Inorg. Chem. **2007**, *46*, 372–374

Inorganic Chemistry
Communication

One-Dimensional Metal–Organic Framework with Unprecedented Heptanuclear Copper Units

Sacramento Ferrer,*,[†] Elena Aznar,[†] Francesc Lloret,[†] Alfonso Castiñeiras,[‡] Malva Liu-González,[§] and Joaquín Borrás[†]

Departament de Química Inorgànica, Universitat de València, 46100 Burjassot, Valencia, Spain,
Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15782 Santiago
de Compostela, Spain, and SCSIE, Universitat de València, 46100 Burjassot, Valencia, Spain

Received October 6, 2006

The reaction of copper(II) sulfate, copper(II) chloride, 3,5-diacetylamino-1,2,4-triazole, and 3-acetylamino-5-amino-1,2,4-triazole in water yields green, plate-shaped crystals of $[[\{Cu_3(\mu_3\text{-}OH_{1/2})L(H_2O)_2Cl\}_2\{\mu\text{-}Cu(H_2O)_2Cl_2\}]\cdot 12H_2O]_n$ (**1**), where L is a new triazole-derived macrocyclic ligand. The structure of **1** consists of heptanuclear $(H)OCu^{II}_3\text{–}Cu^{II}\text{–}Cu^{II}_3O(H)$ entities linked in pairs through symmetric $\mu_3\text{-}O\cdots H\cdots O\text{-}\mu_3$ hydrogen bonds to form a double-stranded one-dimensional network. A significant overall antiferromagnetic behavior has been observed for **1**.

Simple polynuclear paramagnetic clusters are useful in the study of systems in biology and magnetic materials because they allow a better understanding of the electronic and magnetic properties and, thus, the bonding description of more complex analogues. Of these, trinuclear copper complexes with trigonal symmetry are the object of current research because of the existence of multicopper active sites in several oxidades.[1] In this context, compounds containing a $[Cu_3(\mu_3\text{-}X)(\mu\text{-}L)_3]^{n+}$ (X = O, OH, Cl, Br) core with peripheral L bridges have been previously published, where L is a Schiff base,[2a,b] oxime−oximate,[2c,d] pyrazole,[2e−g,3b] or triazole[3a,4] derivative. Some of these pyrazole- and triazole-type complexes exhibited catalytic activity[2f] and interesting magnetic properties related with their character of spin-frustrated systems.[2d,3a,b] In this Communication, we show a novel heptanuclear species formed by two triangular Cu_3O-based units linked by a Cu atom. This heptanuclear species is, in turn, the building block of a one-dimensional (1D) network of formula $[[\{Cu_3(\mu_3\text{-}OH_{1/2})L(H_2O)_2Cl\}_2\{\mu\text{-}Cu(H_2O)_2Cl_2\}]\cdot 12H_2O]_n$ (**1**). The structure of this compound is also unique in the ligand, L, a triazole-containing macrocycle generated in situ from condensation of simple triazole derivatives in the presence of a high ratio of copper(II). We report here its synthesis and characterization.

Reaction of the ligand Haaat (3-acetylamino-5-amino-1,2,4-triazole) with different copper(II) salts yielded trinuclear copper(II) complexes of formula $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}aaat)_3]^{2+}$, as was reported elsewhere.[3a,4b] In contrast, reaction of a mixture of Haaat and Hdaat (3,5-diacetylamino-1,2,4-triazole) with a mixture of copper(II) chloride and copper(II) sulfate in aqueous media (the ratio of ligand/copper(II) is 0.9−1.1:3−3.5) affords a heptanuclear compound, **1**, with two trinuclear copper(II) cores holding each one by a macrocycle, L.[5] The Cu_3O core probably acts as a template in the formation of this new ligand. The synthesis could be reproduced even with some changes in the ligand mixture. Compound **1** is one of the few cases of structurally

---

* To whom correspondence should be addressed. E-mail: sacramento.ferrer@uv.es.

[†] Departament de Química Inorgànica, Universitat de València.

[‡] Universidad de Santiago de Compostela.

[§] SCSIE, Universitat de València.

(1) (a) See a thematic (Biomimetic Inorganic Chemistry) issue of *Chem. Rev.* **2004**, *104* (*2*), 347−1200. (b) Yoon, J.; Mirica, L. M.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **2005**, *127*, 13680−13693.

(2) See references therein: (a) Costes, J. P.; Dahan, F.; Laurent, J. P. *Inorg. Chem.* **1986**, *25*, 413−416. (b) Ray, M. S.; Chattopadhyay, S.; Drew, M. G. B.; Figuerola, A.; Ribas, J.; Díaz, C.; Ghosh, A. *Eur. J. Inorg. Chem.* **2005**, 4562−4571. (c) Agnus, Y.; Louis, R.; Metz, B.; Boudon, C.; Gisselbrecht, J. P.; Gross, M. *Inorg. Chem.* **1991**, *30*, 3155−3161. (d) Stamatatos, T. C.; Vlahopoulou, J. C.; Sanakis, Y.; Raptopoulou, C. R.; Psycharis, V.; Boudalis, A. K.; Perlepes, S. P. *Inorg. Chem. Commun.* **2006**, *9*, 814−818. (e) Mezei, G.; McGrady, J. E.; Raptis, R. G. *Inorg. Chem.* **2005**, *44*, 7271−7273. (f) Casarin, M.; Corvaja, C.; di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F.; Tagliatesta, P. *Inorg. Chem.* **2004**, *43*, 5865−5876. (g) Casarin, M.; Corvaja, C.; di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F. *Inorg. Chem*. **2005**, *44*, 6265−6276.

(3) (a) Ferrer, S.; Lloret, F.; Bertomeu, I.; Alzuet, G.; Borrás, J.; García-Granda, S.; Liu-González, M.; Haasnoot, J. *Inorg. Chem.* **2002**, *41*, 5821−5830. (b) Liu, X.; de Miranda, M. P.; McInnes, E. J. L.; Kilner, C. A.; Halcrow, M. A. *J. Chem. Soc., Dalton Trans.* **2004**, 59−64. (c) Yoon, J.; Solomon, E. *Inorg. Chem.* **2005**, *44* (22), 8076−8086.

(4) (a) Ferrer, S.; Haasnoot, J. G.; Reedijk, J.; Müller, E.; Biagini Cingi, M.; Lanfranchi, M.; Manotti Lanfredi, A. M.; Ribas, J. *Inorg. Chem.* **2000**, *39*, 1859−1867. (b) Ferrer, S.; Lloret, F.; Borrás, J.; Liu-González, M.; García-Granda, S. **2006**, submitted.

(5) $CuSO_4\cdot 5H_2O$ (0.5 mmol, 0.12 g) was mixed with a hot aqueous solution of ligand (0.085 g of Haaat + 0.099 g of Hdaat, 1.1 mmol, in 30 mL) with continuous stirring. A green solution was formed. Then, $CuCl_2\cdot 2H_2O$ (3 mmol, 0.52 g) was added. The resulting dark-green solution was allowed to stand at room temperature. After ca. 1 week, crystals of **1**, suitable for X-ray diffraction, were collected in ca. 40% yield. IR (KBr pellet, cm^{-1}): 3449(m), 3372−3340(sp,w), 3227(sh), 3008(m), 2931(sh), 2870(m), 1640(vs), 1601(s), 1509(s), 1471(w), 1471(w), 1371(m−w), 1291(m−w), 1091(w), 1042(w), 980(m), 861(w), 762(m).

10.1021/ic0619106 CCC: $37.00 © 2007 American Chemical Society
Published on Web 12/15/2006

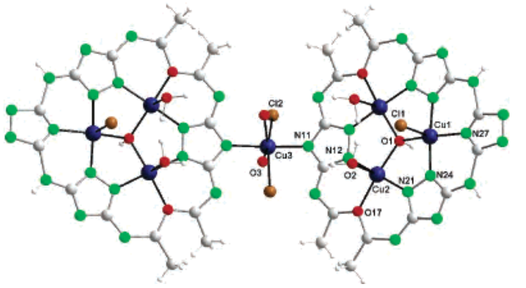

Figure 1. Structure of **1**, with a partial labeling scheme for the asymmetric unit. Solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu1−N27, 2.034(6); Cu1−N24, 1.902(7); Cu1−O1, 1.960(6); Cu1−Cl1, 2.723(3); Cu2−N21, 1.928(5); Cu2−O17, 2.010(5); Cu2−N12, 1.933(5); Cu2−O1, 1.937(3); Cu2−O2, 2.330(5); Cu3−N11, 1.966(7); Cu3−Cl2, 2.405(4); Cu3−O3, 2.161(11); Cu1−O1−Cu2, 115.69(16); Cu2−O1−Cu2$^{\#}$, 117.1(3); N11−Cu3−O3, 85.3(2); N11−Cu3−Cl2, 93.33(15); N11−Cu3−N11$^{\#2}$, 169.6(5); Cl2−Cu3−O3, 156.1(4); O3−Cu3−O3$^{\#}$, 52.4(7); Cl2−Cu3−Cl2$^{\#}$, 100.2(2) [#, −*x*, *y*, *z*; #2, *x*, *y*, −*z* + $^{1}/_{2}$]. Sphere color scheme: blue, Cu; green, N; brown, Cl; red, O; gray, C. This scheme is used throughout.

characterized triazole-containing macrocyclic copper complexes reported to date.[6] Figure 1 shows the structure of **1** together with pertinent bond lengths.[7]

The macrocycle, L, providing one N4-monodentate, two N1,N2-bidentate, and one N1,N2,N4-tridentate 1,2,4-triazole rings,[8] accommodates three copper(II) ions, which are also bonded to a central hydroxo group and located at the corners of an almost equilateral triangle of sides 3.299(1), 3.299(1), and 3.304(2) Å. These edges are slightly shorter than those found in analogous trinuclear clusters not constrained by a peripheral cyclic ligand.[3a,4] The central μ_3-oxygen atom, displaced by 0.387(5) Å over the trigonal plane of the three coppers, exhibits sp^3-distorted hybridization with Cu−O−Cu′ angles of 115.7(2), 115.7(2), and 117.1(3)°. The tridentate triazole ring binds through N4 the unique copper(II) ion, Cu3, which interacts with the μ_3-triazole ring of a second trinuclear cluster to give a heptanuclear unit. Electroneutrality is achieved by deprotonation at the triazole rings; compound **1** represents one of the rare examples of the literature that includes a μ_3-triazolato ligand bonding to copper(II).[9,10] The structure is highly symmetric with a C_2 axis passing through Cu3. The axis corresponds to the intersection between two perpendicular symmetry planes: one includes Cu3, Cl2, and O3, and the second plane includes Cu3, N11, O1, Cu1, Cl1, and N27.

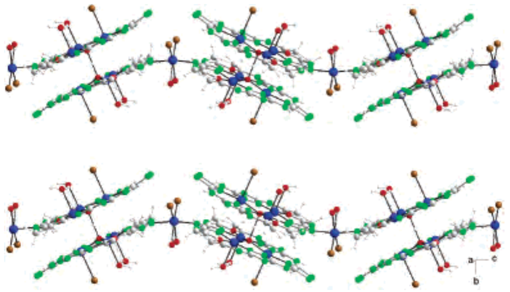

Figure 2. (a) Pairing between alternating heptanuclear "butterfly" units in **1**, with the symmetric hydrogen bonds. (b) 1D network of **1** viewed along the *c* axis (chains of linked convex and concave heptanuclear units, resembling a tiled roof).

The two crystallographically independent copper(II) atoms of the triangular group display square-pyramidal geometries, with a (N, N, N′, O + Cl) chromophore for Cu1 and a (N, N′, O, O′ + O″) chromophore for Cu2. The equatorial bond distances range from 1.902(7) to 2.034(6) Å; the apical bond distances are 2.723(3) and 2.330(5) Å for Cu1−Cl1 and Cu2−O2, respectively. The τ index[11] of Cu1 and Cu2 is <0.10, close to the value of 0 for an ideal square pyramid. The copper atoms lie 0.159(4)−0.151(3) Å over the plane defined by their respective basal donor atoms. The dihedral angle between these planes is 9.8(2)°. The single copper atom, placed on a special position, is six-coordinated, with two short Cu−N$_{\text{triazolato}}$ [1.966(7) Å], two Cu−O$_{\text{water}}$ [2.161(11) Å], and two longer Cu−chloride [2.405(4)Å] contacts; angles corresponding to these positions differ notably from values expected for a regular octahedron (Figure 1). It is remarkable that the Cu3−N11 bonds, which establish the connection between the triangular cores, are strong ones.

The two least-squares planes defined by each of the interlinked trinuclear moieties form a dihedral angle of 47.66(3)° in a way that the resulting heptanuclear unit resembles a butterfly; the single copper atom would be located in the *body*. There is a further pairing of alternate *wings* through an unusual, lineal and symmetric, hydrogen bond, established between the central μ_3-oxygen atoms of two different heptanuclear units (see the Table of Contents synopsis and Figure 2). Therefore, one hydrogen atom is shared by two central μ_3-oxygen atoms [O···O′ distance is 2.528(9) Å], thus generating Cu_3−O−H−O−Cu_3 units. A μ_3-O···H···O-μ_3 group, with an even shorter O···O′ distance, 2.394 Å, was already reported by Watson and Holley.[12] Figure 3 shows in detail atoms and distances concerning this uncommon contact. The overall structure of **1** consists of a 1D arrangement built up by double wavy chains of heptanuclear entities on the *ac* plane, which are piled through the *b* axis via other strong hydrogen bonds involving crystallization water molecules. To our knowledge, only four papers have been published describing the use of triangular copper(II) clusters to form 1D triazole[3a]/pyrazole,[2g] 2D triazole[9]/pyrazole,[2g] or 3D triazole[9,10a] networks. The two 3D polymers reported, generated by solvothermal synthesis, contain, like **1**, μ_3-triazole rings coordinated to copper(II) but, in contrast to **1**, $Cu_3(\mu_3\text{-O})$ planar groups instead of $Cu_3(\mu_3\text{-OH})$ pyramidal groups. Interestingly, the $\{Cu[Cu_3(\mu_3\text{-O})(\mu_3\text{-trz})_3Cl_3\}$ (trz =

---

[6] Depree, C. V.; Beckmann, U.; Heslop, K.; Brooker, S. *J. Chem. Soc., Dalton Trans.* **2003**, 3071−3081.

[7] Crystal data for **1** ($C_{32}H_{65}Cl_4Cu_7N_{36}O_{24}$, fw = 1924.78): orthorhombic, *Cmcm* (No. 63), $a = 15.961(4)$ Å, $b = 13.884(4)$ Å, $c = 27.976(6)$ Å, $V = 6.200(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 2.062$ mg m^{-3}, λ(Cu Kα) = 1.541 804 Å, Bruker Nonius Kappa CCD 2000 diffractometer, $T = 120.0(1)$ K. 21518, reflns colld/unique reflns 21 518/2854 ($R_{\text{int}} = 0.0910$). R1 = 0.0550, wR2 = 0.1709.

[8] Reviews on triazole compounds: (a) Haasnoot, J. G. *Coord. Chem. Rev.* **2000**, *200−202*, 131−185. (b) Klingele, M. H.; Brooker, S. *Coord. Chem. Rev.* **2003**, *241*, 119−132. (c) Beckmann, U.; Brooker, S. *Coord. Chem. Rev.* **2003**, *245*, 17−29.

[9] Zhai, Q.-G.; Lu, C.-Z.; Chen, S.-M.; Xu, X.-J.; Yang, W.-B. *Cryst. Growth Des.* **2006**, *6* (6), 1393−1398.

[10] Ding, B.; Yi, L.; Cheng, P.; Liao, D.-Z.; Yan, S.-P. *Inorg. Chem.* **2006**, *45* (15), 5799−5803. (b) This paper includes copper(I) triazolate networks: Zhang, J.-P.; Zheng, S.-L.; Huang, X.-C.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 206−209.

[11] Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

[12] Watson, W. H.; Holley, W. W. *Croat. Chem. Acta* **1984**, *57*, 467.

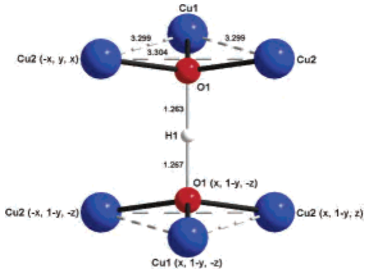

Figure 3. Distances (Å) in the 3 + 3′ antiprisma formed by the coppers of the $Cu_3O\cdots H\cdots OCu_3$ paired groups in the structure of **1**. The Cu2−Cu2(*x*, 1 − *y*, *z*) distance is 3.836 Å. The O1−O1(*x*, 1 − *y*, −*z*) distance is 2.528 Å.

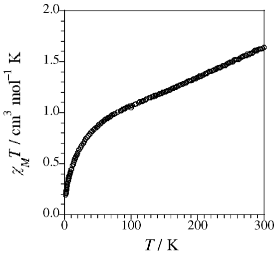

Figure 4. $\chi_M T$ vs T for **1** per heptamer.

1,2,4-triazolate) compound presents one copper(II) atom connecting *three* trinuclear units (*two* in the case of **1**) and, like in the case of **1**, it has also been produced from copper dichloride.[9]

A preliminary magnetic study of **1** has been performed. Magnetic susceptibilities were measured in the 2.0−300 K range with a SQUID magnetometer and are plotted in Figure 4. The value of $\chi_M T$ (χ_M is the magnetic susceptibility per Cu^{II}_7 entity) is 1.65 cm^3 mol^{-1} K at room temperature, and it decreases continuously with decreasing T, reaching a value of 0.19 cm^3 mol^{-1} K at 2.0 K. These features indicate strong antiferromagnetic coupling. In a first approach, the magnetic behavior of **1** must be dominated by the magnetic coupling within the trinuclear core; in fact, similar systems[3a,4] exhibit J values of ca. −200 cm^{-1}, referred to as the Heisenberg−Dirac−van Vleck (HDVV) Hamiltonian $\mathbf{H}_{\mathrm{HDVV}} = -J_{12}S_1S_2 - J_{23}S_2S_3 - J_{13}S_1S_3$. Both in the case of an equilateral triangle ($J_{12} = J_{23} = J_{13}$) and in the case of a distorted triangle ($J_{12} \neq J_{23} \neq J_{13}$), the magnetism curve should follow the Curie law, and a plateau at $\chi_M T = 1.13$ cm^3 mol^{-1} K would be expected [$2\chi_M T(Cu_3) + \chi_M T(Cu) = 1.13$, with $g = 2$]. For **1**, however, below ca. 100 K, the experimental data lie below the theoretical Curie law values (Figure 4). This low-T behavior could be attributed to additional antiferromagnetic interactions and to the antisymmetric exchange (ASE) phenomenon.

The occurrence of ASE [$\mathbf{H}_{\mathrm{ASE}} = G(S_1S_2 + S_2S_3 + S_3S_1)$] may yield magnetic moment values smaller than those expected for the Curie law through the HDVV model.[2d,3] In principle, the low $\chi_M T$ values of **1** could be due to an ASE operating in each triangular unit. As a result of the ASE, the two degenerated spin doublets, which correspond to the low-lying spin state of an equilateral triangle, are split into two Kramers' doublets, with an energy gap of $2G$. The splitting has large effects on the magnetic susceptibility. Mainly, it yields magnetic anisotropy in the ground state: the parallel component of the susceptibility does not change significantly ($\chi_{\|} = \mu_\beta^2 g_{\|}^2/4kT$), while the perpendicular component changes considerably at low fields and at low temperatures ($\chi_\perp = \mu_\beta^2 g_\perp^2/4G$, for $G \gg H$ and $H \ll kT$).[3a] When T tends to zero, $\chi_\perp T$ vanishes and $\chi_{\|} T$ is 0.38 cm^3 mol^{-1} K (for $g = 2$); thus, the contribution of each Cu_3 unit would be $\chi T = (\chi_{\|} T + 2\chi_\perp T)/3 \approx 0.13$ cm^3 mol^{-1} K. In the lack of other interactions, at low temperature, the value of $\chi_M T$ per Cu_7 entity should be $\chi_M T = 2\chi T(Cu_3) + \chi T(Cu) \approx 0.64$ cm^3 mol^{-1} K. This value is larger than the experimental one, which indicates that additional antiferromagnetic interactions contribute to the magnetism of **1**.

The structure of **1** offers two further magnetic exchange pathways. One pathway involves the central copper(II) ion, Cu3, which would interact antiferromagnetically with the four nearest copper atoms, Cu2 and Cu2′, through the *N*,*C*,*N*-triazole bridge. Bridges of this type are known to mediate moderately strong antiferromagnetic interactions ($-J = 40-80$ cm^{-1}).[13] Moreover, the short hydrogen bond that connects triangular units of different heptanuclear entities (Figure 3) is also able to transmit significant antiferromagnetic interactions.[14]

Polycrystalline electron paramagnetic resonance (EPR) spectra of **1** have been recorded in the 2−300 K range, at both the Q- and X-band frequencies. From 300 to 10 K, they are silent. Below this temperature, a weak feature is observed at $g \approx 2.07$. EPR-silent spectra are expected for *equilateral* triangles with important ASE and have already been described for some $[Cu_3(\mu_3\text{-OH})(\mu\text{-L})_3]^{n+}$ compounds.[3a,b,15] The lack of signals for the unique copper(II) indicates a strong antiferromagnetic interaction with the neighboring Cu_3 units.

In summary, we have reported a copper(II) triazole network constructed by unprecedented $Cu^{II}_3-Cu^{II}-Cu^{II}_3$ heptanuclear units, linked by strong symmetric hydrogen bonds between the central μ_3-oxygen atoms to form $Cu^{II}_3-O-H-O-Cu^{II}_3$ species. The favorable interactions between the single Cu^{II} and the two adjacent Cu^{II}_3 groups and between Cu^{II}_3 groups of different heptanuclear units make this unique system appealing for an exhaustive study of its magnetic properties.

Acknowledgment. This work was supported by MCyT (Grant CTQ2004-03735/BQU) and by Xunta de Galicia (Project PGIDIT03PXIC20302PN).

Supporting Information Available: Experimental details for synthesis, spectroscopic characterization, and crystallographic determination; table with selected hydrogen bonds; figure of a packing view normal to the *ab* plane; and a CIF format file for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0619106

---

(13) Pals, W.; Pohlmann, A.; Subramanian, P. S.; Srinivas, D. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1377−1384.

(14) de Munno, G.; Viterbo, D.; Caneschi, A.; Lloret, F.; Julve, M. *Inorg. Chem.* **1994**, *33*, 1585−1586.

(15) In *distorted* Cu^{II}_3 triangles, EPR signals with $g < 2$ are the signature of the existence of important ASE.[3]