

Single-Strand Molecular Wheels and Coordination Polymers in Copper(II) Benzoate Chemistry by the Employment of α -Benzoin Oxime and Azides: Synthesis, Structures, and Magnetic Characterization

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The use of α -benzoin oxime (bzoxH₂) in copper(II) benzoate chemistry, in the absence or presence of ancillary azido ligands, is reported. The reaction of Cu(O₂CPh)₂·2H₂O with one equivalent of bzoxH₂ in *N,N*-dimethylformamide (DMF) affords the decanuclear complex [Cu₁₀(bzox)₁₀(DMF)₄] (**1**) in good yield. Dissolution of **1** in CH₂Cl₂ leads to the subsequent isolation of the solvent-free complex [Cu₁₀(bzox)₁₀] (**2**) in moderate yields. Complexes **1** and **2** are isostructural and possess a loop or single-strand molecular wheel topology. The bzox²⁻ dianions behave as $\eta^1:\eta^1:\eta^2:\mu_3$ ligands, which give rise to an overall [Cu₁₀(μ -ONR)₁₀(μ -OR')₁₀] core. Both **1** and **2** stack to form nanotubular columns with beautiful supramolecular architectures. The reaction of Cu(O₂CPh)₂·2H₂O with bzoxH₂ and NaN₃ in a 1:1:1 molar ratio in MeOH gives the bzoxH₂-free complex [Cu(N₃)(O₂CPh)(MeOH)]_n (**3**), which is a 1D chain. The Cu^{II} atoms in **3** are linked by a

single, end-on N₃⁻ group, a *syn,syn*- $\eta^1:\eta^1:\mu$ PhCO₂⁻ ion, and an oxygen atom from the bridging MeOH ligand. The 1D chains are hydrogen bonded into 2D sheets through N_{azide}...H(O_{MeOH}) interactions. Variable-temperature, solid-state direct-current magnetic studies were carried out on **1**–**3**. The data for **1** and **2** indicate very strong antiferromagnetic exchange interactions and a *S* = 0 ground state, which is expected for even-membered loop arrays of Cu^{II} atoms. In contrast, **3** exhibits ferromagnetic exchange interactions; the data were fitted to the appropriate equation derived from the Hamiltonian $H = -J\sum(S_i \cdot S_{i+1})$, which includes a *zJ'* interchain interaction term. The best-fit parameters were *J* = +49.6(4) cm⁻¹, *g* = 2.067(3), and *zJ'* = 2.3(1) K. The combined results demonstrate the ligating flexibility of both the bzoxH₂ and azido groups and their usefulness in the synthesis of polynuclear Cu^{II} clusters and coordination polymers.

Introduction

There are several reasons for the current interest in the synthesis and study of high nuclearity, molecular clusters and coordination polymers of 3d-metal ions.^[1] Among these is the search for various nuclearity oxide-bridged metal carboxylate clusters to model M_x sites in biomolecules, which includes understanding the growth of the core of the ferritin protein,^[2] elucidating the Mn site of water oxidation within the photosynthetic apparatus of green plants and cyanobacteria,^[3] and modeling the Cu site within the complicated membrane protein ($\alpha\beta\gamma$) methane monooxygenase.^[4] Other reasons for this interest are varied, and include the aesthetically pleasing structures that many such molecular clusters possess^[5] and the search for compounds with interesting magnetic properties.^[6]

Single-strand molecular wheels and closed, cage-like clusters are the two families of polynuclear 3d-metal complexes that have attracted the most intense interest in recent years, and both families include complexes of high nuclearity with beautiful architectures. Of relevance to this work are single-strand Cu^{II} wheels, which almost always contain an even number of metal atoms and are antiferromagnetically coupled with *S* = 0 ground states.^[7] Such molecules represent a rare amalgamation of high nuclearity and high magnetic symmetry, the latter referring to the (often) single type of M₂ (M = 3d-metal ion) pairwise exchange couplings that they contain. Thus, they represent excellent model systems for the study of 1D antiferromagnetism, magnetic anisotropy,^[8] and quantum effects such as coherent tunneling of the Néel vector.^[9] It was recently illustrated for the first time how crystals of Ga₁₀ and Ga₁₈ molecular wheels can be used as nanoporous materials to control diffusive transport of a gas on micrometer scales.^[10] The prototype wheels were [Cr₈F₈(O₂CtBu)₁₆]^[11] and [Fe(OMe)₂(O₂CCH₂Cl)]₁₀.^[12] and the largest known to date is [Ga₂₀(pd)₂₀(O₂CMe)₂₀] (H₂pd = propane-1,3-diol).^[13] Multiple-strand wheels are also known, which are built either from repeating metal cluster units or multiple-layer wheels. These include Ni₁₂,^[14] Mn₂₄,^[15] Mn₁₆,^[16] the giant

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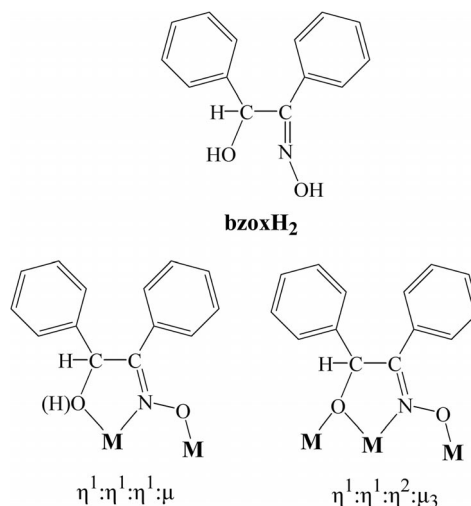
double-decker Mn_{32} ,^[17] and torus-shaped Mn_{84} ,^[5a] Mo_{154} ,^[18] and Mo_{176} ,^[18] most of these wheels possess large S values and are single-molecule magnets.^[5a,14–17]

Coordination polymers are significant from a structural chemistry viewpoint with new, intriguing molecular topologies being discovered, as well as providing numerous examples of interesting phenomena such as the interpenetration of networks.^[19] To date, scientists have realized various applications of coordination polymers in catalysis, electrical conductivity, luminescence, magnetism, nonlinear optics, molecular electronics, sensing, drug delivery, and zeolitic behavior.^[20] The ultimate goal is the transformation of coordination polymers to functional molecular materials. However, the factors that influence the synthesis of coordination polymers are still not completely understood and chemists are always looking for new methods that can lead to predictable products. The two main trends in the field are synthesis by design and nonprogrammed assembly. The former involves the use of rigid, often complicated organic ligands that force or drive the precipitation of the desired product. The latter approach involves the use of more flexible ligands and lacks control over the final product but has proven to be successful in the synthesis of polymeric compounds with interesting structures and properties.^[20,21]

There is a continuing need for new synthetic methods to prepare clusters and coordination polymers, and one approach is the development of new reaction systems using bridging organic ligands that can simultaneously chelate two or more metal ions. One attractive route is to use ligands that contain alkoxido^[22] or oximato^[23] functionalities as these are good bridging groups that can foster the formation of polynuclear or polymeric products. In addition, ancillary ligands such as carboxylates^[24] and/or pseudohalides (e.g. N_3^- , OCN^-)^[25] can either enhance aggregation, which favors the isolation of clusters, or act as linkers for polymer formation. Pseudohalides that bridge in the 1,1-mode (end-on) give ferromagnetic interactions for a wide range of $\text{M}-\text{N}-\text{M}$ angles,^[26] whereas the 1,3-bridging mode (end-to-end) usually promotes antiferromagnetic interactions and leads to multidimensional (1-, 2-, or 3D) coordination polymers.^[27] In Cu^{II} chemistry, for example, we have recently reported Cu^{II}_7 and Cu^{II}_4 clusters, and a unique 1D $(\text{Cu}^{\text{II}}_5)_n$ coordination polymer,^[28] which all bear the anion(s) of pyridine-2,6-dimethanol and acetato groups. Furthermore, the employment of various 2-pyridyl oximes in Cu^{II} carboxylate chemistry has afforded a large family of antiferromagnetically coupled triangular compounds that show antisymmetric exchange phenomena.^[29]

As an extension of this work, we have turned our attention to a new, mixed alkoxide–oximate ligand in 3d-metal cluster chemistry as a potential route to molecular and/or polymeric species with unprecedented structural motifs and interesting physical properties. The ligand chosen, α -benzoin oxime (bzoxH_2), is shown in Scheme 1. It has been sparingly employed in 3d-metal chemistry to yield Mn^{III}_9 ,^[30] Ni^{II}_8 , and Ni^{II}_6 ^[31] complexes. In this work, we have explored binary ($\text{bzoxH}_2/\text{PhCO}_2^-$) and ternary ($\text{bzoxH}_2/\text{PhCO}_2^-/\text{N}_3^-$) reaction schemes in Cu^{II} chemistry

with various solvents. Our systematic investigation has successfully led to a family of decanuclear clusters with a single-strand wheel topology, which bears the dianionic form of the ligand, bzox^{2-} , and a new 1D coordination polymer, which contains bridging benzoato and azido groups. The synthesis, structures, and magnetochemical characterization of the products are described here. A small portion of this work has been previously communicated.^[32]



Scheme 1. Structural formula of bzoxH_2 (top), and the crystallographically established coordination modes of its monoanion (bzoxH^-) and dianion (bzox^{2-}) in transition metal complexes (bottom).

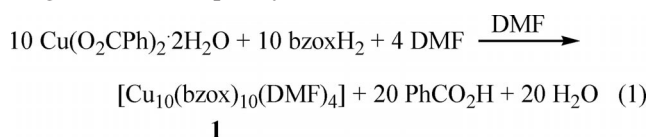
Results and Discussion

Syntheses and IR Spectra

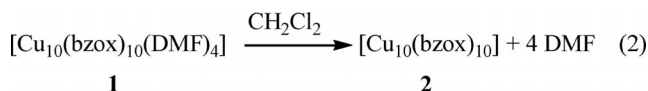
Many synthetic procedures^[33] for polynuclear 3d-metal clusters rely on the reactions of carboxylate starting materials with a potentially chelating/bridging ligand. In some cases, pseudohalides are also incorporated in the reaction mixtures to obtain magnetically interesting species, i.e. high-spin molecules and single-molecule magnets. From our previous work, this general route was also known to yield magnetically and structurally interesting Cu^{II} complexes upon reaction with various pyridyl alcohol ligands and pyridyl oximes and dioximes.^[28–33] In this study we have investigated the reactions of bzoxH_2 , a relatively unexplored alkoxide–oximate ligand, with a simple Cu^{II} carboxylate source, i.e. $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$, in various solvents and in the additional presence of azides. During our synthetic efforts, it was noticed that the addition of external base, e.g. NEt_3 , for the deprotonation of the alcohol and oxime groups of bzoxH_2 was unnecessary and yielded the same products in lower yields, which were occasionally contaminated with amorphous precipitates.

A variety of reactions were explored with different solvents, ratios, and other conditions before the successful procedures were identified. The reaction of $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$

with bzoxH_2 in a 1:1 molar ratio in *N,N*-dimethylformamide (DMF) gave a dark green solution and led to the subsequent isolation of well-formed dark green crystals of the benzoate-free complex $[\text{Cu}_{10}(\text{bzox})_{10}(\text{DMF})_4]$ (**1**) in good yield (ca. 45%). The deprotonation of bzoxH_2 was achieved solely by the PhCO_2^- groups and the formation of **1** is summarized in Equation (1). Small variations in the $\text{Cu}^{\text{II}}/\text{bzoxH}_2$ ratio also gave **1** but in lower yields. DMF was primarily chosen as the solvent to ensure that both solid reagents were completely dissolved.



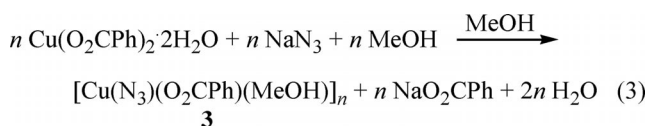
As **1** contains four coordinated DMF molecules (*vide infra*), we wondered if a solvent-free, structurally similar compound could exist. Such a species could be interesting from supramolecular and chemical reactivity viewpoints. To achieve this goal, we used nonpolar solvents with poorly coordinating donor atoms. Thus, dissolution of **1** in CH_2Cl_2 and layering the resulting green solution with Et_2O (Exp. Section, Method A) led to the subsequent isolation of dark green crystals of solvent-free $[\text{Cu}_{10}(\text{bzox})_{10}]$ (**2**) in good yield (ca. 35%). Its formation is summarized in Equation (2). Complex **2** can also be obtained in higher yield (ca. 60%) from the 1:1 reaction between $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ and bzoxH_2 in CH_2Cl_2 under reflux (Method B). The relatively high temperature employed was necessary to enhance the solubility of the starting materials and divert the equilibrium to product formation. Complex **2** can be converted into **1** by dissolution of the former in DMF.



With the identity of **1** and **2** established, and the dependence of the pronounced versatility of their terminal coordination sites on the solvent used (DMF molecules in **1** vs. none in **2**), we undertook the synthetic challenge to link the Cu_{10} wheels into multidimensional coordination polymers using azide ions. Several reactions between **2** and NaN_3 in various molar ratios and solvents were performed but all were unsuccessful and led to dark green, noncrystalline materials, which were not characterized. The addition of salts that contained bulky cations, e.g. Et_4N^+ or $n\text{Bu}_4\text{N}^+$, did not improve the situation. In contrast, the reaction of $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ with bzoxH_2 and NaN_3 in a 1:1:1 molar ratio in MeOH (see Exp. Section, Method A) gave a dark green solution, which led to the subsequent isolation of dark green crystals of the bzoxH_2 -free complex $[\text{Cu}(\text{N}_3)(\text{O}_2\text{CPh})(\text{MeOH})]_n$ (**3**) in low yield (ca. 15%) upon layering the reaction solution with Et_2O . In an attempt to isolate a $\text{Cu}^{\text{II}}/\text{PhCO}_2^-/\text{bzoxH}_2/\text{N}_3^-$ product, we repeated the reaction using different ratios of the reactants (1:2:1, 2:2:1, 1:4:1), however, all of our efforts led to polymeric **3** in even lower yields. It seems that there is a competition between $\text{N}_3^-/\text{PhCO}_2^-$ and bzoxH_2 for Cu^{II} coordination sites. It is likely

that the reaction solution contains several species in equilibrium, with factors such as concentration, relative solubility, lattice energy, crystallization kinetics, and others that determine the identity of the isolated products. In any case, the low yield of **3** cannot be explained easily.

With the identity of **3** established, a convenient high-yield synthesis of **3** was developed by omitting bzoxH_2 from the reaction. Thus, the 1:1 reaction between $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ and NaN_3 in MeOH under reflux gave **3** in ca. 80% yield (Method B). The straightforward formation of **3** is represented by Equation (3).



The use of MeOH as the reaction solvent was crucial for clean product formation; oily products were obtained when the reaction was performed in EtOH, DMF, or MeCN, whereas no significant reaction was observed in CH_2Cl_2 or CHCl_3 .

The IR spectra of vacuum-dried samples of **1** and **2** are similar and dominated by the stretching and deformation bands of the aromatic ring. The band at ca. 1115 cm^{-1} is tentatively assigned to the $\nu(\text{NO})$ vibration of the coordinated oximate groups. Moreover, the IR spectrum of **1** exhibits two very strong bands at 1670 and 696 cm^{-1} , which are assigned to the $\nu(\text{C}=\text{O})$ and $\delta(\text{OCN})$ vibrational modes of the coordinated DMF molecules, respectively.^[34] Upon coordination, the $\nu(\text{C}=\text{O})$ and $\delta(\text{OCN})$ bands are shifted to lower and higher wavenumbers, respectively, compared to the corresponding bands in the spectrum of free DMF.^[34] These bands are absent from the spectrum of **2** as expected.

The presence of a coordinated MeOH molecule in **3** is manifested by one broad band of medium intensity at 3426 cm^{-1} , assigned to $\nu(\text{OH})$; its broadness and relatively low frequency are indicative of hydrogen bonding.^[35] In the spectrum of **3**, the strong bands at 1532 and 1412 cm^{-1} are assigned to the $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ modes of the carboxylate groups, respectively. The difference, Δ [$\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$], is small (120 cm^{-1}) compared with the Δ value for NaO_2CPh (184 cm^{-1}), which is expected for the bidentate bridging PhCO_2^- group.^[36] The intense band at ca. 2090 cm^{-1} is assigned to the asymmetric stretching mode, $\nu_{\text{as}}(\text{NNN})$, of the end-on azide group.^[34,37]

Description of Structures

Complex $\text{1} \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$ crystallizes in the triclinic space group $P\bar{1}$, with the $[\text{Cu}_{10}(\text{bzox})_{10}(\text{DMF})_4]$ molecule in a general position. The structure of the molecule and a stereopair are shown in Figure 1, and a view of its core is presented in Figure 2. Selected interatomic distances and angles are listed in Table 1.

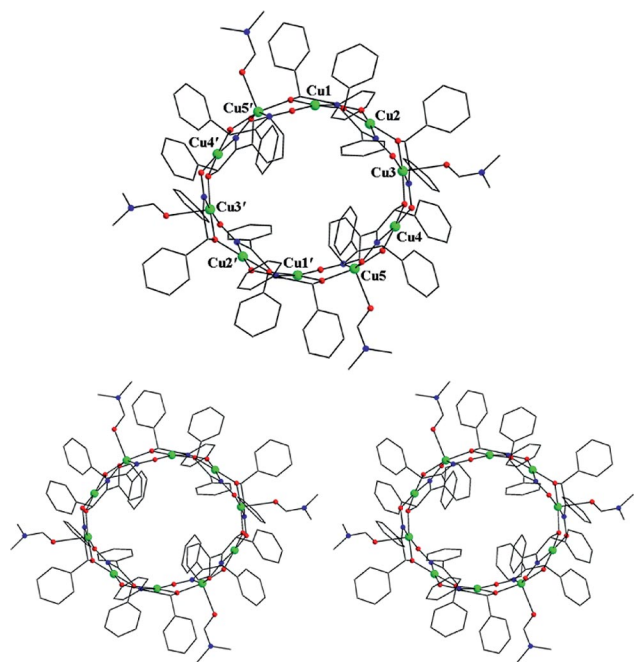


Figure 1. The molecular structure of **1** (top) and a stereopair (bottom). Hydrogen atoms are omitted for clarity. Color code: green Cu^{II}, red O, blue N, gray C.

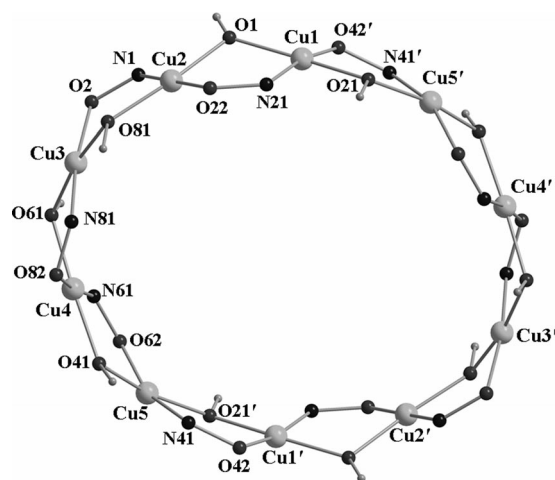


Figure 2. Labeled representation of the $[\text{Cu}_{10}(\mu\text{-ONR})_{10}(\mu\text{-OR}')_{10}]$ core of **1**.

The structure of **1** comprises ten Cu^{II} ions linked through the oximate N–O[−] and alkoxido RO[−] arms of ten bzoX^{2−} groups to form a puckered, single-strand wheel of crystallographic C_i symmetry (Figure 3). It can also be described as a low-symmetry Cu₁₀ loop, with the metal ions bridged by ten $\eta^1:\eta^1:\eta^2:\mu_3$ bzoX^{2−} groups, which lie above and below the Cu₁₀ plane (Scheme 1). Each bzoX^{2−} group chelates a Cu^{II} ion through its O_{alkoxido} and N_{oximate} atoms and bridges two adjacent Cu^{II} centers through its O_{alkoxido} atom and the oximate group. Ligation is completed by four terminal DMF molecules on Cu3, Cu3', Cu5, and Cu5'. The complex therefore contains a $[\text{Cu}_{10}(\mu\text{-ONR})_{10}(\mu\text{-OR}')_{10}]$ core (Figure 2), where RNO and R'O represent the bzoX^{2−} group.

Table 1. Selected interatomic distances [Å] and angles [°] for **1**·12DMF·2H₂O.^[a]

Cu1–O1	1.928(3)	Cu5–O101 ^[b]	2.343(3)
Cu1–O21	1.914(3)	Cu5–N41	1.981(4)
Cu1–O42'	1.902(3)	Cu1...Cu2	3.185(1)
Cu1–N21	1.959(3)	Cu2...Cu3	3.154(2)
Cu2–O1	1.910(3)	Cu3...Cu4	3.137(1)
Cu2–O22	1.897(3)	Cu4...Cu5	3.255(2)
Cu2–O81	1.902(3)	Cu5...Cu1'	3.269(2)
Cu2–N1	1.940(3)	Cu1–O1–Cu2	112.2(1)
Cu3–O2	1.935(3)	Cu2–O81–Cu3	111.2(1)
Cu3–O61	1.938(3)	Cu3–O61–Cu4	108.7(1)
Cu3–O81	1.921(3)	Cu4–O41–Cu5	115.1(1)
Cu3–O111 ^[b]	2.457(3)	Cu5–O21'–Cu1'	115.9(1)
Cu3–N81	1.958(3)	<i>Torsion angles</i>	
Cu4–O41	1.925(3)	Cu1–N21–O22–Cu2	12.2(4)
Cu4–O61	1.923(3)	Cu2–N1–O2–Cu3	17.3(4)
Cu4–O82	1.919(3)	Cu3–N81–O82–Cu4	25.4(3)
Cu4–N61	1.962(3)	Cu4–N61–O62–Cu5	10.6(4)
Cu5–O21'	1.944(3)	Cu5–N41–O42–Cu1'	14.0(4)
Cu5–O41	1.932(3)		
Cu5–O62	1.929(3)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation $2 - x, 1 - y, -z$. [b] O101 and O111 belong to the coordinated DMF molecules.

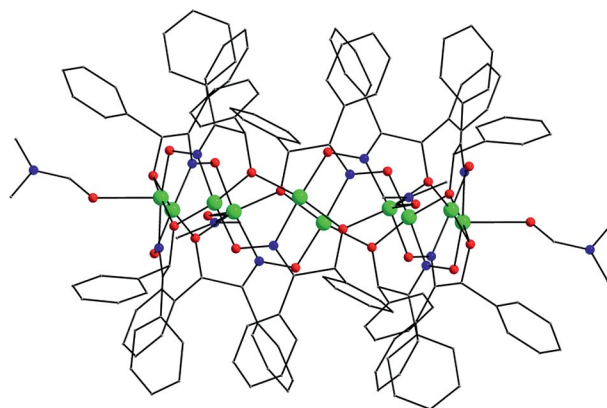


Figure 3. Side view that emphasizes the puckering of the Cu₁₀ wheel in **1**. Color scheme as in Figure 1.

Six Cu^{II} atoms (Cu1, Cu2, Cu4, Cu1', Cu2', Cu4') are four-coordinate with distorted square-planar geometry: the *cis* and *trans* angles lie in the 82.4–95.2 and 169.9–174.5° ranges, respectively, which deviate only slightly from the ideal values of 90 and 180°, respectively, of a square. This deviation is likely due to the formation of a single, five-membered chelating ring around each Cu^{II} ion, which gives rise to a nonsymmetric CuO₃N chromophore. The remaining four Cu^{II} ions (Cu3, Cu5, Cu3', Cu5') are five-coordinate with almost ideal square pyramidal geometry ($\tau = 0.03$ for Cu3 and 0.09 for Cu5, where τ is 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries,^[38] respectively). The coordinated DMF molecules occupy the apical positions, and the Cu^{II} ions lie 0.114 (Cu3) and 0.259 Å (Cu5) above the O₃N least-squares planes towards the apical donor atom. The bonds from Cu3 and Cu5 to the apical DMF oxygen atoms (O101, O111) are longer than those to basal donor atoms, as expected. The Cu...Cu

distances are within the 3.137–3.269 Å range, and the Cu–OR'–Cu angles and Cu–N–O–Cu torsion angles lie in the 108.7–115.9 and 10.6–25.4° ranges, respectively.

Complex **2**·8CH₂Cl₂·2Et₂O crystallizes in the monoclinic space group *P*₂₁/*n*. Selected interatomic distances and angles are listed in Table 2. The molecular structure of **2** (Figure 4) is very similar to that of **1**, the major difference is that all the Cu^{II} ions in **2** are four-coordinate with square-planar geometry; the *cis* and *trans* angles lie in the 82.2–96.0 and 166.5–172.9° ranges, respectively. The Cu···Cu separations range from 3.097–3.228 Å, which is slightly shorter than the corresponding range in **1**, and the Cu–OR'–Cu angles and the Cu–N–O–Cu torsion angles lie in the 106.9–117.0 and 2.9–27.4° ranges, respectively.

Table 2. Selected interatomic distances [Å] and angles [°] for **2**·8CH₂Cl₂·2Et₂O.^[a]

Cu1–O1	1.931(1)	Cu1···Cu2	3.228(1)
Cu1–O3	1.924(1)	Cu2···Cu3	3.228(2)
Cu1–O10'	1.909(1)	Cu3···Cu4	3.168(1)
Cu1–N1	1.954(2)	Cu4···Cu5	3.097(2)
Cu2–O2	1.898(1)	Cu5···Cu1'	3.142(1)
Cu2–O3	1.897(1)		
Cu2–O5	1.889(1)	Cu1–O3–Cu2	115.3(6)
Cu2–N2	1.953(2)	Cu2–O5–Cu3	117.0(6)
Cu3–O4	1.912(1)	Cu3–O7–Cu4	112.3(6)
Cu3–O5	1.897(1)	Cu4–O9–Cu5	106.9(6)
Cu3–O7	1.905(1)	Cu5–O1'–Cu1'	108.8(6)
Cu3–N3	1.964(2)		
Cu4–O6	1.907(1)	<i>Torsion angles</i>	
Cu4–O7	1.910(1)	Cu1–N1–O2–Cu2	13.4(2)
Cu4–O9	1.925(1)	Cu2–N2–O4–Cu3	2.9(2)
Cu4–N4	1.956(2)	Cu3–N3–O6–Cu4	5.4(2)
Cu5–O1'	1.933(1)	Cu4–N4–O8–Cu5	20.9(2)
Cu5–O8	1.915(1)	Cu5–N5–O10–Cu1'	27.4(2)
Cu5–O9	1.931(1)		
Cu5–N5	1.956(2)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation 2 – *x*, –*y*, 1 – *z*.

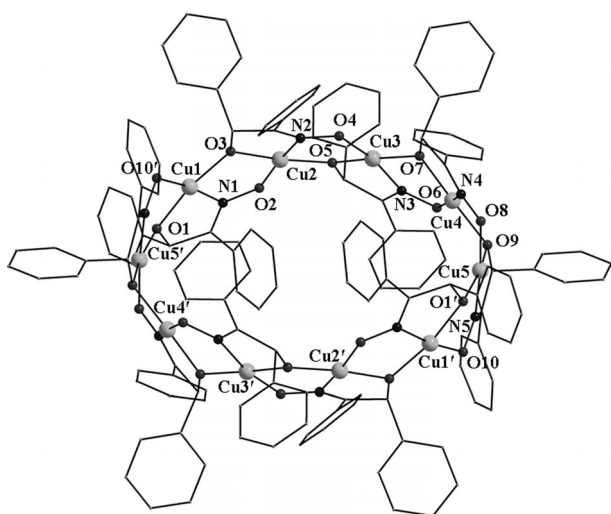


Figure 4. The molecular structure of **2**. Hydrogen atoms are omitted for clarity.

A space-filling representation (Figure 5, top) shows that **1** has a diameter of 23.5 Å, with a central hole of 3.4 Å

diameter defined by the shortest H···H distance; the corresponding values for **2** (Figure 5, bottom) are 23.4 and 3.3 Å, respectively. In **1**, a DMF molecule occupies the central hole of the wheel (Figure 5, top) to form a weak C–H···N hydrogen bond with N61 (N61···C171 3.256 Å). In contrast, **2** contains a disordered CH₂Cl₂ molecule at the center of the wheel, too disordered to be refined. Both wheels **1** and **2** stack to form nanotubular columns (Figure 6).

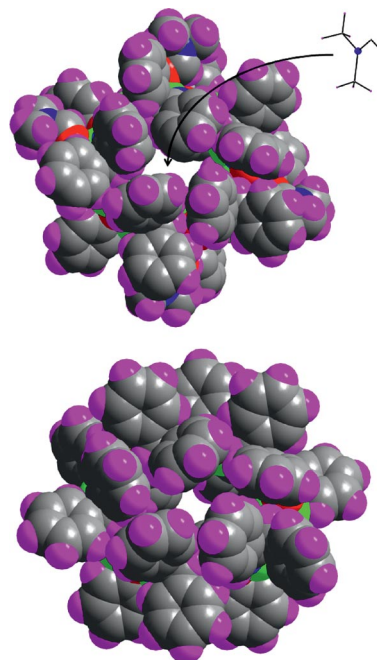


Figure 5. Space-filling representations of **1** (top) and **2** (bottom), which emphasize the position of the DMF molecule in the central cavity of **1**. Color code: green Cu^{II}, red O, blue N, gray C, purple H.

Complexes **1** and **2** join a small family of structurally characterized 3d-metal complexes that contain a form (neutral, mono- or dianionic) of the α -benzoin oxime ligand,^[30–32] and are the first in copper(II) coordination chemistry. The crystallographically confirmed coordination modes of bzoxH[–] and bzox^{2–} in the structurally characterized metal complexes to date are shown in Scheme 1. Complexes **1** and **2** also belong to a relatively undeveloped family of Cu^{II}₁₀ clusters of any structural type with O- and/or N-ligation.^[7c,39] Among these, **1** and **2** are the second and third examples of Cu^{II}₁₀ complexes with a single-strand wheel or loop conformation after [Cu^{II}CIL]₁₀ (L[–] = amino alkoxide),^[7c] and the first with mixed alkoxide/oximate ligation. Finally, **1** and **2** join only a handful of structurally characterized {Cu^{II}_{*x*}} (*x* = various) complexes with a wheel topology.^[7]

A partially labeled representation of **3** is shown in Figure 7. Selected interatomic distances and angles and details of hydrogen bonding are listed in Table 3.

Complex **3** crystallizes in the orthorhombic space group *P*₂₁2₁2₁. Its structure consists of neutral [Cu(N₃)(O₂–CPh)(MeOH)]_{*n*} chains that run along the *a* axis (Figure 7).

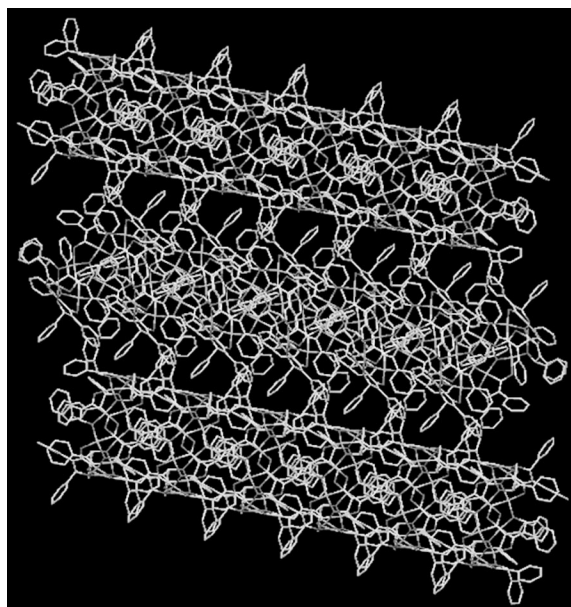


Figure 6. Wireframe representation of the Cu_{10} wheels in **2** and their supramolecular aggregation into ordered nanotubes (excluding H atoms).

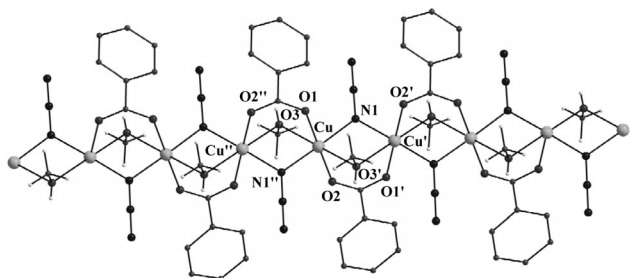


Figure 7. A plot of a portion of the 1D chain in **3**. The aromatic H atoms are omitted for clarity.

Table 3. Selected interatomic distances [Å] and angles [°] for **3**.^[a]

Cu–O1	1.949(3)	O1–Cu–N1''	89.5(1)
Cu–O2	1.948(3)	O2–Cu–O3	94.9(1)
Cu–O3	2.457(4)	O2–Cu–O3'	87.3(1)
Cu–O3'	2.425(4)	O2–Cu–N1	91.5(2)
Cu–N1	2.006(4)	O2–Cu–N1''	90.8(1)
Cu–N1''	1.996(4)	O3–Cu–O3'	177.7(1)
Cu–O3'–Cu'	80.8(1)	O3–Cu–N1	95.8(2)
Cu–N1–Cu'	104.5(2)	O3–Cu–N1''	84.3(2)
O1–Cu–O2	179.4(1)	O3'–Cu–N1	85.0(2)
O1–Cu–O3	85.6(1)	O3'–Cu–N1''	94.9(2)
O1–Cu–O3'	92.2(1)	N1–Cu–N1''	177.7(2)
O1–Cu–N1	88.2(1)		

[a] Singly and doubly primed atoms are related to the unprimed ones by the symmetry transformations: (') = $0.5 + x, 1.5 - y, 2 - z$; (')' = $-0.5 + x, 1.5 - y, 2 - z$.

Adjacent Cu^{II} ions are bridged by a single end-on N_3^- group, a *syn,syn*- $\eta^1:\eta^1:\mu$ PhCO_2^- ion, and an oxygen atom from the neutral bridging MeOH molecule. Thus, three different kinds of bridges are present. The $\text{Cu}\cdots\text{Cu}$ distance within the chain is 3.164(1) Å.

There is one crystallographically independent Cu^{II} ion in the asymmetric unit of **3**. Its coordination geometry is well described as Jahn–Teller distorted octahedral (4+2), with four short bonds formed by the two azido nitrogen atoms [Cu–N1 2.007(4), Cu–N1'' 1.996(4) Å] and two oxygen atoms from two symmetrically ligated PhCO_2^- ions [Cu–O1 1.949(3), Cu–O2 1.948(3) Å]. The equatorial bond angles are only slightly deviated from the ideal value of 90° . The axial coordination sites are occupied by the oxygen atoms from two bridging MeOH molecules, and the Cu–O3 and Cu–O3' bond lengths [2.457(4) and 2.425(4) Å, respectively] are significantly longer than the equatorial ones. Each Cu^{II} center therefore possesses a N_2O_4 chromophore.

Both end-on azido and carboxylato bridges can be considered symmetrical within the crystallographic 3σ criterion. These bridges, together with the bridging MeOH groups, adopt an alternating *all trans* arrangement throughout the chains. The azide ions are almost linear with an N1–N2–N3 angle of $178.3(6)^\circ$ and exhibit nonsymmetric N–N bond lengths. The N2–N3 distance [1.145(7) Å] is shorter than that of N1–N3 [1.211(6) Å].

Compound **3** is the second structurally characterized 1D copper(II) complex in which the Cu^{II} ions are *exclusively* bridged by one end-on $\mu_{1,1}$ N_3^- group, one $\eta^1:\eta^1:\mu$ carboxylato ligand, and one monoatomic bridge from a third ligand; the first such complex is $[\text{Cu}(\text{N}_3)(\text{L})(\text{DMSO})]_n$ ($\text{L}^- = 2$ -thiopheneacetato, DMSO = dimethyl sulfoxide).^[40] The combination of these three bridging ligands is also present in *alternating* 1D copper systems^[40,41] and in the 2D polymer $[\text{Cu}(\text{N}_3)(\text{tp})(\text{MeOH})]_n$, where tp^{2-} is the terephthalato

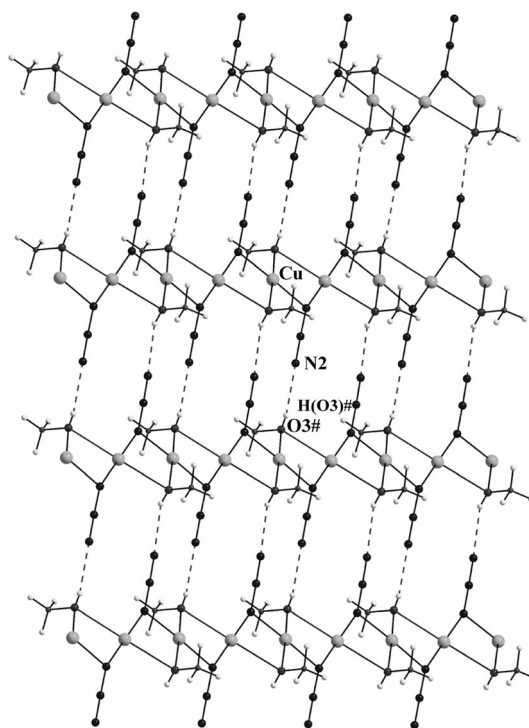


Figure 8. A view of the hydrogen bonding (dashed lines) between chains in **3** along the *c* axis. The benzoate groups are omitted for clarity.

(i.e. a dicarboxylate) ligand.^[42] The double (end-on azido)-($\eta^1:\eta^1:\mu$ -carboxylato) bridging system has also been found in copper(II) coordination polymers of various (1D, 2D, 3D) dimensionalities.^[43]

The 1D chains of **3** are hydrogen bonded into 2D sheets (Figure 8) through $N_{\text{azide}} \cdots H(O_{\text{MeOH}})$ interactions. The dimensions are: $O3\# \cdots N2$ 2.838(7) Å, $O3\#-H(O3\#) \cdots N2$ 158.1(6)° (symmetry code: $\# = 0.5 + x, 0.5 - y, 2 - z$). The closest interchain $\text{Cu} \cdots \text{Cu}$ separation is 7.432 Å.

Magnetochemistry

Solid-state, variable-temperature direct-current (dc) magnetic susceptibility (χ_M) data were collected from vacuum-dried microcrystalline samples of **1**·3DMF·2H₂O and **2**, suspended in eicosane to prevent torquing, in the 5.0–300 K range in a 0.1 T (1000 G) magnetic field. The data are plotted as $\chi_M T$ vs. T in Figure 9, and it can be seen that the overall magnetic response is similar but not identical for the two complexes. $\chi_M T$ at 300 K is 0.32 and 0.54 cm³ K mol^{−1} for **1**·3DMF·2H₂O and **2**, respectively, much lower than the value of 4.13 cm³ K mol^{−1} (calculated with $g = 2.1$) expected for a cluster of ten noninteracting Cu^{II} ions, which indicates the presence of strong antiferromagnetic exchange interactions.

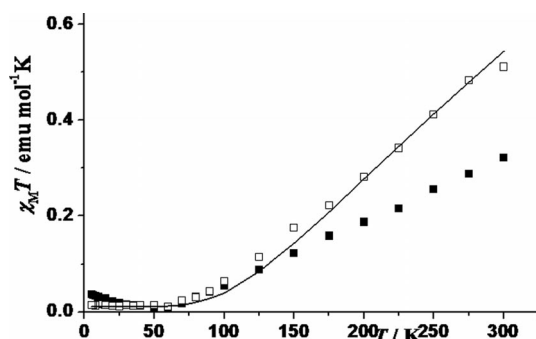


Figure 9. $\chi_M T$ vs. T plot for **1**·3DMF·2H₂O (■) and **2** (□) in the 5.0–300 K range. The solid line represents the best theoretical fit for **2** (see text).

For **1**·3DMF·2H₂O, $\chi_M T$ gradually decreases with decreasing temperature to a minimum of 0.02 cm³ K mol^{−1} at 30 K and then increases very slightly to 0.03 cm³ K mol^{−1} at 5 K. This suggests an $S = 0$ ground state, as expected for antiferromagnetic interactions between an even number of Cu^{II} ions in a single-strand wheel arrangement, and the small increase at the lowest temperature is indicative of a paramagnetic impurity that arises from polymeric Cu^{II} species. For **2**, $\chi_M T$ also decreases upon cooling, and drops to a value of 0.02 cm³ K mol^{−1} at 5 K, consistent with an $S = 0$ ground state with negligible evidence for paramagnetic impurities. The differences in the $\chi_M T$ values between **1**·3DMF·2H₂O and **2**, and consequently in the strength of the antiferromagnetic interactions, are likely due to a combination of the different Cu^{II} environments (combination of square pyramidal and square planar in **1** vs. square planar in **2**) and differences in the metric parameters (i.e. Cu–OR'–

Cu angles and Cu–N–O–Cu torsion angles), among others.^[44] The very small $\chi_M T$ values at 300 K (relative to that expected for ten noninteracting Cu^{II} atoms), particularly for **1**, indicate very strong antiferromagnetic coupling between the Cu^{II} atoms in both wheels even at room temperature.

Analysis of the magnetic data was attempted assuming only one J coupling constant for a ring of ten $S = 1/2$ spins with the CLUMAG program^[45] by applying the Hamiltonian in Equation (4).

$$H = -J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_5 + S_5 \cdot S_6 + S_6 \cdot S_7 + S_7 \cdot S_8 + S_8 \cdot S_9 + S_9 \cdot S_{10} + S_{10} \cdot S_1) \quad (4)$$

The very strong antiferromagnetic coupling present in **1** with a room temperature $\chi_M T$ value lower than 10% for ten noninteracting Cu^{II} centers makes the procedure extremely sensitive to the presence of small amounts of paramagnetic impurities and thus no satisfactory fit was achieved. As an approximation, a fit of the data for the highest T region (200–300 K) suggests a J value of ca. -850 cm^{−1}. In contrast, a good fit was obtained for the highly pure **2** with best-fit parameters of $J = -765$ cm^{−1} and $g = 2.085$. The data indicate that the double (alkoxido)(oximato) bridging system is an extremely strong antiferromagnetic coupler in Cu^{II} chemistry.

Variable-temperature dc magnetic susceptibility data for **3** were collected on a powdered sample of the compound in applied fields of 0.5 T (300–30 K) and 0.05 T (30–2.0 K) to avoid saturation effects. The room temperature $\chi_M T$ value for **3** is 0.49 cm³ K mol^{−1} per formula unit, which is larger than that expected for one isolated $S = 1/2$ spin (0.41 cm³ K mol^{−1} with $g = 2.1$). Upon cooling, the $\chi_M T$ value increases continuously to reach a value of 6.0 cm³ K mol^{−1} at 4 K (Figure 10). The room temperature value and the continuous increase of $\chi_M T$ with decreasing temperature suggest dominant ferromagnetic interactions in **3**.

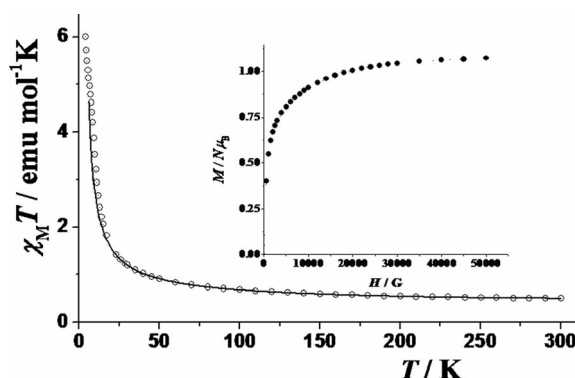


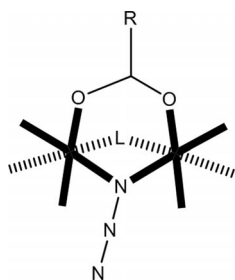
Figure 10. $\chi_M T$ vs. T plot for **3**. The solid line shows the best-fit of the experimental data (see text for fitting parameters). Inset: Magnetization (M) vs. field (H) plot for **3**.

Compound **3** shows a regular pattern of interactions along the 1D chain and thus, analysis of the magnetic data was performed according to the expansion series expression for an homogeneous chain^[46] derived from the Hamiltonian in Equation (5).

$$H = -J\sum_i(S_i \cdot S_{i+1}) \quad (5)$$

This Hamiltonian includes a zJ' interchain interaction term. Best-fit parameters were $J = +49.6(4) \text{ cm}^{-1}$, $g = 2.067(3)$, and $zJ' = 2.3(1) \text{ K}$. Isothermal magnetization at 2 K tends to a quasisaturated value of $N\beta$ equivalent to 1.06 electrons per copper center under the maximum field of 5 T (Figure 10, inset).

From the analysis of the structural data for **3** (Scheme 2) it is clear that the MeOH molecules link the axial coordination sites of the copper ions, and therefore the chain could be considered magnetically as an azido/carboxylato-bridged system. The net superexchange coupling constant of $+49.6(4) \text{ cm}^{-1}$ for **3** corresponds to the combined interactions due to the single *syn,syn* carboxylato and the end-on azido bridges. The single carboxylato bridge is expected to give moderately weak antiferromagnetic exchange,^[40,43a] whereas the small Cu–N–Cu angle of $104.5(2)^\circ$ is expected to lead to weak or moderate ferromagnetic exchange.^[40,43a] The magnetic properties of previously reported examples, which exhibit the copper environment shown in Scheme 2, show strong ferromagnetic coupling in all cases, regardless of the Cu–N_{azide}–Cu bond angles, which range from 105 to 131° .^[40–43] For such a superexchange pathway, molecular orbital calculations have pointed out the countercomplementary character of the superexchange pathways of the two bridging ligands, a feature that gives rise to or enhances the ferromagnetic response of the system even for the largest Cu–N_{azide}–Cu bond angle of 131° .^[43a,47] A few years ago, the experimental ferromagnetic character was studied by DFT calculations performed on copper/azide/carboxylate systems with a Cu–N_{azide}–Cu bond angle of 103.2° (calculated $J = 89 \text{ cm}^{-1}$) and a relatively large bond angle of 116.1° (calculated $J = 70 \text{ cm}^{-1}$).^[41a]



Scheme 2. Coordination environment of a Cu^{II} ion in a triply bridged N₃[−]/RCO₂[−]/L (L = neutral ligand) system where the axial bonds exclusively involve the monoatomic bridge of L. L does not contribute to the magnetic exchange interactions.

Conclusions

The combined use of α -benzoin oxime (bzoxH₂), benzoates, and/or azides in copper(II) chemistry has afforded two new Cu₁₀ molecular wheels and an 1D coordination polymer. [Cu₁₀(bzox)₁₀(DMF)₄] (**1**) and [Cu₁₀(bzox)₁₀] (**2**) contain the bridging dianion of bzox^{2−} with (**1**) or without (**2**) terminal solvate molecules. Wheels **1** and **2** stack to form nanotubular columns with interesting supramolecular

architectures. However, when azides were employed in the reaction mixtures that afforded **1** and **2**, the bzoxH₂-free complex [Cu(N₃)(O₂CPh)(MeOH)]_n (**3**) was obtained. Compound **3** is a 1D chain, in which the Cu^{II} atoms are linked by a single, end-on N₃[−] group, a *syn,syn*- $\eta^1:\eta^1:\mu$ PhCO₂[−] ion, and one monoatomic bridge from a neutral MeOH molecule. The magnetic data for **1** and **2** indicate strong antiferromagnetic exchange interactions and a $S = 0$ ground state, which is expected for even-membered loop arrays of Cu^{II} atoms. In contrast, **3** exhibits ferromagnetic exchange interactions due to the presence of end-on azido ligands with the contribution of countercomplementarity of the superexchange pathways. We anticipate a variety of new 3d-metal clusters and coordination polymers of different nuclearities and dimensionalities from the employment of various ligand combinations that involve bzoxH₂, carboxylates, and/or pseudohalides. Further work is in progress.

Experimental Section

Materials and Physical Measurements: All manipulations were performed under aerobic conditions using chemicals and solvents as received, unless otherwise stated. Cu(O₂CPh)₂·2H₂O was prepared as described elsewhere.^[48]

CAUTION: Azide salts are potentially explosive. Such compounds should be synthesized and used in small quantities and treated with utmost care at all times.

IR spectra were recorded from KBr pellets with a Nicolet Nexus 670 FTIR spectrometer in the 400–4000 cm^{−1} range. Elemental analyses (C, H, N) were performed in-house at the University of Florida Chemistry Department. Variable-temperature dc magnetic susceptibility data for **1** and **2** were collected with a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet operating in the 1.8–300 K range. Variable-temperature magnetic studies for **3** were performed with a DSM5 Quantum Design SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. Samples were embedded in eicosane to prevent torquing. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities (χ_M).

[Cu₁₀(bzox)₁₀(DMF)₄] (1**):** To a stirred solution of bzoxH₂ (0.23 g, 1.0 mmol) in DMF (30 mL) was added solid Cu(O₂CPh)₂·2H₂O (0.35 g, 1.0 mmol). The resulting dark green solution was stirred for 30 min, filtered, and the filtrate was left to evaporate slowly at room temperature. After 10 d, X-ray quality, dark green crystals of **1**·12DMF·2H₂O (0.16 g, 45%) were collected by filtration, washed with cold DMF (2 × 3 mL) and Et₂O (2 × 5 mL), and dried under vacuum over silica gel. **1**·3DMF·2H₂O: C₁₆₁H₁₆₃Cu₁₀N₁₇O₂₉ (3435.69); calcd. C 56.29, H 4.78, N 6.93; found C 56.15, H 4.62, N 7.07. IR (KBr): $\tilde{\nu} = 3460$ (m br.), 2924 (m), 1670 (vs), 1492 (s), 1442 (m), 1406 (m), 1384 (m), 1254 (m), 1190 (w), 1118 (m), 1090 (vs), 1038 (m), 1016 (s), 918 (w), 844 (s), 792 (w), 744 (s), 696 (vs), 658 (s), 618 (w), 596 (m), 562 (w), 504 (m), 466 (w) cm^{−1}.

[Cu₁₀(bzox)₁₀] (2**). Method A:** Solid **1**·3DMF·2H₂O (1.72 g, 0.5 mmol) was dissolved in CH₂Cl₂ (30 mL) to give a green solution. The solution was filtered, and Et₂O (60 mL) was allowed to slowly diffuse into the filtrate over a period of 2 d, during which time green crystals of **2**·8CH₂Cl₂·2Et₂O grew. The crystals were maintained in the mother liquor for X-ray crystallography and

other single-crystal studies, or collected by filtration, washed with CH_2Cl_2 (2×3 mL) and Et_2O (2×2 mL), and dried in air to give solvent-free **2** (0.51 g, 35%). $\text{C}_{140}\text{H}_{110}\text{Cu}_{10}\text{N}_{10}\text{O}_{20}$ (2887.99): calcd. C 58.23, H 3.84, N 4.85; found C 58.02, H 3.76, N 4.97. IR (KBr): $\tilde{\nu} = 2920$ (m), 1497 (s), 1440 (m), 1401 (m), 1390 (m), 1251 (m), 1184 (w), 1111 (m), 1093 (vs), 1045 (m), 1020 (s), 924 (w), 850 (s), 790 (w), 747 (s), 714 (vs), 667 (s), 617 (w), 600 (m), 557 (w), 500 (m), 461 (w) cm^{-1} .

Method B: To a stirred solution of bzoxH_2 (0.23 g, 1.0 mmol) in CH_2Cl_2 (30 mL) was added solid $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ (0.35 g, 1.0 mmol). The resulting blue slurry was heated to reflux for 1 h, during which time the solid dissolved and solution turned green. Layering of the solution with Et_2O (60 mL) gave green crystals of $2 \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$ after 6 d. The crystals were collected by filtration, washed with CH_2Cl_2 (2×3 mL) and Et_2O (2×2 mL), and dried in air; the yield was 60% (0.17 g). The dried solid analyzed satisfactorily as solvent-free. The identity of the product was confirmed by elemental analysis and IR spectral comparison with the authentic sample prepared according to Method A.

[Cu(N₃)(O₂CPh)(MeOH)]_n (3**). Method A:** To a stirred solution of bzoxH_2 (0.23 g, 1.0 mmol) in MeOH (30 mL) was added solid NaN_3 (0.07 g, 1.0 mmol). The mixture was stirred for 15 min before solid $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ (0.35 g, 1.0 mmol) was added with vigorous stirring, which caused a rapid color change from blue to dark green. The resulting solution was stirred for a further 1 h, filtered, and the filtrate was layered with Et_2O (60 mL). After 20 d, X-ray quality, dark green crystals of **3** were collected by filtration, washed with cold MeOH (2×5 mL) and Et_2O (2×5 mL), and dried in air to give **3** (0.04 g, 15%). $\text{C}_8\text{H}_9\text{CuN}_3\text{O}_3$ (258.73): calcd. C 37.14, H 3.51, N 16.24; found C 37.32, H 3.66, N 16.12. IR (KBr): $\tilde{\nu} = 3426$ (m br.), 2094 (vs), 1592 (m), 1532 (vs), 1412 (s), 1266 (w), 1176 (w), 1090 (w), 1052 (w), 1003 (w), 720 (m), 686 (m), 502 (w), 450 (w) cm^{-1} .

Method B: To a stirred solution of NaN_3 (0.07 g, 1.0 mmol) in MeOH (30 mL) was added solid $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ (0.35 g, 1.0 mmol). The resulting blue slurry was heated to reflux for 1 h,

during which time the solid dissolved and the solution turned dark green. Layering of the solution with Et_2O (60 mL) gave dark green crystals of **3** after 2 d. The crystals were collected by filtration, washed with cold MeOH (2×5 mL) and Et_2O (2×5 mL), and dried in air to give **3** (0.21 g, 80%). The identity of the product was confirmed by elemental analysis and IR spectral comparison with the authentic sample prepared according to Method A.

X-ray Crystallography and Structure Solution: Suitable crystals of $1 \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$, $2 \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$, and **3** were attached to glass fibers using silicone grease and transferred to a goniostat where they were cooled to 180, 173, and 293 K, respectively, for data collection. An initial search of reciprocal space revealed a triclinic cell for $1 \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$, a monoclinic cell for $2 \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$, and an orthorhombic cell for **3**; the choice of space groups $P\bar{1}$, $P2_1/n$, and $P2_12_12_1$, respectively, was confirmed by the subsequent solution and refinement of the structures. Data for $1 \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$ and **3** were collected with a Rigaku R-Axis SPIDER Image Plate diffractometer using graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178$ Å). Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11^\circ < 2\theta < 23^\circ$. Intensity data were recorded using a θ - 2θ scan to a maximum 2θ value of 130° . Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization, and psi-scan absorption corrections were applied using CrystalClear^[52] software. Both structures were solved by direct methods using SHELXS-97^[49a] and refined on F^2 by full-matrix least-squares techniques with SHELXL-97.^[49b] All H atoms were either located by Fourier difference maps and refined isotropically or were introduced at calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically. Data for $2 \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$ were collected with a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability

Table 4. Crystallographic data for $1 \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$, $2 \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$, and **3**.

	$1 \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$	$2 \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$	3
Formula ^[a]	$\text{C}_{188}\text{H}_{226}\text{Cu}_{10}\text{N}_{26}\text{O}_{38}$	$\text{C}_{156}\text{H}_{146}\text{Cu}_{10}\text{Cl}_{16}\text{N}_{10}\text{O}_{22}$	$\text{C}_2\text{H}_{2.25}\text{Cu}_{0.25}\text{N}_{0.75}\text{O}_{0.75}$
M [g mol^{-1}] ^[a]	4093.35	3715.43	64.68
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a [Å]	17.6557(3)	16.9401(11)	6.3252(2)
b [Å]	17.9324(3)	27.9757(18)	7.4324(1)
c [Å]	18.0189(3)	16.9907(11)	22.3233(5)
α [°]	67.520(1)	90	90
β [°]	85.575(1)	91.464(1)	90
γ [°]	65.977(1)	90	90
V [Å ³]	4793.97(14)	8049.5(9)	1049.45(4)
Z	1	2	16
T [K]	180(2)	173(2)	293(2)
λ [Å] ^[b]	1.54178	0.71073	1.54178
ρ_{calc} [g cm^{-3}]	1.418	1.533	1.637
μ [mm^{-1}]	1.831	1.626	2.907
Measured/independent (R_{int}); reflections	64502/15688; (0.0753)	53932/18359; (0.0297)	3823/1725; (0.0415)
Observed reflections $I > 2\sigma(I)$	13346	14412	1428
R_1 ^[c,d]	0.0765	0.0324	0.0493
wR_2 ^[e]	0.1892	0.0765	0.1125
GOF on F^2	1.067	1.009	1.107
$(\Delta\rho)_{\text{max, min}}$ [e Å^{-3}]	0.858, −0.818	0.356, −0.280	0.590, −0.594

[a] Including solvate molecules. [b] Graphite monochromator. [c] $I > 2\sigma(I)$. [d] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [e] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

(maximum correction on I was $< 1\%$). Absorption corrections by integration were applied based on measured indexed crystal faces. The structure was solved by direct methods in SHELXTL6,^[50] and refined on F^2 using full-matrix least-squares. The non-H atoms were treated anisotropically, whereas the H atoms were placed in calculated, ideal positions and refined as riding on their respective C atoms. The asymmetric unit of $\mathbf{1} \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$ consists of half of the Cu_{10} cluster, six DMF molecules, and one H_2O molecule of crystallization. None of the water protons could be located in difference Fourier maps and thus were not included in the final refinements. A total of 1378 parameters were refined in the final cycle of refinement using 13346 reflections with $I > 2\sigma(I)$. For $\mathbf{2} \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$, the asymmetric unit also contains the half of the Cu_{10} cluster with four CH_2Cl_2 molecules and one Et_2O molecule of crystallization. All solvent molecules were disordered and could not be modeled properly, thus the SQUEEZE^[51] program was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. It is important to note that one of the disordered CH_2Cl_2 molecules was located at the center of the Cu_{10} wheel cluster. A total of 811 parameters were refined in the final cycle of refinement using 14412 reflections with $I > 2\sigma(I)$. The asymmetric unit of $\mathbf{3}$ contains the one-quarter of the repeating, mononuclear Cu unit, and no solvent of crystallization. A total of 157 parameters were refined in the final cycle of refinement using 1428 reflections with $I > 2\sigma(I)$. Unit cell parameters and structure solution and refinement data for all three complexes are listed in Table 4.

CCDC-717731 (for $\mathbf{1} \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$), -717732 (for $\mathbf{2} \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$), and -839085 (for $\mathbf{3}$) 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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