

A Windmill-Shaped Hexacopper(II) Molecule Built Up by Template Core-Controlled Expansion of Diaquatetrakis(μ_2 -adeninato-N3,N9)-dicopper(II) with Aqua(oxydiacetato)copper(II)

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The windmill-shaped hexanuclear copper(II) cluster $\{(H_2O)_2Cu_2(\mu_3-(Ade)_4[Cu(oda)(H_2O)]_4)\cdot 6H_2O$ (**1-o**) has been synthesized in aqueous medium by in situ core-controlled expansion of the neutral building block $Cu_2(\mu_2-N3,N9-Ade)_4(H_2O)_2$ (**2**) with $Cu(oda)(H_2O)$ (**3-o**) (Ade = adeninato(1-) and oda = oxydiacetato(2-) ligands). Crystal data for **2-b** ($2\cdot 5H_2O$): triclinic, space group $P\bar{1}$; $a = 9.374(1)$, $b = 9.440(1)$, $c = 10.326(1)$ Å; $\alpha = 78.72(1)$, $\beta = 76.77(1)$, $\gamma = 63.51(1)^\circ$; final $R_1 = 0.059$; $T = 100(2)$ K. Crystal data for **1-o**: monoclinic, space group $P2_1/n$; $a = 15.203(2)$, $b = 10.245(1)$, $c = 19.094(2)$ Å; $\beta = 101.61(1)^\circ$; final $R_1 = 0.049$; $T = 293(2)$ K. The X-shaped hexanuclear molecule consists of a central core (**2**) and four terminal arms (**3-o**) linked together by bridging $\mu_3-N3,N7,N9-Ade$ ligands. There are three crystallographic independent metal atoms (two terminals, one central). All Cu(II) atoms exhibit a 4 + 1 coordination, of which one is an aqua apical ligand. The basal coordination sets complete the $CuN_4 + O$ or $CuO_3N + O$ chromophores for the central or terminal metal atoms, respectively. Thermal stability and spectral and magnetic properties were also studied. Analogous compounds to **1-o** with tridentate or tripodal tetradentate ligands L^{2-} , instead of oda, have also been synthesized.

Introduction

In recent years, the use of suitable simple coordination compounds as building blocks for the synthesis of oligomers or polymers has required an increasing effort of inorganic chemists.¹ Indeed, many materials obtained by these self-

assembly synthesis strategies exhibit novel structural topologies and/or profitable optical and/or magnetic properties.^{1,2} A recent paper in this journal^{1b} reports about a 3D polymer ($\{[Cu_2(\mu-Ade)_4(H_2O)_2][Cu(ox)(H_2O)]_2\cdot n\}$) (**4**) built by connecting of the dinuclear molecule "core" $[Cu^{II}_2(\mu-N3,N9-Ade)_4(H_2O)_2]$ (**2**) to $Cu(oxalato)(H_2O)$ (**5**) chelates as peripheral and bridging units. To our knowledge, this interesting polymer represent the first example in which the adeninate(1-) ion simultaneously displays chelating and bridging roles by means of the $\mu_3-N3,N7,N9$ mode.

As a part of our program on molecular recognition processes between metal chelates and the nucleobase adenine

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(AdeH),³ we have also considered the usefulness of studying core-controlled expanding reactions between dinuclear unit **2** and Cu^{II}L chelates **3**, where L²⁻ is a suitable tridentate⁴ or a tripodal tetradentate ligand. In this connection, it should be noted that the structure of **2**, as [Cu₂(Ade)₄(H₂O)]·2H₂O (**2-a**), has been known^{5a} for a long time. Now we report the synthesis and crystal structure of **2** as an higher hydrate form (**2-b**).^{5b} There are not data on the thermodynamic stability of such dinuclear core in solution, but it seems to be stable enough to enable the isolation and X-ray structural determination of closely related derivatives, such as [Cu₂(μ-N3,N9-(AdeH)₄(H₂O)₂](ClO₄)₄·2H₂O⁶ (**6**) or [Cu₂(μ-N3,N9)-AdeH)Cl₂]Cl₂·6H₂O,⁷ with the neutral AdeH, instead of anionic Ade. However, the dinuclear units of these latter compounds seem not to be suitable “cores” for self-assembly or core-controlled expanding purposes because of the nucleobase requirement to be in anionic form (Ade) to supply N3, N7, and N9 as donor atoms, which, indeed, occurs in the above referred 3D polymer.^{1b} On this basis, a workable hypothesis is to use the dinuclear molecule **2** as a template for the binding of four neutral chelates **3** and, in this way, build up hexanuclear Cu^{II} complexes by a core-controlled expansion process. We had to assume that the linking “core-terminal chelate” would require the formation of the bond Cu^{II}(end)–N7(Ade). In this connection, we have shown previously^{3a,b} that such a Cu–N7 coordination bond could be reinforced by one intramolecular, interligand hydrogen bond ⁶N(exocyclic)H···O(acceptor). Keeping that in mind, we have chosen various tridentate⁴ or tripodal tetradentate divalent anions as chelating ligands (vide infra), which could supply terminal carboxylates groups as H-acceptors. A very limited number of hexanuclear copper complexes have been reported, as can easily be appreciated by a SciFinder search (SciFinder Scholar, 2004 ed.). In addition, these compounds are Cu-homonuclear species (including some Cu^I, Cu^{II}-mixed-valence compounds) or Cu^{II}, M^{II}-heteronuclear complex species, which exhibit a variety of topologies as well as spectral or magnetic properties.

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- (5) (a) Sletten, E. *Acta Crystallogr., Sect. B* **1969**, *25*, 1480. (b) Crystal data for **2-b** or **2**·5H₂O: C₂₀H₃₄Cu₂N₂₀O₉, fw 825.75, 100(2) K, λ = 0.710 73 Å, triclinic system, space group P1̄, a = 9.3740(7) Å, b = 9.4395(7) Å, c = 10.3261(8) Å, α = 78.72(1)°, β = 76.77(1)°, γ = 63.51(1)°, Z = 1, D_{calc} = 1.732 Mg·m⁻³, μ = 1.427 mm⁻¹, collected/unique reflections = 9121/3555 for 235 parameters, GOF = 1.048, R₁ = 0.059, wR₂ = 0.075.
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Experimental Section

Synthesis of the Complexes. Well-shaped parallelepipedal crystals of the new core hydrate (**2-b**) can be obtained by reaction of AdeH, a water-soluble Cu(II) salt of weakly coordinating counterion (sulfate, nitrate, or perchlorate) and sodium hydroxide.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with caution. In a typical experiment, AdeH (2 mmol) was dissolved in CO₂-free water (130 mL) with stirring and heating (65 °C). CuSO₄·5H₂O (0.5 mmol) was added, and a muddy solution was formed. A clear solution was obtained after addition of 2 mmol of NaOH, which was filtered without vacuum on a crystallization device and left to evaporate slowly (covered with a plastic film). In a period of 1–10 days many crystals appeared and were collected in successive fractions. Suitable crystals for X-rays diffraction were obtained from one of these samples, but they can also be obtained by recrystallization from water. The compound losses water at room temperature, so the chemical formula and structure were determined by X-ray crystallography at low temperature.

The novel mixed-ligand Cu^{II} complexes were prepared by a general procedure as follows: Cu₂CO₃(OH)₂ (0.375 mmol, green, malachite) and the appropriate ligand H₂L [0.5 mmol, oxydiacetic acid (H₂oda), *N*-methyliminodiacetic acid (H₂MIDA), *N*-benzyliminodiacetic acid (H₂NBzIDA), or *N*-(2-pyridylmethyl)iminodiacetic acid (H₂pmda, prepared as described earlier⁸)] were reacted in water (100 mL) in a Kitasato flask by heating (<70 °C) and stirring (7 h) until a blue-greenish solution was obtained. That solution was slowly filtered over a solution of AdeH (0.5 mmol) in water (80 mL). The reacting mixture was stirred and heated (50 °C) for 1 h. At this point, a fraction of the desired product precipitated and was removed from the blue-gray solution by filtration into a crystallization device, where well-shaped crystals of small size were formed by slow evaporation of the solvent at room temperature. Yields are usually below 50%. Typical yields (%) are 57.2, 45.3, 48.6, or 39.4 for compounds **1-o**, **1-m**, **1-b**, or **1-p**, respectively. Anal. Calcd for **1-o** (H₂L = H₂oda), C₃₆H₅₆Cu₆N₂₀O₃₂: C, 26.01; H, 3.40; N, 16.85; Cu, 22.94. Found: C, 25.91; H, 3.12; N, 14.61; Cu, 22.63. Calcd for **1-m** (H₂L = H₂MIDA), C₄₀H₆₈Cu₆N₂₄O₂₈: C, 28.02; H, 4.00; N, 19.61; Cu, 22.24. Found: C, 27.63; H, 3.56; N, 19.30; Cu, 22.12. Calcd for **1-b** (H₂L = H₂NBzIDA), C₆₄H₈₄Cu₆N₂₄O₂₈: C, 38.07; H, 4.19; N, 16.65; Cu, 18.89. Found: C, 37.82; H, 4.42; N, 16.23; Cu, 18.53. Calcd for **1-p** (H₂L = H₂pmda), C₆₀H₈₀Cu₆N₂₈O₂₈: C, 35.63; H, 3.99; N, 19.39; Cu, 18.85. Found: C, 35.46; H, 3.28; N, 19.57; Cu, 18.77.

Physical Properties. Thermal stability, FT-IR spectra, and electronic spectra were recorded as previously reported.^{3b} Magnetic susceptibility measurements on polycrystalline samples were performed in the temperature range 5–300 K with a Quantum Design MPMS-7 SQUID magnetometer and using an applied field of 0.1 T. Diamagnetic corrections of the constituent atoms were estimated from Pascal’s constants. A Bruker ESP300 spectrometer operating at X- and Q-bands, equipped with standard Oxford low-temperature devices, were used to record the ESR powder spectra at different temperatures. The magnetic field was calibrated using an NMR probe, and the frequency inside the cavity was determined with a Hewlett-Packard 5352B microwave frequency meter.

Crystal Structure Determination. A blue-violet parallelepipedal crystal of **2-b** and a brownish prismatic crystal of **1-o** were mounted

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A Windmill-Shaped Hexacopper(II) Molecule

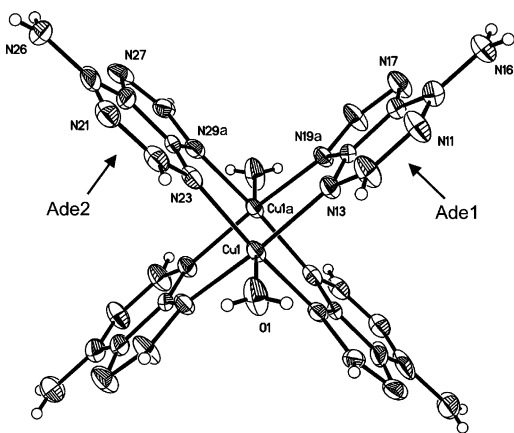


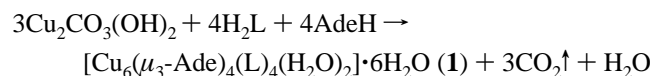
Figure 1. Structure of the “core” **2** in the crystal of **2-b** or **2·5H₂O**. Noncoordinated water is omitted for clarity. Bond lengths (Å): Cu1–N29 2.002(3), Cu1–N19 2.011(3), Cu1–N13 2.023, Cu1–N23 2.025(3), Cu1–O1 2.180(3). Trans-angles (deg): N19–Cu1–N13 165.0(1), N29–Cu1–N23 165.0(1). Cu1···Cu1a separation: 2.950(1) Å. Symmetry code a = $-x + 1, -y + 1, -z$. Structural parameters: τ (%), 0.07; tetragonality T, 0.92.

on a glass fiber and used for data collection⁹ at 100(2) or 293(2) K, respectively, on a Bruker SMART CCD 1000 diffractometer (Mo K α radiation, $\lambda = 0.710\ 73$ Å). The data were corrected for absorption.¹⁰ The structure was solved by direct methods¹¹ and refined by full-matrix least-squares techniques¹² on F^2 . Hydrogen atoms were treated as fixed contributions in positions determined experimentally from difference maps. Molecular graphics were generated with SHELXTL.¹³

Results and Discussion

The blue-violet compound **2-b** seems to be a higher hydrated form compared to that crystallized by Sletten^{5a} (from a 10% ethanol–water mixture), but these crystals differ from a monoclinic one (**2·3.5H₂O**) obtained from a 50% dioxane–water solution.^{5a} Our structural results (Figure 1) for the centrosymmetric core **2** agree reasonably well to those reported by Sletten. In the crystal of **2-b**, noncoordinated water molecules are remarkably disordered.

As far as concern to prepare compound **1** and to minimize undesirable effects of byproducts, we have used the following general reaction in aqueous solution:



This overall process represents a neutralization reaction of the acid protons from the acid H_2L and the nucleobase to give CO_2 (byproduct, easily removed) and water, in such a way that the dinuclear template **2** and the CuL terminal chelate **3** are formed in situ, in the stoichiometric molar ratio required by the hexanuclear molecule (**1**). On the other hand,

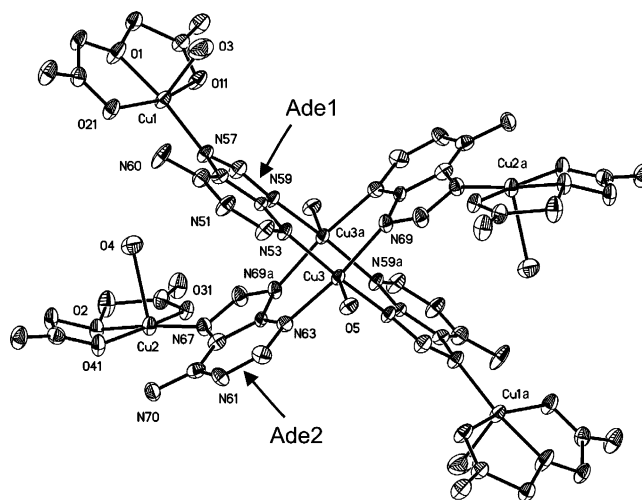


Figure 2. Hexacopper(II) complex molecule of **1-o** with windmill topology, $\{(\text{H}_2\text{O})_2\text{Cu}_2(\mu_3\text{-Ade})_4[\text{Cu}(\text{oda})(\text{H}_2\text{O})_4]\} \cdot 6\text{H}_2\text{O}$. H-atoms and non-coordinated water are omitted for clarity. Bond lengths (Å): Cu1–O21 1.933(3), Cu1–O11 1.951(3), Cu1–N57 1.955(1), Cu1–O1(ether) 1.959(3), Cu1–O3(aqua) 2.227(4); Cu2–O41 1.935(3), Cu2–N67 1.945(3), Cu2–O31 1.959(3), Cu2–O2(ether) 1.959(3), Cu2–O4(aqua) 2.300(3); Cu3–N69 1.991(4), Cu3–N59a 2.001(3), Cu3–N53 2.018(3), Cu3–N63 2.029(4), Cu3–O5(aqua) 2.179(3). Trans-angles (deg): O21–Cu1–O11 160.8, N57–Cu1–O1 169.9, O41–Cu2–O31 163.1, N67–Cu2–O2 175.5, N59a–Cu3–N53 165.1, N69–Cu3–N63 164.5. Cu3···Cu3a separation: 2.944(1) Å. Symmetry code a = $-x + 1, -y, -z + 1$.

the desired CuL chelates are formed free of byproducts by stoichiometric reaction of H_2L acids and copper(II) hydroxy-carbonate. Subsequent reactions of **2-b** with the CuL chelates also give the desired product (**1**). However and until now, suitable crystals for X-ray diffraction studies were only obtained for **1-o**, as described, in the case of the general reaction. In addition, attempts to recrystallize compounds **1** in water or in various alcohol–water mixtures do not yield better crystals. In contrast, the direct synthesis by the above referred reaction also produces well-shaped crystals of **1-m**, **1-b**, and **1-p** but too little in size as for X-ray diffraction purposes. Here, we report the results of structural, thermal, spectral, and magnetic studies of a novel compound of type **1** with $\text{L} = \text{oxydiacetato}(2-)$ ligand (**1-o**). We have found, by appropriate analytical data, that the same reactions apply to the other ligands already referred to in the Experimental Section, namely, H_2MIDA , H_2NBzIDA , and H_2pmda , which produce **1-m**, **1-b**, and **1-p** derivatives, respectively.

Windmill-Shaped Molecular Topology. The crystal¹⁴ of the new hexacopper(II) derivative **1-o** consists of centrosymmetric windmill-shaped molecules (Figure 2) and nonbonded water molecules, according to the general formula **1** ($\text{L} = \text{oda}$) or with $\{(\text{H}_2\text{O})_2\text{Cu}_2(\mu_3\text{-Ade})_4[\text{Cu}(\text{oda})(\text{H}_2\text{O})_4]\} \cdot 6\text{H}_2\text{O}$. The hexanuclear molecule has three nonequivalent Cu^{II} atoms from a crystallographic point of view, two terminal Cu1 and Cu2 atoms and the core Cu3 atom. All metal atoms exhibit a square base pyramidal coordination (type 4 + 1) of which one, an aqua ligand, occupies the apical site. The Cu3 or

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(14) Crystal Data for **1-o**: $\text{C}_{36}\text{H}_{56}\text{Cu}_6\text{N}_{20}\text{O}_{32}$, fw 1662.25, 293(2) K, $\lambda = 0.710\ 73$ Å, monoclinic system, space group $P2_1/n$, $a = 15.203(2)$ Å, $b = 10.245(1)$ Å, $c = 19.094(2)$ Å, $\beta = 101.61(1)^\circ$, $Z = 2$, $D_{\text{calc}} = 1.895$ Mg·m $^{-3}$, $\mu = 2.263$ mm $^{-1}$, collected/unique reflections = 16 552/6650 for 424 parameters, GOF = 0.867, $R_1 = 0.049$, $wR_2 = 0.075$.

Table 1. Structural Comparison of Data (Å) in the Dinuclear Core Cu₂(Ade)₄(H₂O)₂ or Cu₂(AdeH)₄(H₂O)₂ of the Compounds **1-o**, **2**, and **4** or in Compound **6**, Respectively

param	1-o	2-b ^{5b}	4 ^{1b}	6 ⁶
σ , ^a Å	0.267	0.263	0.264	0.264
Cu–O (aqua, apical), Å	2.179(3)	2.180	2.179(6)	2.166
Cu···Cu, Å	2.944(1)	2.950(1)	2.938(2)	2.951(4)
α , ^b deg	74.53	85.27	76.5	90.10

^a Distance from the metal atom to the mean basal coordination plane.

^b Dihedral angle defined by the mean planes of two crystallographically nonequivalent nucleobases.

Cu3a atoms of the core [Cu₂(μ ₃-Ade)₄(H₂O)₂] in **1-o** are separated by 2.944(1) Å (transformation $a = -x + 1, -y, -z + 1$) and have structural parameters¹⁵ [τ (%) 0.9, tetragonality T 0.92, Cu–P(1) Cu–basal plane distance σ 0.266 Å, and Cu–O(aqua) distance 2.179(3) Å], which revealed a lower distortion than those of the terminal Cu1 [τ 15.3%, T 0.88, σ 0.15 Å, Cu–O(aqua) 2.227(4) Å] and Cu2 [τ 20.6%, T 0.85, σ 0.06 Å, Cu–O(aqua) 2.300(3) Å] atoms, respectively. The basal plane of the core Cu3 atoms is defined by two trans-sets of N3 and N9 donor atoms from the four μ ₃-Ade ligands. Given the N3–Cu3–N9 angles ($\approx 165^\circ$), the largest observed σ distance, the shortest Cu–O(aqua) bond length thus far recorded, and the lowest distortion toward a trigonal bipyramidal coordination known, it seemed instructive to carry out structural comparisons with those of closely related windmill molecules. For that purpose, Table 1 shows the Cu–basal plane distance (σ), the Cu···Cu separation, the Cu–(aqua) apical bond distance, and the dihedral angle α between nonequivalent nucleobases (Ade/Ade for compounds **1-o**, **2-b**, and **4** or AdeH/AdeH for compound **6**) in the windmill cores Cu₂(Ade)₄(H₂O)₂ or Cu₂(AdeH)₄(H₂O)₂, respectively. We can appreciate that irrespective of the anionic (Ade) or neutral (AdeH) form of the nucleobase, all these compounds have close similar σ , Cu–aqua, or Cu···Cu distances, with averaged values of 0.267, 2.178, and 2.946 Å, respectively. However, the available data for **1-o** and **4** revealed that their values of α [(Ade/Ade) $\sim 75^\circ$] are significantly below the estimated value for the core in **2-b** (85.27°) or for compound **6** (90.10°). It seems, therefore, that such a change should be attributed to structural consequences from the bridging tridentate mode, μ ₃-N3,N7,N9, of Ade in **1-o** or **4** versus that of the bridging bidentate mode, μ ₂-N3,N9, of the neutral nucleobase in **6**. In this connection, one should emphasize the remarkably similar windmill topology of the hexanuclear molecule of **1-o** and of the 3D polymer **4**, which we can now justify by the formation of the appropriate peripheral Cu–N7(Ade) bonds with the central core **2**.

The basal coordination plane of each terminal Cu1 or Cu2 atom is supplied by the N7 donor atom of a bridging Ade ligand and by the three O-donor atoms of the oda chelating ligand, which exhibits an unprecedented *mer*-O₃(equatorial) conformation, forming three Cu–O bonds rather close to 2 Å. The dihedral angle, defined by the mean planes of the

corresponding chelate rings (φ) is 2.6 or 10.4° for the terminal Cu1–oda or Cu2–oda moieties, respectively. In contrast, oda exhibits a *fac*-O₂ + O(ether, apical) conformation in [Cu(oda)(H₂O)]_n,^{16a} in [Cu(oda)(2,2'-bpy)(H₂O)]·4H₂O,^{16b} or in relatives of this latter compound,^{16c} with two nearly perpendicular chelate rings. A *mer*-O(ether, equatorial) + O₂(carboxylato, apical) was also reported for [Cu(oda)-(terpy)]·2H₂O^{16d} (ϕ 3.8°), but in this case, the Cu(oda) moiety exhibits the shortest Cu–O(ether) bond (2.070 Å) and the two longest, trans-apical Cu–O(carboxylato) bonds (2.202 and 2.313 Å).

The internal stability and windmill molecular topology of the new hexanuclear complex molecule of **1-o** is reinforced, as expected,^{3a,b} by interligand ⁶N(exocyclic)–H···O(oda) hydrogen-bonding interactions, namely, N60–H60a···O21 (2.79 Å, 168°) and N70–H70a···O41 (2.88 Å, 153°) or their symmetry-related ones, obtained with the above-mentioned transformation, a. The crystal packing involves many other H-bonds. For example, the aqua ligands have O(aqua)–H···O(aqua) and O(aqua)–H···O(carboxylato) bridges in a 3:1 ratio, whereas all noncoordinated water and the remaining ⁶N(exocyclic)–H bond form H-bonds with O(carboxylato) acceptor atoms, mostly from adjacent asymmetric units. In the observed windmill molecular topology, the planes of the two nonequivalent adeninato ligands (Ade1/Ade2) define a dihedral angle α of 74.5°. Other relevant dihedral angles, defined by the Ade ligands and the corresponding basal coordination planes (P1), are as follows: Ade1/P1(Cu1) 22.1°, Ade2/P1(Cu2) 32.9°, Ade1/P1(Cu3) 88.7°, and Ade2/P1(Cu3) 88.3°. These data revealed that the windmill molecular topology is due to the cooperative effects of the rigid “core” (which impose dihedral angles α Ade1/Ade2 $\approx 75^\circ$ and Ade/P1(Cu3) $\approx 90^\circ$) and the arms (where each (oda)Cu–N7(Ade) bond is reinforced by one N6–H···O bridge) giving a dihedral angle P1(Cu1 or Cu2)/Ade of 22 or 33°. This unique molecular topology produces similar, and large, intramolecular separations Cu1–Cu3 7.116(1), Cu2–Cu3 7.069(1), and Cu1–Cu2 6.893(1) Å (excepting that Cu3···Cu3a within the central core).

Thermal, Spectral, and Magnetic Properties. The thermal decomposition of **1-o** indiscriminately releases coordinated and lattice waters from the compound (air-dry flow of 100 mL/min) according to an actual total water contents of 11 H₂O, instead of 12 H₂O required by its formula (first step: rt (room temperature) –165 °C, expt 11.850%, calcd 12.053% for a total amount of 11 H₂O in the studied sample). The next three steps of pyrolysis of organic ligands (215–315, 315–380, and 380–435 °C) lead to a final residue of CuO (expt 29.574%, calcd 29.027%). The released gases (identified by series of 5 or 6 FT-IR spectra/each step) strongly suggest that ignition of the anhydrous residue Cu₂(Ade)₄(oda)₄ is initiated by the oda ligand of the terminal

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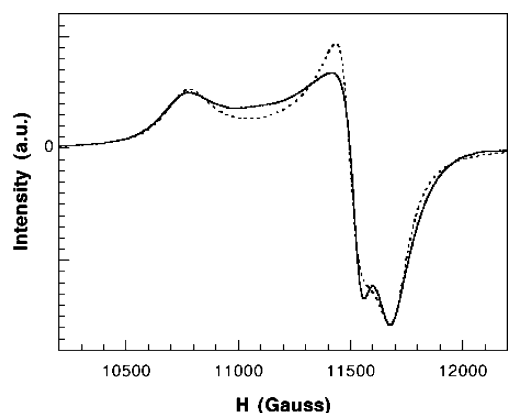


Figure 3. Q-band ESR powder spectra of compound **1-o**. Dotted lines correspond to the simulated spectrum.

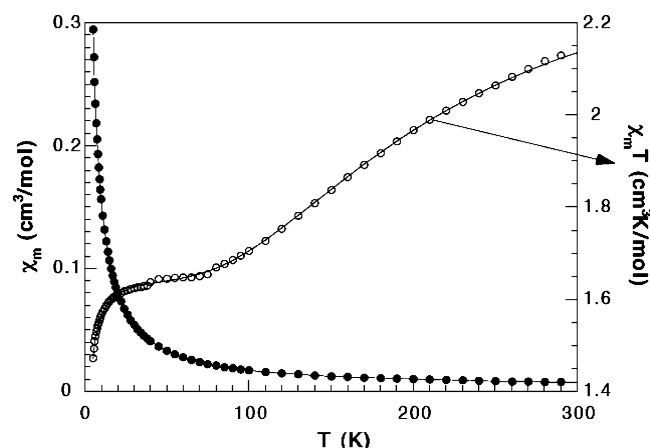


Figure 4. Thermal evolution of the magnetic susceptibility and $\chi_m T$ product for compound **1-o**. Continuous lines correspond to the best least-squares fit to the data using eq 4.

arms (with production of CO_2 , H_2O , H_2CO , and CO in the corresponding step).

The FT-IR spectrum shows the bands expected of the characteristic chromophores, namely, Ade, oda, and H_2O . We can easily identify the modes $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of oda at 1601 and 1398 cm^{-1} , respectively, as well as $\pi(\text{C}-\text{H})$ of Ade at 794 cm^{-1} . The electronic spectrum exhibits a d-d absorption with two maxima at 567 and 840 nm (17 640 and 11 900 cm^{-1}), probably due to the $\text{CuN}_4 + \text{O}$ and $\text{CuO}_3\text{N} + \text{O}$ chromophores, respectively.

X-band EPR powder spectra show a single broad featureless band. Although there is some change in the line shape, there is no increase in resolution with temperature change. On the contrary, low-temperature Q-band spectra exhibit the characteristics of a rhombic \mathbf{g} tensor with main values: $g_1 = 2.257$, $g_2 = 2.115$, and $g_3 = 2.080$ (see Figure 3). The observation of a unique signal indicates that appreciable magnetic exchange is operative between different Cu(II) chromophores. Therefore, the calculated g values correspond to the average of the local g -factors. It is to note that no evidence of a well-isolated $S = 1$ state, such as half-field signals or fine structure, has been found in all the studied temperature range.

The thermal evolution of the magnetic molar susceptibility and the $\chi_m T$ product, being $\chi_m T = \mu_{\text{eff}}^2/8$, are shown in Figure

Table 2. Expressions for the Energy Levels and Multiplicities (W) of the Various Spin States for a Hexanuclear Arrangement of Cu(II) Ions with Windmill Topology

S_A	$\Sigma\Delta$	ΣT	Ω	E
1	2	3	1	0
1	2	2	1	$3J'$
1	2	1	1	$5J'$
1	1	2	3	$J' + 2J''$
1	1	1	3	$3J' + 2J''$
1	1	0	3	$4J' + 2J''$
1	0	1	2	$2J' + 3J''$
0	2	2	1	$J' + 2J'$
0	1	1	3	$J' + 2J' + 2J''$
0	0	0	2	$J' + 2J' + 3J''$

4. The effective magnetic moment at room temperature ($4.14 \mu_B$) is lower than that expected for six uncoupled $S = 1/2$ spins ($4.56 \mu_B$ for $g = 2.15$) and decreases rapidly with decreasing temperature, reaching a value of ca. $3.6 \mu_B$ at 80 K, which is close to the theoretical value expected for four independent Cu(II) ions. Between approximately 80 and 20 K, the effective magnetic moment remains practically constant, but it decreases again when the system is cooled to 5 K. This behavior suggests the existence of strong antiferromagnetic interactions between the copper(II) ions within the dimeric core, resulting from the four $\text{Cu3}-\text{N3}-\text{C4}-\text{N9}-\text{Cu3a}$ bridges, whereas only weak couplings affect the peripheral ions.

Taking into account the structure of this compound, we used the following Heisenberg Hamiltonian to describe the low-lying electronic states:

$$H = -JS_1S_2 - J'[S_1S_3 + S_1S_4 + S_1S_5 + S_1S_6 + S_2S_3 + S_2S_4 + S_2S_5 + S_2S_6] - J''[S_3S_4 + S_3S_5 + S_3S_6 + S_4S_5 + S_4S_6 + S_5S_6] \quad (1)$$

Here J , J' , and J'' refer to the “core-to-core”, “peripheral-to-core”, and “peripheral-to-peripheral” exchange parameters, respectively. Within the framework of the model described by eq 1, it is possible to generate an operator-equivalent expression by using the Kambe method of momentum coupling:¹⁷

$$H = (-J/2)S_A^2 - (J'/2)[S_T^2 - S_D^2 - S_A^2] - (J''/2)S_D^2 \quad (2)$$

This equation was obtained by a vector coupling of spin operators, being $S_A = S_1 + S_2$, $S_B = S_3 + S_4$, $S_C = S_5 + S_6$, $S_D = S_B + S_C$, and $S_T = S_A + S_D$. The energies of the spin-states in this coupling scheme are given by

$$E = -J/2[S_A(S_A + 1)] - J'/2[S_T(S_T + 1) - S_D(S_D + 1) - S_A(S_A + 1)] - J''/2[S_D(S_D + 1)] \quad (3)$$

A total of 20 spin states with ST ranging from 0 to 3 are generated by eq 3 for a hexanuclear complex of Cu(II) ions ($S = 1/2$), and they are described in Table 2. Finally, the application of Van Vleck's approach,¹⁸ considering equal and isotropic g -values for all the Cu(II) ions, gives the following analytical expression for the magnetic susceptibility:

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$$\chi_m = \frac{Ng^2\beta^2}{3kT} \left[\frac{30 \exp(x+2y) + 18 \exp(x+2y+2z)}{5 \exp(x+2y) + 9 \exp(x+2y+2z) + 2 \exp(x+2y+3z)} + \frac{30 \exp(3y) + 6 \exp(5y) + 90 \exp(y+2z)}{5 \exp(3y) + 3 \exp(5y) + 15 \exp(y+2z)} + \frac{18 \exp(3y+2z) + 12 \exp(2y+3z) + 84}{9 \exp(3y+2z) + 3 \exp(4y+2z) + 6 \exp(2y+3z) + 7} \right] \quad (4)$$

Here $x = -J/kT$, $y = -J'/kT$, and $z = -J''/kT$ and the other symbols have their usual meanings. Least-squares fits of eq 4 to the experimental data were performed by minimizing the following function:

$$R = \left\{ \sum_{i=1}^{NP} [c_m(\text{exp})_i - \chi_m(\text{cal})_i]^2 / (NP - NV) \right\}^{1/2} \quad (5)$$

Here NP is the number of data points and NV is the number of variable parameters. The best fit (solid lines in Figure 4) was obtained with the parameters $J = -274 \text{ cm}^{-1}$, $J' = -2.6 \text{ cm}^{-1}$, $J'' = 0.55 \text{ cm}^{-1}$, and $g = 2.103$, showing a very good agreement between experimental and calculated data ($R = 3.4 \times 10^{-4}$). The resulting order of the lowest lying spin states for this combination of parameters gives a two degenerate $ST = 0$ ground state with three $ST = 1$ states at 0.55 cm^{-1} and a $ST = 2$ state at 1.65 cm^{-1} at higher energy.

To compare the above results with those previously reported for related complexes, it is necessary to consider that usually magnetic interactions involving terminal ions have been neglected (i.e. $J' = J'' = 0$). Within this approximation, eq 4 reduces to the well-known Bleaney–

Bowers equation for a Cu(II) dimer¹⁹ with a paramagnetic term resulting from four isolated Cu(II) ions. Therefore, the calculated $J = -274 \text{ cm}^{-1}$ can be compared with the singlet–triplet energy values near -300 cm^{-1} that have been reported for related complexes.^{5,6,7,20,21} Moreover, the consideration of “peripheral-to-core” and “peripheral-to-peripheral” couplings allow us to fit the low temperature decrease (below 20 K) of the effective magnetic moment, and it is in good agreement with the observed exchange EPR spectra.

Conclusion

The use of Cu^{II}L neutral chelates with tridentate or tripodal tetradentate ligands instead of bridging Cu(oxalato)(H₂O) units as terminal blocks for the neutral core [Cu^{II}₂(μ-N3,N9-Ade)₄(H₂O)₂] enables the self-assembly preparation of novel hexanuclear copper(II) complexes. The crystal structure determination of one of these oligomers revealed an unprecedented windmill molecular topology.

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Supporting Information Available: FT-IR spectrum, electronic spectrum, X-band RSE spectrum, TGA curves, and X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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