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Two Triazole-Based Metal–Organic Frameworks Constructed from Nanosized Cu_{20} and Cu_{30} Wheels

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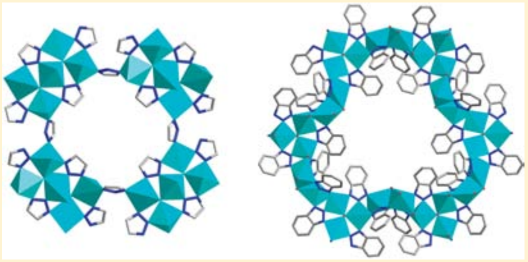
Supporting Information

ABSTRACT: Two metal–organic frameworks constructed from nanosized Cu_{20} and Cu_{30} wheels have been obtained under hydrothermal conditions based on 1,2,3-triazole and 1-*H*-1,2,3-benzotriazole, respectively. Crystal structure analysis shows that their differences in the size and nuclearity of Cu_{20} and Cu_{30} wheels are attributed to the steric effect of ligands.



INTRODUCTION

The exploratory synthesis and investigation of properties of high-nuclearity clusters have received much interest because of their beautiful architectures and properties.[1−3] A particularly intriguing type within this class is the molecular wheel, driven largely by their potential applications, such as magnetic materials, sensors for small molecules or anions, and new classes of catalysts.[4,5] Although a number of molecular wheels have been reported, the rational design of molecular wheels is also synthetically challenging because of the difficulty to control the size and nuclearity of the wheels.[6]

Recent studies have shown that small molecular and anionic species, such as toluene, Cl^-, Br^-, I^-, and NO_3^-, are effective templates to construct molecular wheels, especially for low-nuclearity wheels.[7−9] For example, Raptis et al. obtained a series of copper wheels $[Cu(\mu_2\text{-OH})(pz)]_n$ ($n = 6, 8, 9, 12, 14$), templated by Cl^-, CO_3^{2-}, and SO_4^{2-} anions, based on the pyrazole (pz) ligand.[9] However, high-nuclearity wheels are still very rare due to the instability of large hydrophobic or hydrophilic inner cavities.

One feasible avenue to increase the nuclearity of wheels is introducing large volume template anions, such as polyoxometalates (POMs), which have large volume, high charge, and inherent structural feature. Another attainable approach is to increase the steric effect of ligands, leading to expansion of the ring size.[4c] To investigate the steric effect, the 1,2,3-triazole (taH) and 1-*H*-1,2,3-benzotriazole (btaH) ligands were selected to construct high-nuclearity wheels because the three nitrogen atoms of 1,2,3-triazole will be a good candidate not only for interconnecting metals to assemble wheel compounds through adjacent N atoms[10] but also for linking the wheels to frameworks via the third N atom.[11,12] Here, two metal–organic frameworks $[Cu_{13}(ta)_{16}(\mu_3OH)_4(H_2O)_6]\cdot 2PMo_{12}O_{40}\cdot 14H_2O$ (**1**) and $[Cu_{12}(bta)_{12}(\mu_3\text{-OH})_5(\mu_2\text{-}H_2O)_6]\cdot PMo_{12}O_{40}\cdot 2HPMo_{12}O_{40}\cdot 18H_2O$ (**2**) were obtained under hydrothermal conditions. X-ray crystallographic analysis shows that the three-dimensional compound **1** consists of Cu_{20} wheels with a pentanuclear $[Cu_5(ta)_4(\mu_3\text{-OH})_2]^{4+}$ cluster and linear trinuclear $[Cu_3(ta)_4]^{2+}$ cluster as building units (Figure 1a and 1b), while the two-dimensional compound **2** is constructed from larger Cu_{30} wheels with triangular $[Cu_3(bta)_3(\mu_3\text{-OH})]^{2+}$ and dinuclear $[Cu_2(bta)_2(\mu_2\text{-OH})]^+$ units as building blocks (Figure 1c and 1d). Structural analysis indicates that the differences in the size and nuclearity of Cu_{20} and Cu_{30} wheels are attributed to the steric effect of ligands.

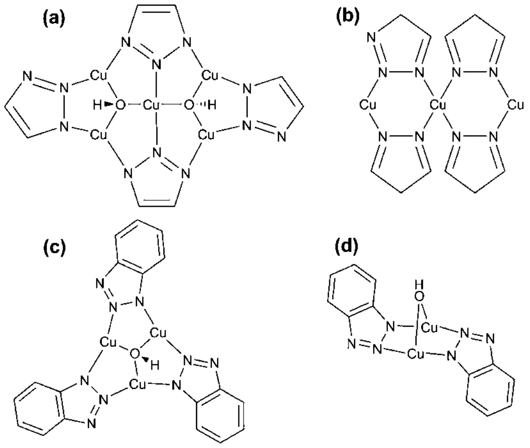


Figure 1. Schematic view of the pentanuclear $[Cu_5(ta)_4(\mu_3\text{-OH})_2]^{4+}$ cluster in **1** (a), linear trinuclear $[Cu_3(ta)_4]^{2+}$ in **1** (b), triangular trinuclear $[Cu_3(bta)_3(\mu_3\text{-OH})]^{2+}$ cluster in **2** (c), and dinuclear $[Cu_2(bta)_2(\mu_2\text{-OH})]^+$ cluster in **2** (d).

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■ EXPERIMENTAL SECTION

Materials and Methods. All reagents were of commercial origin and used as received. C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR330 Spectrophotometer with pressed KBr pellets. Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID).

Synthesis and Characterization of $[Cu_{13}(ta)_{16}(\mu_3\text{-}OH)_4(H_2O)_6]\cdot 2PMo_{12}O_{40}\cdot 14H_2O$ (1). A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.24 g, 1 mmol), $H_3PMo_{12}O_{40}$ (0.23 g, 0.125 mmol), and 1,2,3-triazole (0.12 g, 1.79 mmol) was dissolved in 20 mL of distilled water at room temperature. Green block crystals were obtained in 63% yield (based on $H_3PMo_{12}O_{40}$). Anal. Calcd. for $C_{32}H_{76}Cu_{13}N_{48}O_{104}P_2Mo_{24}$ (%, fw = 5987.93): C, 6.41; N, 11.23; H, 1.27. Found: C, 6.26; N, 11.10; H, 1.27. IR (KBr, cm^{-1}): 3441 (vs), 1630 (w), 1560 (w), 1418 (m), 1384 (s), 1146 (w), 1121 (m), 1109(m), 1085 (w), 626 (m).

Synthesis and Characterization of $[Cu_{12}(bta)_{12}(\mu_3\text{-}OH)_5(\mu_2\text{-}H_2O)_6]\cdot PMo_{12}O_{40}\cdot 2HPMo_{12}O_{40}\cdot 18H_2O$ (2). A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.24 g, 1 mmol), $H_3PMo_{12}O_{40}$ (0.23 g, 0.125 mmol), and 1-*H*-1,2,3-benzotriazole (0.12 g, 1 mmol) was dissolved in 20 mL of distilled water at room temperature. Then it was sealed in a 25 mL Teflon-lined Parr vessel, heated at 140 °C for 5000 min, and slowly cooled down to room temperature for 4500 min. Dark green block crystals were obtained in 56% yield (based on $H_3PMo_{12}O_{40}$). Anal. Calcd for $C_{72}H_{103}Cu_{12}N_{36}O_{149}P_3Mo_{36}$ (%, fw = 8166.13): C, 10.59; N, 6.17; H, 1.27. Found: C, 10.60; N, 6.31; H, 1.32. IR (KBr, cm^{-1}): 3441 (vs), 1636 (m), 1560 (s), 1476 (w), 1419 (w), 1384 (s), 1143 (w), 1121 (s), 1108 (m), 1082 (m), 636 (m).

Single-Crystal X-ray Structure Determination. Data for compounds **1** and **2** were collected on a Bruker SMART Apex CCD diffractometer with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) at 173 K for **1** and 273 K for **2**. Absorption corrections were applied using the multiscan program SADABS. Structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL-97 program. The hydrogen atoms of the organic ligand were generated geometrically (C–H, 0.96 A). Crystal data as well as details of data collection and refinement for the complexes are summarized in Table 1. The CCDC contains the supplementary crystallographic data for this paper with deposition numbers of CCDC 866573 and 866574 for **1** and **2**, respectively. Crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Selected bonds and angles for **1** and **2** are summarized in Tables S1 and S2, Supporting Information.

Table 1. Crystal Data and Details of Data Collection and Refinement for Complexes 1 and 2

complex	1	2
formula	$C_{32}H_{76}Cu_{13}N_{48}O_{104}P_2Mo_{24}$	$C_{72}H_{103}Cu_{12}N_{36}O_{149}P_3Mo_{36}$
M_r	5987.93	8166.13
cryst syst	triclinic	trigonal
space group	*P*-1	$R\bar{3}c$
a/Å	15.325(6)	20.758(12)
b/Å	16.472(6)	20.758(12)
c/Å	17.072(6)	158.36(13)
α/deg	70.144(7)	90.00
β/deg	64.567(7)	90.00
γ/deg	67.516(7)	120.00
V/Å^3	3516(2)	59 094(68)
Z	1	12
D_c/g cm^{-3}	2.828	2.754
μ/mm^{-1}	4.122	3.611
data/params	12 028/1027	11 524/950
θ/deg	1.37–25.00	0.77–25.00
obsd reflns	8614	9234
R_1 $[I > 2\sigma(I)]^a$	0.0780	0.1423
wR_2 (all data)^b	0.1833	0.2938

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^bwR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

■ RESULTS AND DISCUSSION

Description of the Crystal Structure of Compound 1. Compound **1** was synthesized under hydrothermal conditions using a mixture of 1,2,3-triazole, $Cu(NO_3)_2$, and $H_3PMo_{12}O_{40}$ and crystallized in the $P\bar{1}$ space group. Compound **1** consists of two types of building blocks, planar Cu_5 and linear Cu_3 (Figures 2a–d). The Cu_5 unit is composed of five Cu^{2+} cations, four ta^- ligands, and two $\mu_3\text{-}OH^-$ anions, forming a planar pentanuclear $[Cu_5(ta)_4(\mu_3\text{-}OH)_2]^{4+}$ cluster, similar to the reported $[Cu_5(bta)_4(\mu_3\text{-}OH)_2]^{4+}$.[12] The linear Cu_3 unit, formulated as $[Cu_3(ta)_4]^{2+}$, is made up of three Cu^{2+} and four ta^- ligands. Four Cu_5 clusters are linked by four ta^- ligands, forming a nanosized Cu_{20} wheel of $[Cu_{20}(ta)_{20}(\mu_3\text{-}OH)_8]^{12+}$ (Figure 2e). Adjacent Cu_{20} wheels are connected by sharing the Cu_5 cluster, leading to a 2D 4^4-network of $[Cu_5(ta)_6(\mu_3\text{-}OH)_2]_n^{2n+}$ (Figure 2f) in which the Cu_5 unit acts as a four-connected node. The 3D structure of **1** can be viewed as a set of parallel 2D structures of $[Cu_5(ta)_6(\mu_3\text{-}OH)_2]_n^{2n+}$ linked by Cu_3 units through three Cu–N bonds (Cu6–N19 = 2.046(6) Å, Cu6–N17 = 2.185(7) Å, and Cu6–N9 = 2.009(8) Å) (Figure 2g). In this regard, the Cu_5 and Cu_3 units can be viewed as 6-connected and 4-connected nodes (Figure 2h), respectively. As a result, the 3D framework of **1** can be assigned to a $(3^2.6^2.7^2)(3^2.4^4.5^4.6^4.7)_2$ topology symbol. Acting as counter-anions, the $PMo_{12}O_{40}^{3-}$ anions locate on the voids between 2D layers, through hydrogen bonds (O1W···O22 = 2.833(2) Å and O26···C13 = 3.211(1) Å) (Figure S1, Supporting Information). The bond lengths of Cu–N and Cu–O are 1.860(8)–2.225(7) and 1.970(5)–2.432(8) Å, comparable to those in the reported Cu–POM complexes.[12–14]

Description of the Crystal Structure of Compound 2. Compound **2** was crystallized in the *R*–3*c* space group. As shown in Figure 3a and 3b, three Cu^{2+} ions, three bta^- ligands, and one $\mu_3\text{-}OH^-$ forms a triangular Cu_3 cluster of $[Cu_3(bta)_3(\mu_3\text{-}OH)]^{2+}$, while two Cu^{2+} ions, two bta^- ligands, and one $\mu_2\text{-}OH^-$ produce a Cu_2 unit of $[Cu_2(bta)_2(\mu_2\text{-}OH)]^+$. Six Cu_3 clusters and six Cu_2 are linked alternately by two bta^- ligands of adjacent units, leading to a nanosized hexagonal Cu_{30} wheel of $[Cu_{30}(bta)_{30}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_6]^{18+}$ (Figure 3c). One $PMo_{12}O_{40}^{3-}$ is located in the cavity of the Cu_{30} wheel, and its presence can be readily appreciated in terms of the templating effects. As shown in Figure 3d, adjacent Cu_{30} wheels are connected through sharing the one side of the hexagon of Cu_{30}, generating a 2D 6^3-network in which the Cu_3 clusters serve as a three-connected node and the Cu_2 units act as two-connected linkers. The 3D framework can be viewed as constructing from the 2D 6^3 networks and two parts of the $PMo_{12}O_{40}^{3-}$ anions through the covalent bond (O11–Cu4, 2.469(12) Å). In addition, the third of the $PMo_{12}O_{40}^{3-}$ anions locate on the voids between 2D layers through hydrogen bonds (Figure S2, Supporting Information). The bond lengths of Cu–N and Cu–O are range of 1.974(15)–2.062(15) and 1.990(9)–2.469(12) Å, respectively, comparable to those in the reported Cu–POM complexes.[12–14]

It is interesting to observe that the use of 1,2,3-triazole yields a Cu_{20} wheel in **1**, while the presence of the 1-*H*-1,2,3-benzotriazole

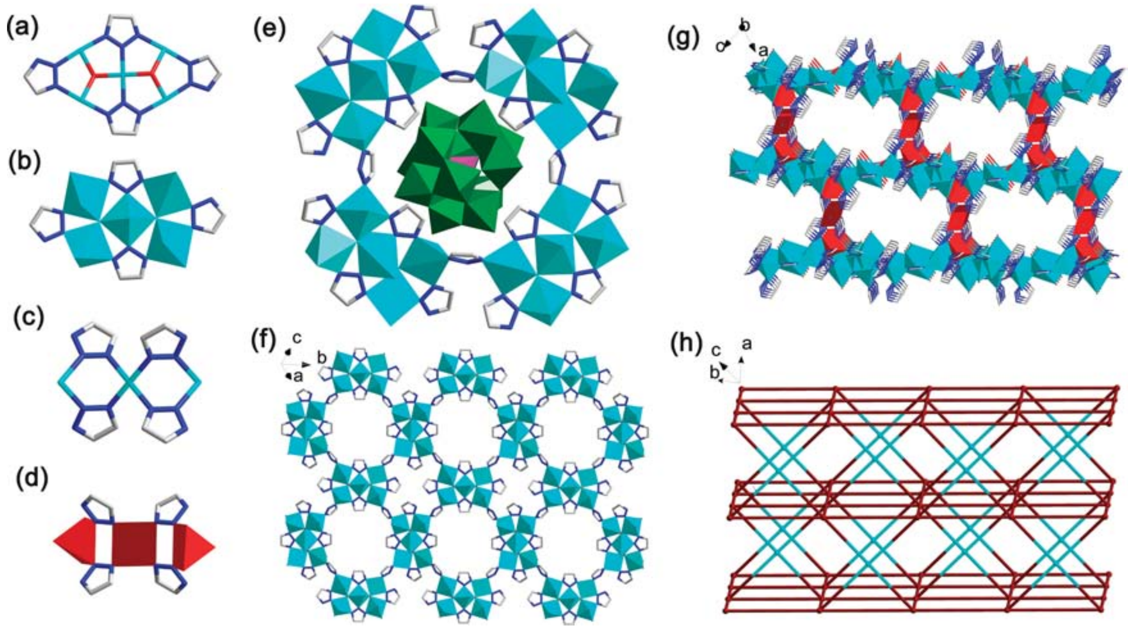

Figure 2. Cu_5 cluster of $[Cu_5(ta)_4(\mu_3\text{-OH})_2]^{4+}$ in **1** (a,b), Cu_3 cluster of $[Cu_3(ta)_4]^{2+}$ (c,d), Cu_{20} wheel of $[Cu_{20}(ta)_{20}(\mu_3\text{-OH})_8]^{12+}$ (e), 4^4 network of $[Cu_5(ta)_6(\mu_3\text{-OH})_2]_n^{2n+}$ (f), 3D framework of $[Cu_{13}(ta)_{16}(\mu_3\text{-OH})_4(H_2O)_6]_n^{6n+}$ (g), and 3D topology structure of **1** (cyan, Cu_3 units; wine-red, Cu_5 units) (h).

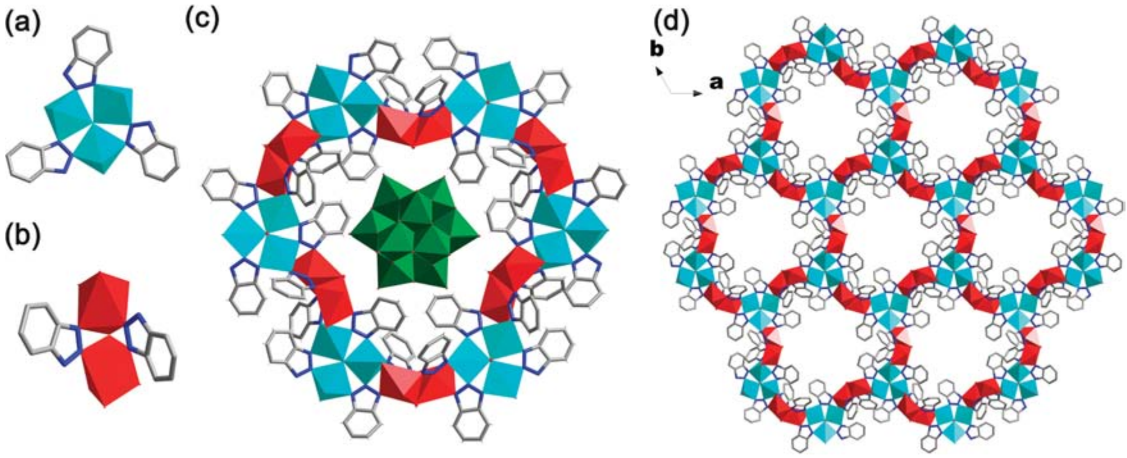

Figure 3. Polyhedral views of the triangular Cu_3 of $[Cu_3bta_3(\mu_3\text{-OH})]^{2+}$ in **2** (a), Cu_2 unit of $[Cu_2(bta)_2(\mu_2\text{-OH})]^+$ (b), Cu_{30} wheel of $[Cu_{30}(bta)_{30}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_6]^{18+}$ (c), and 6^3-network of $[Cu_{12}(bta)_{12}(\mu_3\text{-OH})_5(\mu_2\text{-H}_2O)_6]_n^{7n+}$ (d).

gives a Cu_{30} wheel in **2**, revealing that the steric exclusion of ligand forces the 20-membered copper wheel into an expanded 30-membered copper wheel. Although locating in the void between two layers, the $PMo_{12}O_{40}^{3-}$ anion also has a template effect through the hydrogen bond. Structural analysis suggests that the inside diameters of Cu_{20} and Cu_{30} wheels are approximately equal. However, the steric repulsion between the phenyl group and the $PMo_{12}O_{40}^{3-}$ anion leads to expansion of the copper wheel from the outside diameter of the Cu_{20} wheel with about 25.2 Å to the Cu_{30} wheel with about 32.3 Å (Figure 4). Notably, introduction of the phenyl group not only leads to expansion of the copper wheel but also accompanies the structural modifications in building blocks.

Magnetic Properties. Magnetic susceptibility data for **1** and **2** were measured in a temperature range of 2−300 K with an applied magnetic field of 1000 Oe. The field dependence of magnetization plots for **1** and **2** are shown in Figures S5 and S6, Supporting Information, and plots of the temperature dependence of $\chi_M T$ vs T for **1** and **2** are shown in Figure 5. For **1**, the

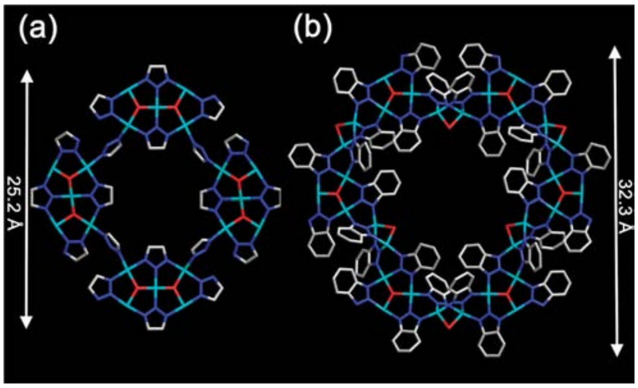

Figure 4. Stick views of the Cu_{20} wheel (a) and Cu_{30} wheel (b).

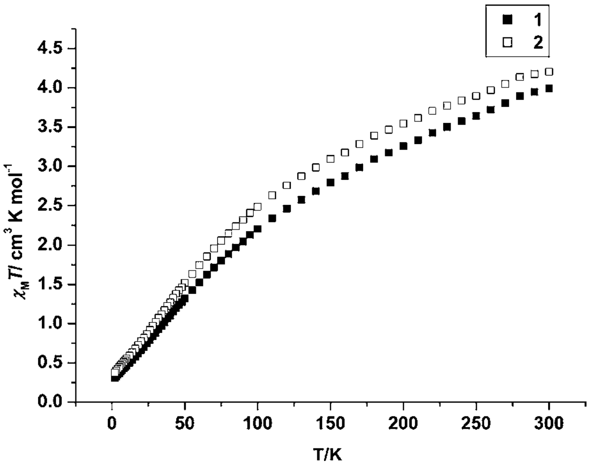

Figure 5. Plots of the temperature dependence of $\chi_M T$ vs T for **1** and **2** under 1000 Oe dc field.

observed $\chi_M T$ value of 3.99 cm^3 mol^{-1} K at room temperature is smaller than the calculated value of 4.875 cm^3 mol^{-1} K for 13 isolated spin-only Cu^{II} ions for $S = 1/2$, $g = 2.00$. Upon cooling, the $\chi_M T$ value decreases slowly to 0.31 cm^3 mol^{-1} K at 2 K, indicating antiferromagnetic behavior. The similar antiferromagnetic behavior has been found in compound **2**. For **2**, the $\chi_M T$ value at 300 and 2 K is 4.21 and 0.31 cm^3 mol^{-1} K, respectively. Data in the range of 50−300 K can be fitted to the Curie−Weiss law, yielding $C = 6.61$ cm^3 K mol^{-1} and $\theta = -202.4$ K for **1** and $C = 6.4$ cm^3 K mol^{-1} and $\theta = -161.2$ K for **2**. The negative θ is consistent with an overall antiferromagnetic coupling.

■ CONCLUSION

In summary, two triazole-based metal−organic frameworks constructed, respectively, from nanosized Cu_{20} and Cu_{30} wheels have been obtained. Crystal structure analysis shows that the $PMo_{12}O_{40}^{3-}$ anions may play a template role on formation of the larger Cu wheels. The steric effect of ligands has caused copper wheel expansion from Cu_{20} to Cu_{30} system. Further investigations on the preparation of various new polynuclear copper clusters constructed from triazole ligands with substituted groups are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray powder diffraction data and detailed structural and magnetic data for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Notes. The authors declare no competing financial interest.

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