Inorganic Chemistry

Communication

[NaCu^{II}₄] Cluster from Alkali Template Assembly of Two Asymmetric End-On Azido-Bridged [Cu^{II}₂] Units

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The cluster [NaCu₄L₂(N₃)₂](ClO₄) [**1**; H₃L is 2-(2′-hydroxyphenyl)-1,3-bis[3′-aza-4′-(2″-hydroxyphenyl)prop-4′-en-1′-yl]-1,3-imidazolidine] has been synthesized and structurally characterized. Complex **1** is formed by the template assembly of two [Cu₂L(N₃)] neutral fragments through their weak oxophilic interactions with a central Na$^+$ cation as observed in metallacrowns. The cluster exhibits a combination of ferro- and antiferromagnetic interactions. End-on N₃$^−$ bridging of copper ions within the [Cu^{II}₂] units facilitates stabilization of $S = 1$ magnetic subunits that mutually cancel via antiferromagnetic coupling as mediated by the O⋯Na$^+$⋯O bridges.

Crown ethers[1] have been known for decades as size-specific cation-binding species, and their study has greatly helped to enrich host−guest chemistry.[2,3] Metallacrowns are the inorganic analogues of crown ethers. These form inorganic guest−host complexes with cations that have potential applications in analytical chemistry, catalysis, or magnetic materials.[4] A major difference between crown ethers and metallacrowns is that the former are covalent stable species whereas the latter are coordination compounds formed by self-assembly. For many of the metallocrown−cation complexes, the metallic−organic frame does not exist independently without the associated cation, with the latter thus playing the role of template.[5,6] This template effect has been exploited for the construction of transition-metal clusters with interesting structures and properties that would not form otherwise.[7,8] The assembly of polynuclear complexes using

Chart 1
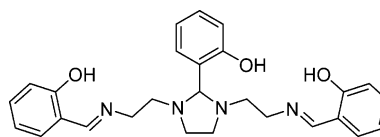
main-group cations as a template requires, besides the metals, ligands capable of both coordinating and bridging transition metals and interacting with the templating ion. We report here the synthesis and magnetic properties of the cluster [NaCu₄L₂(N₃)₂](ClO₄) (**1**; H₃L is the binucleating ligand in Chart 1), from the assembly by Na$^+$ of two neutral 1,1-azido-bridged [Cu₂L(N₃)] fragments.

We have been exploring H₃L or its derivatives for the assembly of dinuclear Cu^{II} complexes with various exogenous bridging ligands. A bridge of special interest is the 1,1-N₃$^−$ group, known to generally mediate ferromagnetic interactions.[9,10]

The reaction in a CH₂Cl₂/MeOH mixture of Cu(ClO₄)₂·6H₂O with H₃L[11] and NaN₃ in the presence of NEt₃ using the 1:2:1:3 molar ratio leads to a green product that precipitates directly from the reaction mixture. The elemental analysis and solution electrical conductivity data in dimethylformamide are consistent with the formula [NaCu₄L₂(N₃)₂]-(ClO₄)·H₂O (**1**), and the yield was thus calculated as 85%. The IR spectrum of **1** shows strong absorption bands at 2076 and 1274 cm^{-1} corresponding to the ν_{as} and ν_s stretching vibrations of the μ-1,1-N₃$^−$ group.

The structure of **1** (Figures 1 and 2) was determined from crystals obtained by slow evaporation of a MeCN/MeOH (1:1) solution (see the Supporting Information for the crystallographic data for **1**). It revealed a very interesting

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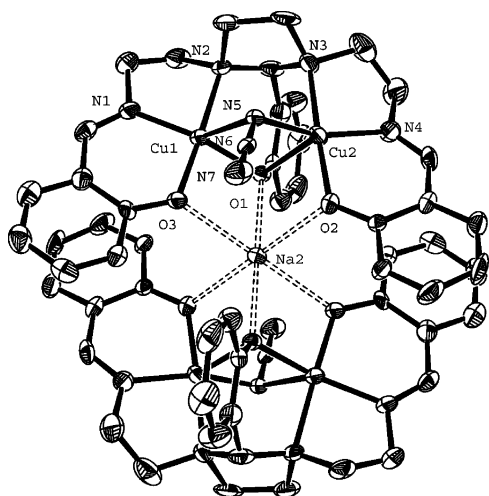
Figure 1. ORTEP representation of **1** at the 40% probability level. H atoms are omitted for clarity. Only independent non-C atoms are labeled.
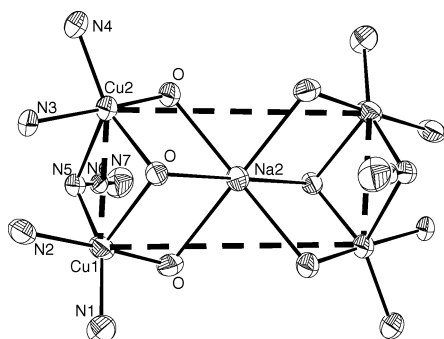
Figure 2. ORTEP representation of the core of **1** at the 40% probability level, emphasizing the topology of the metals. Independent atoms are labeled.

multicomponent complex arising from the assembly of two neutral $[Cu_2L(N_3)]$ fragments through the intermediacy of an intercalated Na^+ cation, located at a crystallographic center of symmetry. Two Cu^{II} ions are held together within each binuclear unit by one heptadentate μ-L^{3-} ligand through central bridging imidazolidine and phenoxide moieties and one exogenous end-on N_3^- group. One imine N atom and one terminal phenoxide from each arm of the L^{3-} ligand complete five coordination around each of the Cu^{II} metals. Electroneutrality is ensured by one non-coordinated ClO_4^- anion. Other related $[Cu_2L'(X)]$ moieties (L' is a ligand equal or related to L; X^- is AcO^-, NO_3^-, Cl^-, OMe^-, etc.) have been reported in the literature[12–14] as independent species, suggesting that the dinuclear components assembled to form **1** may be stable as discrete molecules. The intra- and interdimer Cu···Cu distances in the rectangular $[Cu_4]$ core of **1** (Figure 2) are 3.040(9) and 6.009(12) Å, respectively. The N_3O_2 coordination environment around the Cu^{II} ions is between square-pyramidal and trigonal-bipyramidal (τ is

Chart 2
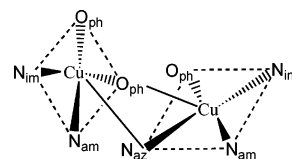
0.463 and 0.365 for Cu1 and Cu2, respectively).[15] The only clearly identifiable apical position of Cu1 is occupied by N5 [Cu1−N5, 2.333(11) Å], the bridging atom of the μ-N_3^- group, which takes, by contrast, an equatorial position of Cu2 [apical−basal bridging, a,b; Cu2−N5, 1.980(11) Å]. In turn, the bridging phenoxide O atom binds to the long axial position of Cu2 [Cu2−O1, 2.260(7) Å] and uses an equatorial site of Cu1 [basal−apical, b,a; Cu1−O1, 1.995-(8) Å; see Chart 2]. Despite the large number of reported complexes featuring the $[Cu(\mu$-N)$(\mu$-O)Cu] moiety, this distribution ($a,b + b,a$) has only been seen in two previous examples,[16,17] and **1** is the first case involving bridging phenoxide. Important parameters are the bridging angles $Cu-O_{PhO}-Cu$ and $Cu-N_{az}-Cu$, which are 91.0(3) and 89.3(4)°, respectively, with the latter being one of the lowest ever observed for single end-on azido-bridged Cu^{II} complexes.[18] The particular arrangement of L^{3-} around the Cu^{II} ions leads to the formation of a $[-O-Cu-O-Cu-O-]$ moiety properly disposed so as to provide three facial donors of a distorted octahedral coordination environment around a Na^+ cation, an extremely common feature in inorganic chemistry (643 hits on the CCDC). The other equivalent three donors are delivered by one such moiety located on the opposite side. The distances to Na2 fall within the interval observed on other metallacrowns or metallacriptates.[5,19] The supramolecular $[Cu_2L(N_3)]$···Na^+···$[Cu_2L(N_3)]$ arrangement is further held together by means of $\pi-\pi$ interactions established between terminal phenyl rings of the ligands. These can be seen in Figure S1 in the Supporting Information, and the distances between the calculated centroids of the interacting rings are 3.713 Å, while they form an angle of 10.79°. The staggered face-to-face orientation of the O donors of each ligand in $Cu_2L(N_3)$ is responsible for the generation of the cavity during packing in which Na^+ ions are fitting nicely (Figure S2 in the Supporting Information). The perchlorate anion is a disordered one.

Compound **1** is an unprecedented system from the magnetic point of view. The nature of the magnetic exchange within the cluster was investigated by means of bulk magnetization measurements under a constant magnetic field of 1 T between 2 and 300 K. A plot of $\chi_m T$ vs T per mole of **1** is represented in Figure 3, where the experimental values have been corrected for the diamagnetic contribution of the complex and the sample holder, and a temperature-independent paramagnetism (TIP) of 240×10^{-6} cm^3/mol has been subtracted. The product $\chi_m T$ near room temperature

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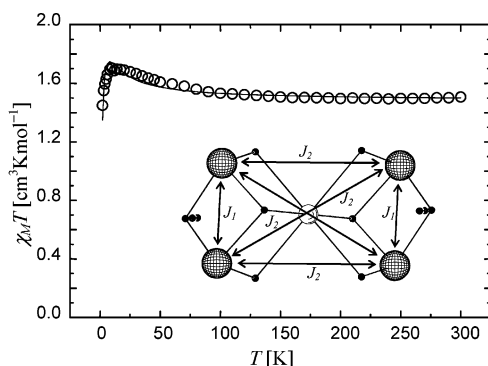
Figure 3. Plot of $\chi_m T$ vs T for complex **1**·H_2O. Data have been corrected for diamagnetic contributions and TIP. The solid line is a fit of the data to a theoretical expression of the susceptibility. The inset shows the core of the complex with the spin-coupling scheme.

(1.5 cm³·K/mol) is the expected value for four noncoupled Cu^{II} centers ($S = \frac{1}{2}$) with $g = 2$ and remains almost constant upon cooling until ca. 80 K, where it starts to gradually increase to reach a maximum of 1.75 cm³·K/mol at 8 K, before decreasing again down to 1.35 cm³·K/mol at 2 K. The maximum value attained is below that expected for two independent $S = 1$ spin magnetic moments. This could indicate that the system can be described as two pairs of Cu^{II} ions displaying intradimer ferromagnetic coupling, with weak antiferromagnetic interactions between pairs, to lead to a total spin ground state of $S = 0$. This behavior was modeled quantitatively by considering the Heisenberg spin Hamiltonian $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4)$, according to the scheme depicted on the inside of Figure 3. Under this framework, all interactions between Cu^{II} ions from different [Cu^{II}_2] dimeric units (expected to be very weak) are presumed to be equal, and thus the value obtained from the fit must be regarded as an averaged number. Thus, the experimental data were fit by matrix diagonalization by using the irreducible tensor operator approach by means of the program CLUMAG.[20] This provided the parameters $J_1 = +5.43$ cm⁻¹, $J_2 = -0.32$ cm⁻¹, and $g = 1.99$. The value of g is only slightly lower than expected. It is often difficult to obtain accurate g values from bulk measurements, and thus we prefer to use the value obtained by powder X-band electron paramagnetic resonance at 4 and 298 K ($g = 2.08$). It is important to analyze the moderate ferromagnetic coupling observed within the [Cu^{II}_2] units in **1** in light of previously characterized systems. On the one hand, several cases of such a type of interaction between Cu^{II} centers bridged by the same N−C−N moiety as that in **1** have been previously reported.[12,13,21] In many cases, the

coupling was observed to be significantly stronger (J up to +48 cm⁻¹).[13] This was studied and rationalized theoretically by density functional theory (DFT) calculations.[21] However, a comparison of complex **1** with those previously studied is precluded by the fact that the asymmetric bridging mode of L (see Chart 2) is unprecedented among these kinds of compounds. On the other hand, it is well-known that 1,1-μ-N_3 bridges between paramagnetic metal ions generally lead to ferromagnetic exchange.[9] Nonetheless, in the exceptional cases where the bonding occurs asymmetrically in an apical−basal manner (as in **1**), the coupling is more often antiferromagnetic.[22] It is thus difficult to establish the exact reason for the moderate ferromagnetic coupling found within the dimers of **1**. DFT calculations will be used to clarify this point. The observed weak magnetic interaction through the intermediacy of Na^+ is, in turn, not unexpected because such a type of exchange has been documented.[23−25]

In conclusion, the Na^+-mediated assembly of two neutral [Cu^{II}_2] fragments bridged by a 1,1-N_3^- group and a dinucleating ligand leads to the new cluster **1**. This composite complex features a combination of both ferro- and antiferromagnetic interactions that would not be observed in the absence of Na^+. The independent existence of the [$CuL(N_3)$] neutral components, as well as the possible formation of other self-assembled complexes with different cations and bridging groups, is currently being investigated. On the other hand, a rationalization for the exact reasons for the ferromagnetic interaction observed in **1** will be sought through theoretical calculations.

Supporting Information Available: Crystallographic data (CIF), tables of selected bond lengths and angles, Figures S1 and S2, and the synthesis and characterization of ligand H_3L and complex **1**·H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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