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Self-Assembly of High-Nuclearity Copper Cages: Tricorne Cu_{21} and Saddlelike Cyclic Cu_{16}

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Abstract: Reaction of cupric salts with H_2Rppz (R = H, Me; H_2ppz = 3-(2-hydroxyphenyl)pyrazole; H_2Meppz = 3-(2-hydroxy-5-methylphenyl)pyrazole) in the presence of sodium azide and triethylamine as bases gave two high-nuclearity copper cage compounds $[HNEt_3]_2\cdot[Cu_{21}(CH_3CN)_2(H_2O)(\mu_2\text{-}N_3)_6(\mu_3\text{-}N_3)_2(ppz)_{18}]\cdot(H_2O)_3\cdot(EtOH)_2$ (**1**) and $[Cu_{16}(EtOH)_2(H_2O)_2(Meppz)_{16}]\cdot 9.5\,H_2O$ (**2**), respectively. X-ray crystallographic studies revealed that molecular skeletons of **1** and **2** are unique tricorne Cu_{21} and saddlelike cyclic Cu_{16} aggregates, respectively. The magnetic properties studies showed overall antiferromagnetic interactions in **1** and **2**. Quantum Monte Carlo simulations by using a 3-*J* model for **1** and a 2-*J* model for **2** were performed, which indicated that the magnetic couplings within the triangular copper units in **1** are ferromagnetic and those between other copper ions are antiferromagnetic, whereas in **2** all magnetic couplings between adjacent copper ions are exclusively antiferromagnetic.

Keywords: ab initio calculations · azides · copper · magnetic properties · metallocages

Introduction

Polynuclear transition-metal clusters continue to attract much attention in the field of coordination chemistry, not only on account of their fascinating chemical and physical properties but also the architectural beauty of their structures.[1] Furthermore, when regarded as predefined building units with a necessary shape and geometry, they can possibly be assembled into extended frameworks with expected topologies.[2] An interesting subarea of homometallic cluster chemistry, metallocyclic cage chemistry has been a small but growing family of research interests in recent years.[3] Of the 3D metal ions, the most spectacular cage is the Mn_{84} giant wheel,[4] which crystallizes into supramolecular nanotubes and exhibits magnetic relaxation and quantum tunneling of magnetization. Other 3D metal-ion cyclic cages, such as Ni_{24},[5] Fe_{18}[6], and Co_{12} wheels,[7] and so forth, with interesting properties have also been found. However, to the best of our knowledge, large cage structures involving copper(II) ions are relatively rare. Cu_{44} is the largest homometallic aggregate containing paramagnetic Cu^{II} centers reported to date.[8] In addition, two high-nuclearity Cu_{36} aggregates have been reported; one of them shows a cubic-based, cagelike structure, in which there are twelve copper atoms on each shared face. This means that each face can be considered to be a Cu_{12} cycle.[9] The other one formed around a central $\{KCl_6\}^{5-}$ unit.[10] Several other small cyclic copper cages with different characters have also been reported—for example, Cu_6,[11] Cu_8,[12] and Cu_x (x = 6, 8, 9, 12, and 14)[13]—that encapsulate small molecules or anions in their central cavities. Another octanuclear copper cycle $[Cu_8(\mu\text{-dmpz})_8(\mu\text{-OH})_8]$ (Hdmpz = 3,5-dimethylpyrazole)[14] shows catalytic activity in the oxidation of organic substrates, and other copper cages, such as the Cu_{10} wheel[15] and Cu_{12} “flywheel”,[16] show antiferromagnetic properties. A 4×4 gridlike Cu_{12} cage also displays interesting magnetic phenomena.[17] It is worth noting that there is a resemblance between most cyclic copper cages in that copper centers are usually connected by pyrazolato bridges and/or accessorial ligands of X^- (X = F, Cl, Br, and OH). Herein we employ versatile N,N,O-che-

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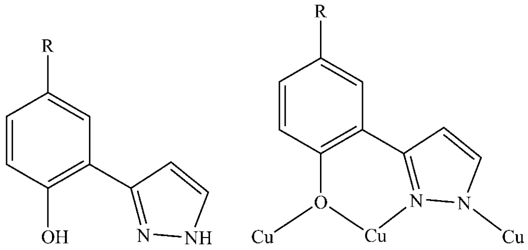
lating and bridging ligands that hold pyrazole and phenol groups and successfully obtain two high-nuclearity copper cages. They are unique tricorne Cu_{21} $[HNEt_3]_2\cdot[Cu_{21}(CH_3CN)_2(H_2O)(\mu_2\text{-}N_3)_6(\mu_3\text{-}N_3)_2(ppz)_{18}]\cdot(H_2O)_3\cdot(EtOH)_2$ (**1**) with N_3^- ions as coligands and saddlelike cyclic Cu_{16} $[Cu_{16}(EtOH)_2(H_2O)_2(Meppz)_{16}]\cdot 9.5\,H_2O$ (**2**) (H_2ppz = 3-(2-hydroxyphenyl)pyrazole and H_2Meppz = 3-(2-hydroxy-5-methylphenyl)pyrazole) (see Scheme 1). It should be mentioned that a heterometallic aggregate containing sixteen copper ions, $Li_8[Cu_{16}(\text{D-SorbH}_{-6})_4(\text{D-Sorb1,2,3,4H}_{-4})_4]\cdot$ca. $46\,H_2O$ (D-Sorb = D-sorbitol), featuring a planar structure has been reported by Klüfers.[18]



Scheme 1. H_2Rppz (R = H, Me) (left) and its coordination modes in **1** and **2** (right).

Results and Discussion

Single-crystal X-ray structural analysis shows that compound **1** crystallizes in the orthorhombic space group *Pccn* and contains a Cu_{21} tricorne anionic backbone (Figure 1a). The charge balance of the compound is completed by the two disordered protonated triethylamine molecules, which can be further confirmed by the elemental analysis result. The structure is disposed around a crystallographic twofold axis, therefore there are only half molecular segments (Figure 1b) in the asymmetric unit that consists of ten-and-a-half Cu^{2+} ions, one end-on $\mu_3\text{-}N_3^-$, three end-on $\mu_2\text{-}N_3^-$ ions, nine ppz^{2-} ligands in the $\eta^2{:}\eta^1{:}\eta^1\text{-}\mu_3$ coordination mode (Figure 1b and Scheme 1), half of a water molecule, and one acetonitrile molecule. According to the structural character, ten-and-a-half Cu^{2+} ions can be divided into near-arc Cu_3 (Cu8, Cu9, Cu11), triangular Cu_3 (Cu1, Cu2, Cu7), and vaulted Cu_5 (Cu3–Cu6, Cu10) subunits (Figure 1b) that are connected by end-on $\mu_2\text{-}N_3^-$ bridges and μ_2-pyrazolato bridges. Actually, the near-arc Cu_3 unit is just the same as half of the vaulted Cu_5 unit, so the structural role and coordination geometry of Cu8 is equivalent to that of Cu4 or Cu5, that of Cu9 is equivalent to Cu3 or Cu6, and that of Cu11 is equivalent to Cu10. Thus, only half of the vaulted Cu5 unit (Cu3, Cu4, and Cu10) is representatively discussed in detail. Cu3 and Cu4 are four-coordinated and lie in a highly distorted square-planar coordination sphere with different coordination atoms: for Cu4, one oxygen atom and three nitrogen atoms come from three different pyrazolato ligands and one end-on $\mu_2\text{-}N_3^-$ ion, respectively, whereas for Cu3 two oxygen atoms and two nitrogen atoms come from two different pyrazolato ligands. Cu10 is five-coordinated in distorted trigonal-bipyramidal geometry with two oxygen atoms and three nitrogen atoms from four pyrazolato ligands and one aceto-

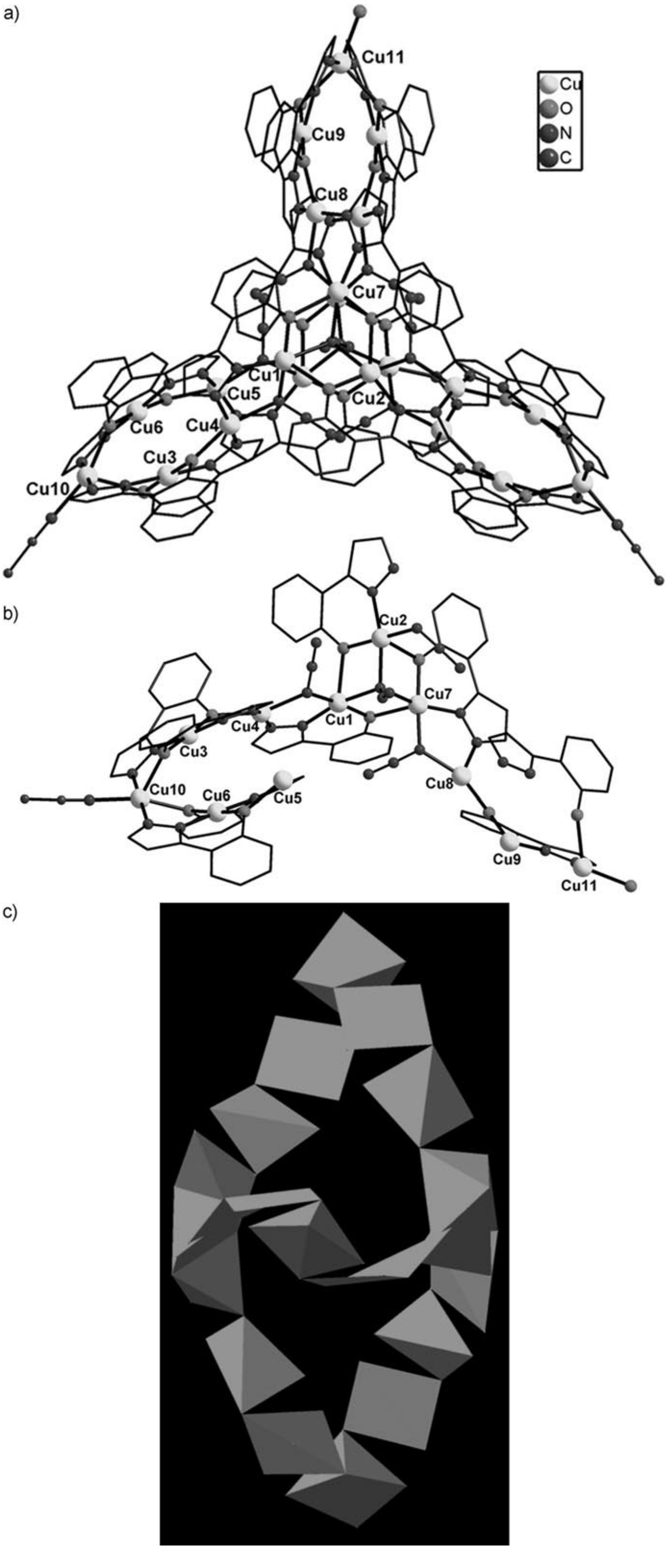


Figure 1. a) The tricorne framework structure of **1**. b) The asymmetric unit of **1**. Hydrogen atoms and lattice molecules are omitted for clarity. c) The tricorne polyhedral Cu_{21} cage of **1**.

nitrile molecule, respectively. The bridges within near-arc Cu_3 and vaulted Cu_5 units are μ_3-fashion pyrazolato ligands with Cu···Cu separations falling in range of 3.280–3.309 Å. Cu1, Cu2, and Cu7 in the triangular unit have almost the same coordination environments, which are five-coordinated in slightly distorted square-pyramidal geometry with two oxygen atoms and three nitrogen atoms from two pyrazolato ligands, one end-on μ_3-N_3^- and one end-on μ_2-N_3^- ion. The vertices in this triangular unit are bridged not only by three μ_2-$O_{phenoxo}$ atoms but also by an end-on μ_3-N_3^- ion that is located above the unit, within which the Cu···Cu distances span the range of 3.180–3.213 Å, somewhat shorter than those in the near-arc trinuclear unit. However, the average bond length of Cu−$O_{phenoxo}$ (2.057(3) Å) in the triangular unit is slightly longer than that in the near-arc unit (2.010(3) Å). The Cu−N_{azide} bond lengths fall in the range of 1.980(4)–2.134(4) Å and are evidently longer than those of Cu−$N_{pyrazolato}$ (1.888(4)–1.939(4) Å), which is similar to the expected values for typical Cu−$N_{azide/pyrazolato}$ bond lengths.[13,19] The triangular unit (Cu1, Cu2, and Cu7) acts as a node that connects three adjacent arc units through end-on μ_2-N_3^- bridges in three orientations to finally form the tricorne Cu_{21} core through an inversion operation. Figure 1c shows the polyhedral copper cage in which each edge of the tricorne cage is a 14-membered copper cycle.

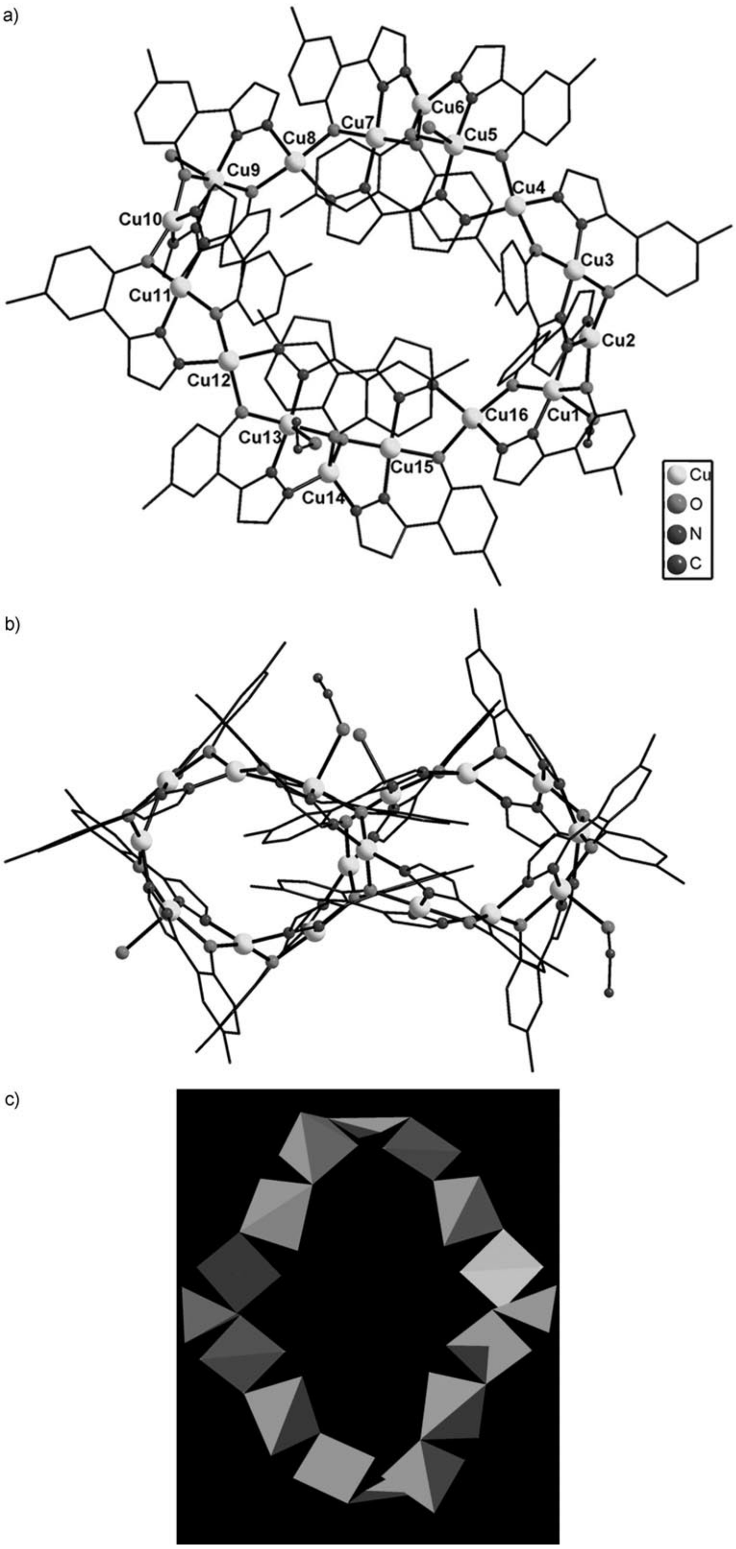


Figure 2. a) The cyclic framework structure of **2**. b) Perspective view of the saddlelike structure of **2**. c) The cyclic polyhedral Cu_{16} cycle of **2**.

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with a whole hexadecanuclear cycle in the asymmetric unit (Figure 2a), which consists of sixteen bridging $Meppz^{2-}$ groups, sixteen Cu^{2+} ions, and two water, as well as two ethanol molecules. In the 16-membered copper ring, all $Meppz^{2-}$ groups alternate in approximately in-cycle and out-of-cycle orientations and feature a η^2:η^1:η^1-μ_3 coordination mode as in compound **1** (Scheme 1). Each one bridges three neighboring Cu^{2+} ions. Due to the considerable steric hindrance between adjacent $Meppz^{2-}$ groups, this large copper ring is not a nearly planar sheet but rather a saddlelike structure as shown in Figure 2b. This greatly distorted skeleton is believed to cause the diverse coordination geometries around copper ions in compound **2**. According to the different coordination geometries of copper ions (Figure 2a), this 16-membered ring can be divided into four tetranuclear copper subunits (Cu1 to Cu4, Cu5 to Cu8, Cu9 to Cu12, and Cu13 to Cu16) in which Cu1, Cu5, Cu9, and Cu13 are five-coordinated. Each subunit is linked to adjacent ones by phenoxo oxygen atoms; the resulting polyhedral copper cycle is shown in Figure 2c. In the {Cu_4} fragment, here exemplified by Cu1 to Cu4, Cu1 lies in a slightly distorted square-pyramidal coordination sphere, whose equatorial plane is occupied by nitrogen and oxygen atoms from two $Meppz^{2-}$ groups. The remaining apical coordination site is occupied by one ethanol molecule. On the apical positions of Cu5, Cu9, and Cu13 in other {Cu_4} fragments, the coordination molecules are water, water, and ethanol, respectively. The three other copper ions (Cu2 to Cu4) are in a distorted-square coordination geometry; the Cu2 and Cu4 ions are coordinated by two oxygen atoms and two nitrogen atoms from four $Meppz^{2-}$ groups, whereas the Cu3 ion is coordinated by two oxygen atoms and two nitrogen atoms from two $Meppz^{2-}$ groups. In other subunits the coordination environment of the Cu6/Cu8, Cu10/Cu12, and Cu14/Cu16 ions resembles those of Cu2/Cu4 ions, whereas those of the Cu7, Cu11, and Cu15 ions are similar to that of the Cu3 ion. The bond lengths of Cu–O$_{water}$/O$_{ethanol}$ (2.310(8)–2.456(6) Å) are distinctly longer than those of Cu–O$_{phenoxo}$ (1.914(6)–1.992(6) Å), indicating that the solvent molecules are weakly coordinated to copper ions. The Cu–N bond lengths lie in the range of 1.890(9)–1.949(8) Å, close to those of Cu–N$_{pyrazolato}$ in compound **1**. Moreover, it is noteworthy that the distortion of copper coordination geometries can also be viewed through O/N-Cu–O/N bond angles, which alter from 93.20 to 179.09°.

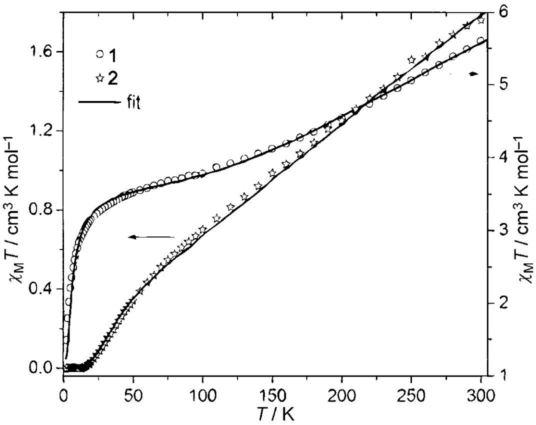


Figure 3. Magnetic susceptibilities of compounds **1** and **2** measured under an applied field of 5 kOe for **1** and 2 kOe for **2**, and quantum Monte Carlo simulation of **1** and **2** with 3-*J* model and 2-*J* model (—— = simulated).

Magnetic susceptibilities of **1** and **2** were measured under fields of 5 kOe (for **1**) and 2 kOe (for **2**) in the temperature range of 2–300 K (Figure 3). The observed $\chi_M T$ values at room temperature are 5.61 and 1.76 cm^3 K mol^{-1} for **1** and **2**, respectively, which are much less than the theoretical values of 7.875 and 6.0 cm^3 K mol^{-1} for twenty one and sixteen uncoupled Cu^{2+} ions, respectively. Upon cooling, the $\chi_M T$ value of **1** gradually decreases and reaches a value of 3.78 cm^3 K mol^{-1} at 100 K, where it keeps approximately constant until 30 K and then sharply falls to reach a minimum at 2 K, whereas the $\chi_M T$ value of **2** rapidly decreases in a nearly straight line to reach a plateau of 0.005 cm^3 K mol^{-1} at around 15 K and remains almost unchangeable until 2 K, which indicates strong antiferromagnetic interactions in **2** and that the net ground state is zero. The data of χ_M^{-1} above 150 K fit well with the Curie–Weiss law to give $C = 8.93$ cm^3 K mol^{-1} and $\theta = -187.60$ K for **1** and $C = 5.36$ cm^3 K mol^{-1} and $\theta = -820.92$ K for **2**. The large negative Weiss constants indicate antiferromagnetic interactions in **1** and **2**, and evidently the antiferromagnetic couplings in **2** are much stronger than those in **1**. The difference in magnitude between the magnetic exchanges between **1** and **2** may be due to the counter compensation of antiferro- and ferromagnetic couplings propagated by the magnetically active bridges of ppz^{2-} and N$_3^-$ in **1**, which may also lead to the appearance of a sort of plateau in $\chi_M T$ versus T plots of **1** in the 100–30 K temperature range. Generally, copper–azide/phenoxo compounds show ferromagnetic exchanges when the Cu-(end-on-N$_{azide}$)-Cu angle is less than 108° and Cu-O$_{phenoxo}$-Cu angle less than 99°, whereas the magnetic interactions beyond these angles become antiferromagnetic in nature.[20,21] So for **1** the coupling interactions in the triangle Cu$_3$ unit with Cu-μ_3-N$_3^-$-Cu bond angles of 100.14, 100.30, and 101.90°, respectively, should be ferromagnetic by means of the end-on μ_3-N$_3^-$ bridge, whereas the vaulted Cu$_5$ subunit should be antiferromagnetic through the end-on μ_2-N$_3^-$ because the Cu-μ_2-N$_3^-$-Cu angles are over 108° (117.21, 117.5, and 117.79°) and the Cu-μ_2-O$_{phenoxo}$-Cu angles are beyond 99° (105.62–115.1°), such that the antiferromagnetic interactions should dominate in **1**. In **2**, however, the pyrazolato and μ_2-O$_{phenoxo}$ (Cu-O-Cu 109.59–116.39°) bridges are expected to propagate strong antiferromagnetic exchanges, which is consistent with the magnetic experimental results.

Quantum Monte Carlo simulations: To evaluate the magnetic interactions between copper ions in compound **1**, we simulated the magnetic properties by using a model with four coupling parameters, taking into consideration the couplings propagated by the different bridges in Figure 4 [the corresponding Hamiltonian ($\mathscr{H}$) is described in Equation (1)], in which the J_1 concerns interactions within the triangular Cu$_3$ units bridged by end-on μ_3-N$_3^-$ and phenoxo oxygen atoms, J_2 represents the exchange couplings of Cu⋯Cu bridged by end-on μ_2-N$_3^-$ and pyrazolato, J_3 and J_4 are the exchange parameters of Cu⋯Cu interactions bridged by pyrazolato and phenoxo oxygen bridges, and S represents the Cu^{II} S = 1/2 spin.

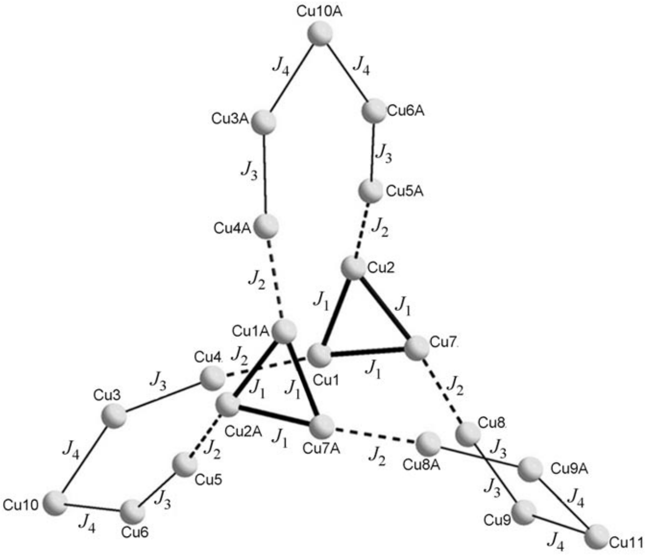


Figure 4. Highlight of the coupling model of compound **1** with four *J* exchange parameters.

$$\begin{aligned}\mathcal{H} = &-2J_1(S_1S_2 + S_1S_7 + S_2S_7 + S_{1A}S_{2A} + S_{1A}S_{7A} + S_{2A}S_{7A})\\ &-2J_2(S_1S_4 + S_2S_{5A} + S_7S_8 + S_{1A}S_{4A} + S_{2A}S_5 + S_{7A}S_{8A})\\ &-2J_3(S_3S_4 + S_5S_6 + S_8S_9 + S_{3A}S_{4A} + S_{5A}S_{6A} + S_{8A}S_{9A})\\ &-2J_4(S_3S_{10} + S_6S_{10} + S_9S_{11} + S_{3A}S_{10A} + S_{6A}S_{10A} + S_{9A}S_{11A})\end{aligned} \tag{1}$$

To avoid overparameterization, we made the assumption that $J_3 = J_4$, because both J_3 and J_4 represent the exchanges between copper ions bridged by the pyrazolato and phenoxo groups. Although the value of $|J_4|$ (Cu-μ_2-$O_{phenoxo}$-Cu 105.62–108.57°) may be relatively larger or less than that of $|J_3|$ (Cu-μ_2-$O_{phenoxo}$-Cu 113.68–115°), according to the Cu-O-Cu angles, they are still antiferromagnetic because the Cu-O-Cu angles exceed 99°. On the other hand, the Cu···Cu distances regarding J_3 and J_4 vary in a small range (3.280–3.309 Å), which implies that J_3 can be assumed to be equal to J_4. Concerning the susceptibility equation, we have to take into account the temperature-independent paramagnetism (TIP) parameter due to the large number of paramagnetic centers.

It was not possible to apply the well-known irreducible tensor operators (ITO) method due to the large dimensions of the energy matrix. More explicitly, its total dimension (2097152×2097152) can be reduced (for point symmetry reasons) to S-block matrices in which the maximum size is also very large (90440×90440) and CPU time intensive. Therefore a quantum Monte Carlo (QMC) study was carried out based on the algorithms and libraries for physical simulations (ALPS) project to simulate the magnetic behavior of the compound (see the Experimental Section).

The final result of the simulations is shown as a solid line in Figure 3. According to the applied 3-J model the best simulated values are $J_1 > 340\ \text{cm}^{-1}$, $J_2 = -290(20)\ \text{cm}^{-1}$, $J_3 = -3(1)\ \text{cm}^{-1}$, $g = 2.07(1)$, and $\text{TIP} = 1000 \times 10^{-6}\ \text{cm}^3\text{mol}^{-1}$. There is a clear uncertainty concerning the large ferromagnetic value of the J_1 parameter. From our simulations this value varies between 340 to 620 cm^{-1}. This uncertainty is much smaller in the case of the large antiferromagnetic J_2 interaction, whereas J_3 is well defined. In a previously reported paper, a series of dicopper compounds in which only end-on μ_2-azide and N–N groups serving as bridges showed antiferromagnetic exchanges, with $-2J$ falling in the range of 40–1100 cm^{-1},[22] which indicates that the end-on μ_2-azide bridge can propagate antiferromagnetic coupling between two copper centers if the bridge angle is large enough, and therefore confirming the possibility of a large J_2 value of compound **1**. In a phenoxo- and pyrazolato-bridged dicopper compound with Cu-$O_{phenoxo}$-Cu = 117.1° and Cu···Cu = 3.358 Å,[23] however, the strength of the exchange coupling was as large as $-2J = 448\ \text{cm}^{-1}$, which is much larger than the J_3 value in **1**. Indeed, the superexchange can be $J > 0\ \text{cm}^{-1}$, $-J \leq 50\ \text{cm}^{-1}$, or even $-J \leq 150\ \text{cm}^{-1}$ regarding the phenoxo bridging angle.[24] In the case of **1**, the Cu-$O_{phenoxo}$-Cu angles are greater than 105°, which indicates moderate antiferromagnetic interactions between copper ions (J_3 or J_4).

To evaluate the magnetic interactions between copper ions in compound **2**, we simulated the magnetic properties by using a model with two coupling constants, taking into consideration the nearest Cu···Cu distances (Figure 5). The corresponding Hamiltonian is described in Equation (2). Concerning the susceptibility equation, we also had to take into account the TIP parameter due to the large number of paramagnetic centers.

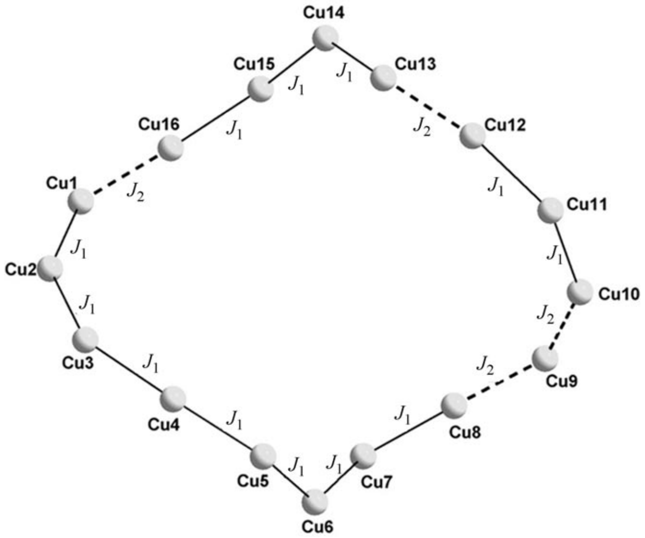


Figure 5. Highlight of the coupling model of compound **2** with two J exchange parameters. Distances of Cu···Cu [Å]: Cu1···Cu2 3.213(6), Cu2···Cu3 3.206(7), Cu3···Cu4 3.254(2), Cu4···Cu5 3.239(6), Cu5···Cu6 3.178(8), Cu6···Cu7 3.236(2), Cu7···Cu8 3.173(9), Cu8···Cu9 3.297(9), Cu9···Cu10 3.281(1), Cu10···Cu11 3.184(8), Cu11···Cu12 3.250(4), Cu12···Cu13 3.336(3), Cu13···Cu14 3.257(8), Cu14···Cu15 3.179(5), Cu15···Cu16 3.237(10), Cu16···Cu1 3.305(8).

$$\begin{aligned}\mathcal{H} = &-2J_1\left[\left(\sum_{i=1-7} S_i \times S_{i+1}\right) + S_{11}(S_{10} + S_{12}) + \left(\sum_{i=13-15} S_i \times S_{i+1}\right)\right]\\ &-2J_2[S_9(S_8 + S_{10}) + S_{12}S_{13} + S_1S_{16}]\end{aligned} \tag{2}$$

Two different approaches were used: 1) The well-known ITO method, according to which the dimension of the exchange matrix, 65536×65536, is formed by S-block matrices with a maximum size of 3640×3640. In the second case it is not possible to employ this method because the dimension of the energy matrix is 2097152×2097152 and the maximum size of the S-block matrix is 90440×90440. 2) A QMC study was carried out based on the ALPS project to simulate the magnetic behavior of the compound. The final result of the simulations is shown as a solid line in Figure 3. According to the applied 2-J model, the best simulated values are $J_1 = -368(2)\ \text{cm}^{-1}$, $J_2 = -53(2)\ \text{cm}^{-1}$, $g = 2.04(2)$, and $\text{TIP} = 1000 \times 10^{-6}\ \text{cm}^3\text{mol}^{-1}$. The large negative J values indicate strong antiferromagnetic interactions in **2** propagated through phenoxo and pyrazolato groups, which were consistent with those in other copper compounds with similar bridge ligands.[11c,23,25]

Conclusion

In summary, we have successfully synthesized two high-nuclearity copper cages, tricorne Cu_{21} and saddlelike cyclic Cu_{16}, by a one-pot reaction of copper salts with polydentate H_2Rppz ligands (R = H, Me). Magnetic studies and quantum Monte Carlo simulations of **1** and **2** indicate the presence of ferromagnetic and antiferromagnetic interactions in **1** and strong antiferromagnetic interactions in **2** between copper centers within the clusters. Further investigations on the preparation of various new polynuclear metal clusters constructed with analogous ligands $Rppz^{2-}$ with substituted groups R and/or with other ionic bridges such as X^- (X = F, Cl, Br and OH) within the system are in progress.

Experimental Section

Materials and physical measurements: All starting materials were obtained commercially and were used without further purification. Elemental analyses for C, H, and N were performed by using a Perkin-Elmer 240Q elemental analyzer. The IR spectra were recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Nicolet 5DX spectrometer. The magnetic measurements were carried out using a Quantum Design SQUID MPMS-XL instrument. Crystal data were collected using an Oxford diffractometer ($Cu_{K\alpha}$, $\lambda = 1.54178$ Å). The ligands 3-(2-hydroxyphenyl)pyrazole (H_2ppz) and 3-(2-hydroxy-5-methylphenyl)pyrazole (H_2Meppz) were prepared by following a modified literature method according to reference [26].

Magnetic simulations and fitting procedure: Monte Carlo (MC) simulations are powerful numerical tools for high-precision studies of many-body systems, both in the classical and quantum regime. Especially near second-order phase transitions where physical length scales diverge, it is essential to simulate large systems, which has become possible due to significant algorithmic advances within the last 15 years. In classical simulations, conventional MC algorithms sample the canonical partition function by making local configuration updates. While being straightforward, this approach tends to slow down simulations near phase transitions and gives rise to long autocorrelation times in the measurement of the relevant physical observables. For classical spinlike systems, this critical slowing down can be overcome by using cluster algorithms, which update large clusters of spins in a single MC step.

The generalization of these nonlocal update schemes to the case of QMC simulations was initiated by the development of the loop algorithm in world-line representation. This very efficient method has been used in many studies, in which it allowed the simulation of large systems at very low temperatures. In the original formulation (either in discrete or continuous imaginary time), however, the loop algorithm has a major drawback: to work efficiently, its application is restricted to specific parameter regimes. In the case of quantum spin models, for example, it suffers from severe slowing down upon turning on a magnetic field.

An alternative QMC approach, which is not based upon the world-line representation, is the stochastic series expansion (SSE),[27] a generalization of Handscomb's algorithm[28] for the Heisenberg model. Although local MC updates were used in the original implementation,[27] Sandvik later developed a cluster update called the operator-loop update for the SSE representation,[29] which allows for nonlocal changes of MC configurations. Within this SSE approach one can efficiently simulate models for which the world-line loop algorithm suffers from slowing down.

A QMC study using the SSE and the loop algorithm was carried out instead of the usual ITO method to simulate the magnetic behavior of compounds **1** and **2.** The reason for using the QMC method instead of the classical Monte Carlo (CMC) method is the quantum nature of the Cu^{II} ion ($S = 1/2$). The QMC calculations are based on the ALPS project.[30] For each site 5×10^6 Monte Carlo steps were performed and 10% of them were discarded as the initial transient stage.

Caution! Sodium azide is potentially explosive and should be treated with care and in small quantities.

Synthesis of 1: A solution of H_2ppz (0.016 g) and NaN_3 (0.013 g, 0.2 mmol) in ethanol (10 mL) was laid upon a solution of $Cu(ClO_4)_2\cdot6H_2O$ (0.037 g, 0.1 mmol) in ethanol (5 mL) in a test tube. Three days later black crystals of **1** were collected. Suitable crystals for X-ray diffraction study were obtained through recrystallization of the crude products from ethanol/acetonitrile (v/v 2:1, 12 mL). Yield: 58% (based on H_2ppz); elemental analysis calcd (%) for $C_{182}H_{166}N_{64}O_{24}Cu_{21}$: C 44.00, H 3.37, N 18.04; found: C 44.00, H 4.09, N 18.02.

Synthesis of 2: A solution of H_2Meppz (0.017 g, 0.1 mmol), $Cu(BF_4)_2\cdot6H_2O$ (0.034 g, 0.1 mmol), and triethylamine (50–100 μL) in ethanol (30 mL) was stirred under ambient conditions for 15 min. The solution was then filtered and left for slow evaporation. Black block crystals of **2** were obtained after 5 d. Yield: 28% (based on H_2Meppz); elemental analysis calcd (%) for $C_{164}H_{163}N_{32}O_{29.5}Cu_{16}$: C 48.38, H 4.04, N 11.01; found: C 48.16, H 4.13, N 10.95.

Crystallographic studies: X-ray crystallographic data were collected with a $Cu_{K\alpha}$ radiation source ($\lambda = 1.54178$ Å) by using an Oxford diffractometer equipped with a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares calculations (F^2) by using SHELXT-97 software.[31] All non-hydrogen atoms were refined in the anisotropic approximation against F^2 for all reflections. All H atoms were placed at their calculated positions and refined in the isotropic approximation. Owing to severe disorder or partial occupancy, some parts of the structures (guest and solvent molecules) of **1** were removed from the data with the SQUEEZE procedure.[32]

Compound 1: $C_{182}H_{166}N_{64}O_{24}Cu_{21}$; $M_r = 4968.2$; orthorhombic; *Pccn*; $a = 25.3726(2)$, $b = 29.3066(3)$, $c = 36.9638(3)$ Å; $V = 27485.7(4)$ Å^3; $Z = 4$; $\mu = 2.136$ mm^{-1}; $S = 0.996$; $T = 173(2)$ K; $\rho_{calcd} = 1.121$ $Mg\,m^{-3}$; $R_1 = 0.0504$, $wR_2 = 0.1612$.

Compound 2: $C_{164}H_{163}N_{32}O_{29.5}Cu_{16}$; $M_r = 4070.9$; monoclinic; $P2_1/n$; $a = 14.293(5)$, $b = 49.503(5)$, $c = 28.513(5)$ Å; $V = 19993(8)$ Å^3; $Z = 4$; $\mu = 2.338$ mm^{-1}; $S = 1.081$; $T = 173(2)$ K; $\rho_{calcd} = 1.352$ $Mg\,m^{-3}$; $R_1 = 0.0978$, $wR_2 = 0.2682$.

CCDC 696638 and 696639 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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