Tetranuclear Cu(II) complex supported by a central μ_4-1,1,3,3 azide bridge†

Prasant Kumar Nanda,[a] Guillem Aromí*[b] and Debashis Ray*[a]

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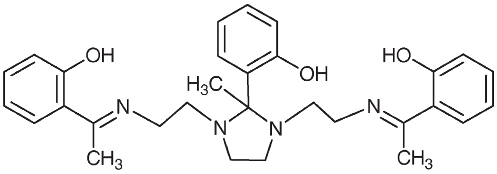
The new cluster $[Cu_4L_2(N_3)]Cl\cdot16H_2O$ (1) has been synthesized and characterized; it features a unique μ_4-1,1,3,3 bridging mode for azide, whose capacity to mediate magnetic coupling has been examined through bulk magnetic measurements and numeric fitting procedures.

The azide ligand has been a prominent actor in the development of molecular magnetism since its inception.[1] Primarily, this group has functioned as a structural bridge and magnetic coupler of paramagnetic metal ions within one-, two- or three-dimensional extended coordination arrays, rather than discrete molecules, unveiling interesting phenomena such as ferrimagnetism within homometallic chains,[2] or sheets.[3] Of these polymers, the vast majority feature the ligand (N_3^-) in the μ-1,1 (end-on, EO) or the μ-1,3 (end-to-end, EE) coordination mode. The former strongly favors the ferromagnetic coupling[1,4–6] between metals while the latter mostly facilitates antiferromagnetic interactions,[1,7,8] albeit these rules do not apply under certain specific circumstances (see below). Only recently, these properties have been increasingly exploited in the formation of discrete polynuclear complexes,[9–11] coinciding with the renewed eclosion of cluster coordination chemistry caused by the discovery of Single-Molecule Magnets.[12] This has revealed a variety of coordination modes of N_3^-, in many cases unprecedented, including μ_3-1,1,1,[13] μ_4-1,1,1,1,[14] μ_3-1,1,3,[15] or the very rare μ_4-1,1,3,3.[16] The study of the magnetic exchange mediated by this ligand in its different bridging modes is often hampered by the presence of additional bridging ligands.

We report here the preparation, structure and properties of a tetranuclear Cu^{II} cluster, $[Cu_4L_2(N_3)]Cl\cdot16H_2O$ (**1**), formed by two pairs of $[Cu_2L]^+$ units exclusively bridged by an unsupported μ_4-1,1,3,3 azide ligand (L is a dinucleating phenol–imine–amine ligand, Scheme 1).‡[17] This coordination mode has been reported only for one class of $[Ni^{II}_4]$ cluster where the quadruply bridged central μ_4-azide is supported by additional ligands.[16] Complex **1** represents thus a unique example where two dinuclear Cu^{II} moieties are connected structurally and magnetically by only one N_3^- group.



Scheme 1 H_3L.

We and others have been exploring the coordination properties of the dinucleating ligand L (and derivatives) with Cu^{II}, and studied the relevance of the resulting products in areas related to bioinorganic chemistry or molecular magnetism.[17–19] It has been established that this family of ligands invariably chelate and bridge pairs of Cu^{II} ions, leaving one coordination site on each metal for exogenous bridging in the formation of $[Cu_2LX]$ complexes (X = AcO, OMe, OH *etc.*). In some cases, aggregation into tetranuclear entities has been observed either through further bridging by the exogenous ligand (*e.g.* CO_3^{2-}),[20] or through the template action of a Na^+ cation.[21]

We have examined the possibility of including the N_3^- ligand into the growing family of X groups by replacement of H_2O from the complex $[Cu_2L(H_2O)]Cl\cdot2H_2O$ (**2**). Treatment of **2** with NaN_3 indeed resulted in the replacement of H_2O by N_3^-, and this was accompanied by the linkage of two $[Cu^{II}_2]$ moieties to form the tetranuclear cluster **1**. This compound can also be formed directly from its components in good yield by the reaction in air of H_3L, $CuCl_2\cdot2H_2O$, NaN_3 and NEt_3 in the 1 : 2 : 1 : 2 molar ratio. The complex was characterized by analytical, electrochemical and spectroscopic techniques. Thus, compound **1** behaves as a 1 : 1 electrolyte in DMF and its IR spectrum showed a unique strong absorption band at 2043 cm^{-1} caused presumably by the μ_4-N_3^- ligand. Also, a sharp peak is present at 1601 cm^{-1}, characteristic of the CH_3–C=N– functionalities of L^{3-}.

Single crystals of **1** suitable for X-ray diffraction were obtained by diffusion of MeOH into a MeCN solution of the product. The structure of the cation (Fig. 1)§ consists of a tetranuclear arrangement of four crystallographically equivalent Cu^{II} ions as two pairs of metal ions. The tetramer cation has crystallographic $2/m$ symmetry; the central azide N atom (N4) is at the $2/m$ center. Within each $[Cu_2]$ pair, the metal ions are bridged and chelated by one μ-L^{3-} ligand. These dinuclear units are in turn linked exclusively by one unsupported N_3^- ligand in the μ_4-1,1,3,3 bridging mode.

Within each dinuclear unit, the polydentate ligand L^{3-} bridges the metal ions *via* one imidazolidine and one phenoxide moiety while further coordinating the cations through two terminal phenoxide and imine groups. Each $[Cu^{II}_2]$ pair is also bridged in EO fashion by one end of the μ_4-N_3^- ligand. The four Cu^{II} ions are thus pentacoordinated and feature a highly distorted square pyramidal N_3O_2 environment (τ = 0.42).[22] In this pyramid, one

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[a] *Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India. E-mail: dray@chem.iitkgp.ernet.in; Fax: 91-3222-82252; Tel: 03222-283324*
[b] *Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647 08028-Barcelona, Spain. E-mail: guillem.aromi@qi.ub.es; Fax: +34 93 490 7725; Tel: +34 93 402 1273*

† Electronic supplementary information (ESI) available: Figure S1, showing the packing of **1** in the solid state. See DOI: 10.1039/b604502b

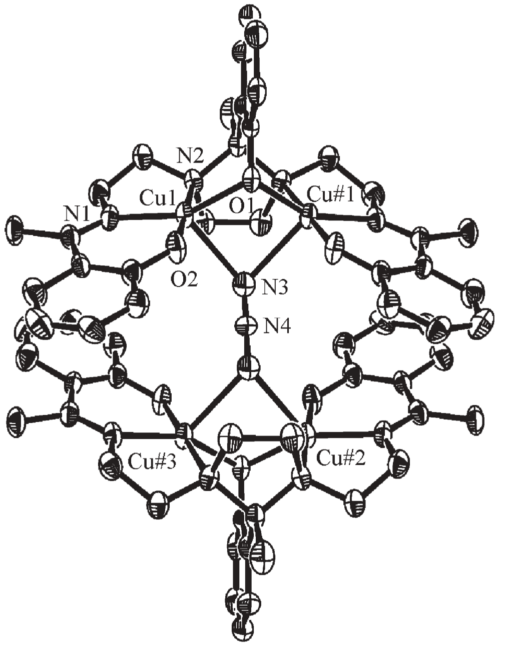
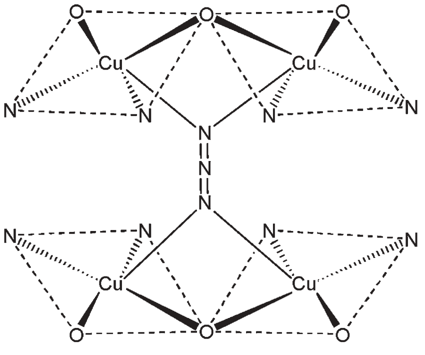
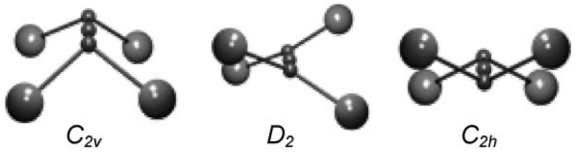


Fig. 1 ORTEP representation at the 40% level of the cation of **1**, $[Cu_4L_2(N_3)]^+$. Hydrogen atoms are not shown and the unique non-carbon atoms are labelled. Selected parameters (Å or °): Cu1–O1, 1.987(4); Cu1–O2, 1.880(5); Cu1–N1, 1.945(6); Cu1–N2, 2.072(6); Cu1–N3, 2.406(8); Cu1···Cu#1, 3.157(2); Cu1···Cu#3, 5.578(3); Cu1···Cu#2, 6.409(3); Cu1–O1–Cu#1, 105.2(3); Cu1–N3–Cu#1, 82.0(3). "#1", "#2" and "#3" denote symmetry operations [x, 1 − y, z], [−x, 1 − y, −z] and [−x, y, −z].



Scheme 2



Scheme 3 Molecular view of the eclipsed (C_{2v}), gauche (D_2) and staggered (C_{2h}) conformation of the $[M_4(\mu_4\text{-}N_3)]$ bridged unit (M = Ni (C_{2v},D_2) or Cu (C_{2h})).

N-atom from N_3^- occupies the apical position (see Scheme 2 and caption in Fig. 1 for metric parameters). The intermetallic distances within the perfect $[Cu_4]$ rectangle featured by **1** are 3.157(2) Å within each $[Cu_2]$ pair and 5.578(3) and 6.409(3) Å, respectively, as spanned by the μ_4-N_3^- ligand through the *cis*-EE and *trans*-EE bridges. The μ_4-1,1,3,3-N_3^- coordination mode is extremely rare. It has only recently been reported for two types of $[Ni_4]$ clusters where the central μ_4-azide is supported by additional ligands.[16] Thus, complex **1** is the first case where two pairs of metals are bridged exclusively by a single μ_4-N_3^- group without participation of additional bridging ligands. The μ_4-1,1,3,3-N_3^- conformation in **1** is different from the two previously reported cases (Scheme 3) with respect to its symmetry. In the compound reported here, the symmetry is strictly C_{2h} and thus, the Cu–N bonds are staggered, with the appearance of a propeller when viewed along the linear N–N–N axis (N–N–N angle, 180°). The other two preexisting cases feature idealized C_{2v} (eclipsed) and D_2 (gauche) symmetry. By virtue of the symmetry, both N–N bond distances in **1** are identical (1.136(11) Å) and the *trans* Cu–N_3–Cu torsion angles are exactly 180°. On the other hand, the Cu–(μ-1,1-N_3)–Cu angle featured in **1** (Cu1–N3–Cu#1, 82.0(3)°) is exceptionally low, and one of the lowest ever observed in any coordination compound.[23] Each molecule of **1** is interacting in the crystal lattice with four equivalent such molecules on the *a*–*b* plane, through π–π interactions involving the terminal phenoxide rings of L^{3-}. The resulting sheets are thus stacked along the *c* direction, separated by chloride ions and water molecules (see Figure S1).

Of particular interest is the capacity of this unusual bridging mode of azide to mediate magnetic interactions between the four Cu^{II} ions bound to it. Thus, we carried out bulk magnetization measurements on a sample of **1** between 2 and 300 K within a constant magnetic field of 1 T. The results are represented in Fig. 2 in the form of $\chi_M T$ *vs.* T and χ_M *vs.* T (inset) plots, where χ_M is the paramagnetic susceptibility per mol of **1** after correction for diamagnetic contributions and temperature independent paramagnetism. The value of $\chi_M T$ at 300 K nearly corresponds to that expected for a molecule with four magnetically dilute Cu^{II} centers with average $g = 2.2$ (~ 1.8 cm^3 K mol^{-1}). This value remains almost constant upon cooling and starts to decrease noticeably below 100 K with an increasingly pronounced slope, down to 0.3 cm^3 K mol^{-1} at 2 K. This shows that the system is dominated by antiferromagnetic interactions. The plot of χ_M is consistent with this, since it shows a maximum near 10 K. This plot features a

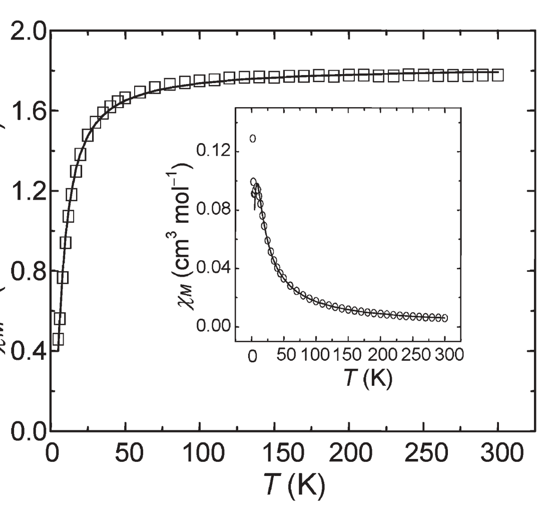


Fig. 2 Plot of $\chi_M T$ *vs.* T (χ_M *vs.* T in the inset) per mol of **1**. The solid lines are fits to the experimental data using numerical procedures (see text for details).

small tail at the lowest temperatures that is attributed to a small amount of paramagnetic impurities. This is a very common occurrence in this type of system and its visibility is magnified at very low temperatures, especially if they are antiferromagnetic. A quantitative description of the coupling facilitated by the μ_4-N_3^- ligand (and the other bridges present in the cation of **1**) was carried out by applying a numerical fitting procedure based on the full matrix diagonalization of the spin Hamiltonian of the system by applying the irreducible tensor operator (ITO) formalism.[24] For this, the following isotropic Heisenberg spin Hamiltonian was used, $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_1S_3 + S_2S_4) - 2J_3(S_1S_4 + S_2S_3)$, where $S_i = 1/2$, which results from considering the C_{2h} symmetry of the cluster. In order to avoid the influence of the small amount of paramagnetic impurity, the fit was carried out with data measured at 5 K and above. The fit (Fig. 2, solid lines) yielded the parameters $J_1 = +0.61$, $J_2 = -3.98$ and $J_3 = -3.07$ cm^{-1}, as well as $g = 2.20$. A similar, and more accurate value of g was obtained with X-band, solid state EPR at various temperatures ($g = 2.11$). Given the symmetry of the cluster, it is not straightforward to assign the J values obtained here to the different exchange pathways. It is tempting to attribute the ferromagnetic interaction to the Cu_2 pairs bridged by the azide in EO, since this coordination mode has almost always yielded this type of interaction. However, this rule breaks down for μ-1,1-N_3^- bridges that do not take up two equatorial positions of the metal ions.[25,26] On the other hand, it has been previously reported that the imidazolidine, such as that in L^{3-}, usually facilitates ferromagnetic interactions even in combination with exogenous bridging ligands known to favor antiferromagnetism.[18,20] A case is even documented for a geometry such as that observed in **1** (Scheme 2).[19] Thus, J_1 shall be assigned here to this bridge. Under this hypothesis, it is assumed that both the *cis* and *trans* EE-bridges in **1** lead to very weak antiferromagnetic coupling. As mentioned before, this type of connection is well known to usually cause antiferromagnetic coupling. This only applies however for *basal–basal* type bridges, since it has become clear otherwise that asymmetric linkages (*i.e. basal–apical*) can give both types of coupling.[25] On the other hand, there are only very few examples of *apical–apical* μ-EE-N_3^- bridged Cu^{II} systems. They all feature either additional bridging ligands between the metal ions that are responsible for stronger magnetic couplings and thus mask the contribution of the bridge of interest,[27] or other dominating antiferromagnetic pathways that cancel the spin within the molecule and thus play the same role.[28] Compound **1** is certainly unique in this sense, since it has no other ligands supporting this μ_4-bridge, and indeed, reveals the coupling through an *apical–apical* μ-EE-N_3^- pathway to be very weak and antiferromagnetic.

In conclusion, the use of the dinucleating ligand H_3L to form [Cu_2] moieties with the possibility of binding a bridging exogenous ligand has allowed the incorporation of an unprecedented μ_4-1,1,3,3 coordination mode of N_3^- within a tetranuclear Cu_4 cluster. The magnetic susceptibility study has revealed that unsupported *cis* and *trans* EE bridging modes on axial positions facilitate only weak antiferromagnetic coupling.

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Notes and references

‡ 2-(2′-Hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azapent-3-enyl]-2-methyl-1,3-imidazolidine.

§ Crystallographic data for **1**, $C_{60}H_{98}N_{11}O_{22}ClCu_4$: M_r = 1614.52, monoclinic, space group *C*2/*m* (No. 12), a = 14.769(4), b = 18.012(8), c = 13.517(9) Å, β = 103.60(2)°, V = 3495.0(3) Å^3, ρ_{calcd} = 1.504 g/cm^3 and Z = 2. With the use of 3079 unique reflections collected at 293 K with Mo Kα radiation (λ = 0.71073 Å) out to θ range = 2.16 to 24.97° on a Bruker-Nonius Mach3 CAD4 single-crystal X-ray diffractometer, the structure was solved by using the SHELX-97 programme and refined by full-matrix least squares methods. The refinement converged to final $R1$ = 0.0810, $wR2$ = 0.1915; and GOF = 0.997 with the largest difference peak and hole as 0.899 and −0.980 e Å^{-3} respectively. CCDC number 292303. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604502b

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