cu_6 cluster is that it is roughly planar. The six metal centers lie approximately in the same plane, with the deviations from the mean plane, defined by Cu2, Cu2a, Cu3, and Cu3a, being +0.302 Å (Cu1) and −0.302 Å (Cu1a) (S12 in the SI). The whole ligand system is nearly planar, although the pyridine rings, more external, tend to bend out of the planar $\{Cu1(N1-N2)_2Cu1a\}$ fragment, forming with it dihedral angles of ±9.5° and ±16.9° (py−py′ dihedral angles are 21.7°). This type of planarity imposed by the ligand system has also been described for a Cu_4 "1 + 2 + 1" tetranuclear copper compound constructed with a related triazole-based ligand.[7a]

In **1**, the central Cu atoms (Cu1 and Cu1a) exhibit, in a first approach, square-planar CuN_2O_2 geometries. As shown in Figure 1 and S8 in the SI, Cu1 and the symmetry-related Cu1a ions are four-coordinated by the N1 and N2 atoms from two different triazole rings (at 1.96 and 1.96 Å) and by two oxygen carbonyl atoms (O17 and O27) from two different HdiV ligands (at 1.92 and 1.95 Å). In addition, one water O atom (O1) establishes a weaker interaction in the apical position (at 2.43 Å). Finally, one perchlorate anion (Cl1) approaches the $\{Cu1(N1-N2)_2Cu1a\}$ plane to fill the sixth coordination position at a Cu1−O11 distance of 2.81 Å (S9 in the SI).

The four peripheral Cu atoms (Cu2, Cu2a, Cu3, and Cu3a) present, in the first instance, square-pyramid environments, which afford CuN_2O_2 + O cores. The equatorial positions are occupied by the N pyridine and N acetamido atoms of one HdiV ligand (distances from 1.98 to 2.04 Å) and by two water O atoms (O2 and O3 in Cu2; O5 and O7 in Cu3; bond lengths in the range 1.98−2.01 Å). The axial site is occupied by another water O atom (O4 and O6; at 2.27 and 2.33 Å). A further contact is produced with one perchlorate O atom (O21/Cl2 and O31/Cl3) at longer distances (2.52 and 2.58 Å).

In the crystal lattice, the perchlorate Cl1 anion forms two moderate hydrogen bonds, one with the water molecule axially (weakly) bonded to the Cu1a [d(O14···O1) = 3.03 Å] atom and another one with the water molecule equatorially coordinated to the peripheral Cu2* (from a neighboring hexanuclear unit) atom [d(O13···O3*) = 2.76 Å], thus connecting two different units (S9 and S10 in the SI). Finally, the fourth type of perchlorate anion (Cl4) links two different units through two hydrogen bonds established with coordinated/semicoordinated water molecules belonging to two different Cu_6 units [d(O43···O5) = 2.95 Å and d(O41···O4*) = 2.90 Å] (S10 in the SI). In this way, a 3D supramolecular network is generated (S11 in the SI).

As expected, the hexanuclear cation of **1** presents many different crystallographically independent Cu···Cu distances, i.e., d(Cu1···Cu1a) = 3.83 Å, d(Cu1···Cu2) = 5.37 Å, d(Cu1···Cu3) = 5.36 Å, d(Cu2···Cu3) = 10.50 Å, d(Cu3···Cu2a) = 5.87 Å, and d(Cu2···Cu2a) = 12.05 Å.

The thermal dependence of the $\chi_M T$ product (χ_M being the magnetic susceptibility per Cu_6 unit) is given in Figure 2. At room temperature, the $\chi_M T$ value is 2.31 $cm^3\cdot K/mol$, which is

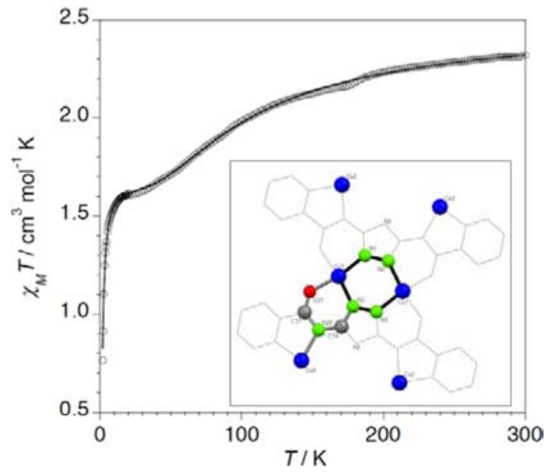

Figure 2. $\chi_M T$ vs T plot for complex **1** (values per Cu_6 unit). The solid line corresponds to the best-fit parameters obtained from the Hamiltonian (1). Inset: Cu_6 cluster with the two exchange pathways emphasized [black, J_1 = −234.4(3) cm^{-1}; gray, J_2 = −35.4(1) cm^{-1}].

close to the value expected for six independent $\mathrm{Cu^{II}}$ $S = {}^1/_2$ ions. Upon cooling, the $\chi_M T$ product decreases to give a plateau with a 1.61 $\mathrm{cm^3{\cdot}K/mol}$ value (at 30−15 K), which corresponds to four independent $\mathrm{Cu^{II}}$ ions. Below 15 K, $\chi_M T$ decreases sharply to reach a value of 0.75 $\mathrm{cm^3{\cdot}K/mol}$ at 2 K.

From structural analysis (vide supra), this behavior can be understood in terms of two stages. First, the high-temperature region (300−30 K) reveals the presence of a moderate-to-strong antiferromagnetic interaction within the "dimeric unit" between the two central Cu1−Cu1a atoms, doubly bridged through the triazole N1−N2 diazinic atoms. This bridging mode is well-known to lead to significant antiferromagnetic coupling.[1,2,4] Second, at lower temperatures (15−2 K), a weaker antiferromagnetic exchange involving the pairs Cu1−Cu2, Cu1−Cu3, Cu1a−Cu2a, and Cu1a−Cu3a occurs. This weak antiferromagnetic interaction is produced through the double NCN + NCO bridge, in a trans-bridging mode (anti−syn conformation, following the carboxylate bridges literature[15]). Taking into account all of these features, the following Hamiltonian was used:

$$H = -J_1 S_1\cdot S_{1a} - J_2(S_1\cdot S_2 + S_1\cdot S_3 + S_{1a}\cdot S_{2a} + S_{1a}\cdot S_{3a}) \qquad (1)$$

The best-fit parameters obtained from this Hamiltonian were $J_1 = -234.4(3)\ \mathrm{cm^{-1}}$, $J_2 = -35.4(1)\ \mathrm{cm^{-1}}$, and $g = 2.11(1)$. These coupling parameters are comparable to those observed for (respective) analogous bridges.[1,4,7]

In summary, a new tetrachelating triazole ligand has been designed and synthetized, $\mathrm{H_3diV}$. In the presence of an excess of $\mathrm{Cu^{II}}$, the assembly of two dideprotonated HdiV ligands has allowed one to isolate a novel almost planar hexanuclear copper(II) cluster (**1**), which exhibits well-defined magnetic behavior consisting of two different antiferromagnetic interactions. Finally, this polynuclear compound, water-soluble, is currently being tested as a DNA binding and cleavage agent because the presence of several metallic centers should favor the electrostatic interactions with the negatively charged double helix.[8]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and additional experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(9) Synthesis of $\mathrm{H_3diV}$: 3,5-diamino-1,2,4-triazole = guanazole (10.1 mmol, 1 g) and ethyl 2-picolinate (50.5 mmol, 6.8 mL) were mixed in a glass oven at 210 °C. The mixture was stirred (rotated) for 4 h. A brown solid was isolated, then washed with hot ethyl acetate, dried, and crystallized from hot methanol. Yield: 1.6 g, 51%. Further details and full characterization are given in S1 in the SI.

(10) Synthesis of complex **1**: A methanolic solution (10 mL) of $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$ (0.97 mmol, 0.360 g) was added dropwise to a hot methanolic solution (30 mL) of $\mathrm{H_3diV}$ (0.16 mmol, 0.050 g) (the reactant ratio $\mathrm{H_3diV/Cu^{II}}$ is 1:6). Immediately, a pale-green precipitate was formed. After filtration, the resulting green solution was placed in a crystallizing dish. Prismatic sea-blue crystals suitable for X-ray analysis were obtained after ca. 2 months. Yield: ca. 0.11 g (ca. 30%). Further details and full characterization are given in S2−S13 in the SI.

(11) Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 10.7330(3)$ Å, $b = 13.2580(3)$ Å, $c = 15.4740(5)$ Å; $\alpha = 67.589(2)°$, $\beta = 76.747(2)°$, $\gamma = 71.487(2)°$; $V = 1915.52(9)$ Å^3; $T = 298(2)$ K; $Z = 1$; $D_c = 1.928$ g/cm^3; $F(000) = 1122$; $\mu = 2.041\ \mathrm{mm^{-1}}$; 13807 reflections measured, 8744 unique ($R_{int} = 0.0339$); final R1 = 0.0940, wR2 = 0.2985. CCDC 918812. A full crystal report and details are given in S3 and S4 in the SI.

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