

Initial employment of α -benzoin oxime as a route to high-nuclearity metal clusters: decanuclear Cu^{II} complexes with a wheel topology†

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Received 30th January 2009, Accepted 5th March 2009

First published as an Advance Article on the web 17th March 2009

DOI: 10.1039/b901990a

The initial employment of α -benzoin oxime (bzoXH_2) in metal cluster chemistry has provided access to a new family of decanuclear Cu^{II} complexes with a loop or single-strand wheel topology; the $\text{Cu}^{\text{II}}_{10}$ clusters are antiferromagnetically-coupled with an $S = 0$ spin ground state, as expected for even-membered loop arrays of Cu^{II} atoms.

Molecular 3d-metal cluster chemistry has been attracting intense interest during the last two decades.¹ Among the diverse reasons for this are (i) the aesthetically pleasing structures that many such molecular clusters possess,² and (ii) the search for models of metallosites in biology³ and compounds with interesting magnetic properties.⁴ There is thus a continuing need for new synthetic methods to such molecules, and one approach is the development of new reaction systems using chelating organic ligands. One attractive approach is to use chelates containing alkoxide⁵ or oximate⁶ functionalities since these are good bridging groups that can foster formation of polynuclear products. Indeed, alkoxide-based ligands such as pyridyl alcohols,⁷ diols⁸ and triols,⁹ and oximates such as 2-pyridyl oximes,^{6b,10} R-substituted salicylaldoximes¹¹ and dioximes,¹² have yielded a number of 3d metal clusters with various structural motifs and interesting magnetic properties. For example, we have recently reported $\text{Mn}^{\text{II/III}}_{10}$,^{7c} and $\text{Mn}^{\text{II,III,IV}}_{25}$ ^{7a} cages bearing 2-pyridyl alkoxides and possessing large ground state spin values of 44/2 and 61/2, respectively, as well as the initial examples of triangular Mn^{III} single-molecule magnets⁴ from the use of various 2-pyridyl oximes.^{10a,b}

As an extension to this work, we are now employing a new, mixed alkoxide-oximate ligand in 3d-metal cluster chemistry as a potentially new route to high nuclearity molecular species with unprecedented structural motifs. The molecule chosen, α -benzoin oxime (bzoXH_2), is shown in Chart 1. This has never previously been employed in 3d-metal chemistry, only once in Mo chemistry,¹³ and we therefore investigated its use initially in Cu^{II} cluster chemistry. We herein report that the $\text{Cu}^{\text{II}}/\text{bzoXH}_2/\text{PhCO}_2^-$ reaction system has provided access to a new family of decanuclear clusters with a loop or single-strand wheel structure, containing the dianionic form of the ligand, bzoX^{2-} . We believe this compound

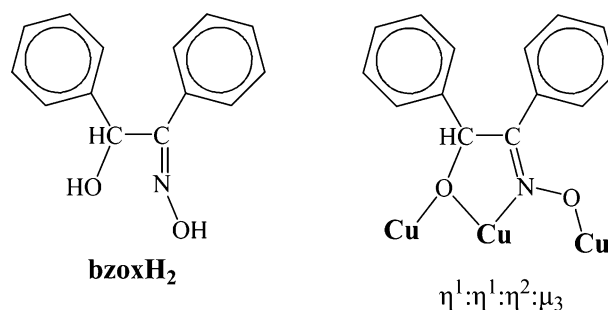


Chart 1 Structural formula and abbreviation of α -benzoin oxime (left) and the crystallographically established coordination mode of its dianion (bzoX^{2-}) in complexes **1** and **2** (right).

is the prototype of a rich new area of high nuclearity metal clusters derived from the amalgamation of oximate/alkoxide groups within the same ligand.

The reaction of $\text{Cu}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ and bzoXH_2 in a 1 : 1 molar ratio in dimethylformamide (DMF) gave a dark green solution that upon slow evaporation at room temperature for several days gave dark green crystals of $[\text{Cu}_{10}(\text{bzoX})_{10}(\text{DMF})_4] \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$ ($1 \cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$) in 45% yield.‡ Dissolution of **1** $\cdot 12\text{DMF} \cdot 2\text{H}_2\text{O}$ in CH_2Cl_2 , and layering of the resulting green solution with Et_2O , gave green crystals of the DMF-free $[\text{Cu}_{10}(\text{bzoX})_{10}] \cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$ (**2** $\cdot 8\text{CH}_2\text{Cl}_2 \cdot 2\text{Et}_2\text{O}$) complex in 35% yield.‡

The structure§ of **1** (Fig. 1, top) comprises ten Cu^{II} ions linked through the oximate $\text{N}-\text{O}^-$ and alkoxide RO^- arms of ten bzoX^{2-} groups to form a puckered (Fig. S1 in ESI†), single-strand wheel of crystallographic C_{10} symmetry. It can be alternatively described as a low-symmetry Cu_{10} loop, with the metal ions bridged by ten $\eta^1:\eta^1:\eta^2:\mu_3$ bzoX^{2-} groups (Chart 1); the latter alternate above and below the Cu_{10} plane. The complex thus contains a $[\text{Cu}_{10}(\mu\text{-ON})_{10}(\mu\text{-OR})_{10}]$ core (Fig. 1, bottom). Six Cu^{II} atoms ($\text{Cu}1, \text{Cu}2, \text{Cu}4, \text{Cu}1', \text{Cu}2', \text{Cu}4'$) 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, deviating only slightly from the 90° and 180° values, respectively, of an ideal square plane. The remaining four Cu^{II} atoms ($\text{Cu}3, \text{Cu}5, \text{Cu}3', \text{Cu}5'$) are five-coordinate with almost ideal square pyramidal geometry ($\tau = 0.03$ and 0.09, where τ is 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries,¹⁴ respectively); the coordinated DMF molecules occupy the apical positions, while the Cu^{II} atoms lie 0.114 ($\text{Cu}3$) and 0.259 Å ($\text{Cu}5$) above the O_3N least-squares planes. The $\text{Cu} \cdots \text{Cu}$ distances are within the 3.137–3.269 Å range, whereas the $\text{Cu}-\text{OR}-\text{Cu}$ angles and the $\text{Cu}-\text{O}-\text{N}-\text{Cu}$ torsion angles lie in the 108.9–115.9 and 10.4–25.2° ranges, respectively.

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† Electronic supplementary information (ESI) available: Additional molecular structures. CCDC reference numbers 717731 and 717732. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901990a

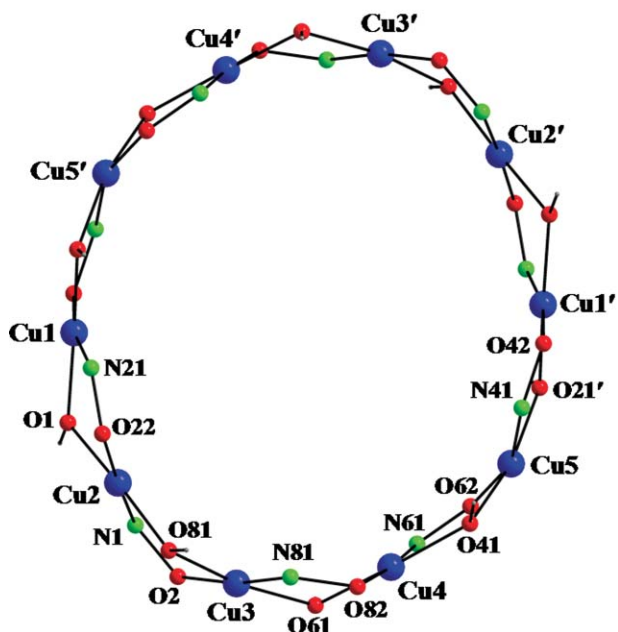
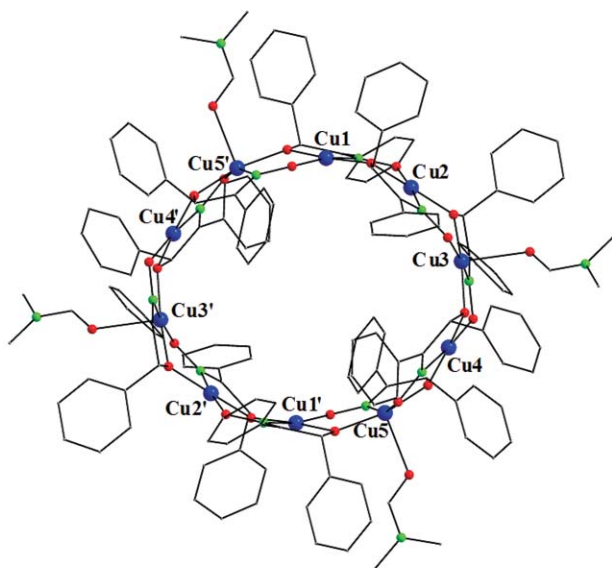


Fig. 1 The structure of the Cu_{10} wheel **1**: (top) the complete molecule with Cu atom labels; (bottom) the labelled $[\text{Cu}_{10}(\mu\text{-ON})_{10}(\mu\text{-OR})_{10}]$ core. Hydrogen atoms have been omitted for clarity. Colour code: Cu blue, O red, N green, C grey.

The structure of **2** (Fig. S2 in ESI[†]) is very similar to that of **1**, with the major difference being 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 $\text{Cu}\cdots\text{Cu}$ separations span the range 3.097–3.228 Å, slightly shorter than the corresponding values found in complex **1**, while the $\text{Cu}\text{-OR}\text{-Cu}$ angles and the $\text{Cu}\text{-O}\text{-N}\text{-Cu}$ torsion angles lie in the 106.9–117.0 and 2.9–27.4° ranges, respectively.

A space-filling representation (Fig. 2, top) shows that **1** has a diameter of 23.5 Å, with a central hole of 3.4 Å diameter defined by the shortest $\text{H}\cdots\text{H}$ distance; the corresponding values for **2** (Fig. S3 in ESI[†]) are 23.4 Å and 3.3 Å, respectively. In complex **1**, there is a DMF molecule occupying the central hole of the

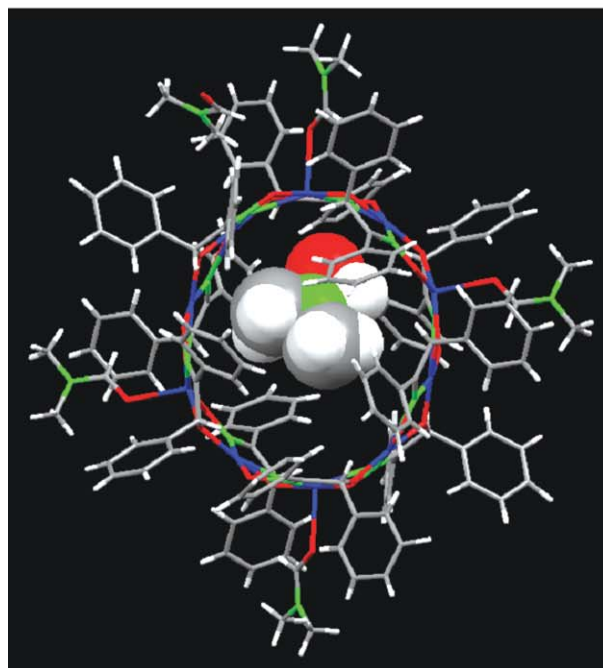
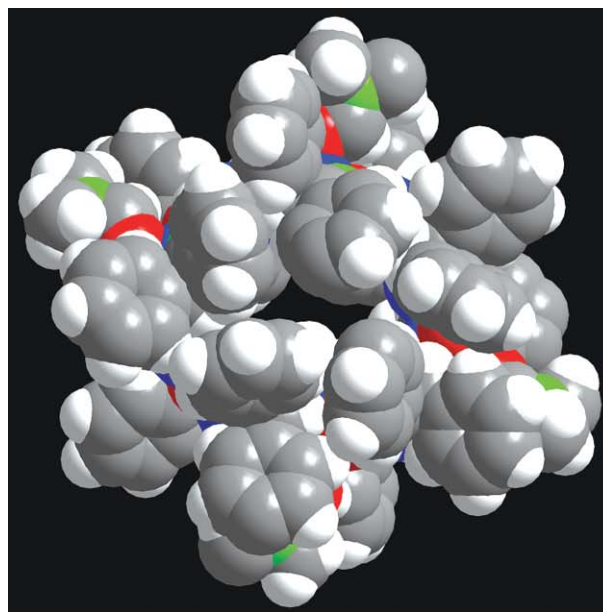


Fig. 2 (top) A space-filling representation of **1**; (bottom) wireframe representation of **1** showing the DMF molecule in the central cavity as a space-filling representation. Colour code: Cu blue, O red, N green, C grey, H white.

wheel (Fig. 2, bottom), forming a weak $\text{C}\text{-H}\cdots\text{N}$ hydrogen-bond with N61 ($\text{N61}\cdots\text{C171} = 3.256$ Å). In contrast, complex **2** contains a disordered CH_2Cl_2 molecule at the center of the wheel, too disordered to be refined. Both wheels **1** and **2** stack to form nanotubular columns.

Complexes **1** and **2** are the first structurally characterized 3d-metal complexes to contain any form (neutral, mono- or dianionic) of the α -benzooin oxime ligand, and join only a very small family of $\text{Cu}^{\text{II}}_{10}$ clusters of any structural type with O- or/and N-ligation.¹⁵ 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 the [Cu^{II}CIL]₁₀ (L⁻ is an amino alkoxide ligand) wheel from the Reedijk group,^{15b} and the first ones with a mixed alkoxide/oximate ligation. Note that wheel complexes are of interest for reasons other than just structural aesthetics: for example, even-membered, antiferromagnetic wheels of paramagnetic 3d metal atoms represent model systems for studying one-dimensional antiferromagnetism, magnetic anisotropy, and quantum effects such as coherent tunnelling of the Néel vector.¹⁶ Complexes **1** and **2** join only a handful of structurally characterized {Cu^{II}_x} (x = various) complexes with a wheel topology.^{15b,17}

The solid-state dc magnetic susceptibilities (χ_M) of 1·3DMF·2H₂O and **2** were measured in the 5.0–300 K range in a 1 kG (0.1 T) field, and they are plotted as $\chi_M T$ vs. T in Fig. 3. $\chi_M T$ at 300 K is 0.32 and 0.78 cm³ K mol⁻¹ for 1·3DMF·2H₂O and **2**, respectively, much lower than the 4.13 cm³ K mol⁻¹ value (calculated with $g = 2.1$) expected for a cluster of 10 non-interacting Cu^{II} ions, indicating the presence of strong antiferromagnetic exchange interactions. For 1·3DMF·2H₂O, $\chi_M T$ gradually decreases with decreasing T 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 indicates an $S = 0$ ground state, as expected for antiferromagnetic interactions between an even number of Cu^{II} ions in a single-strand wheel arrangement,^{15b,17} while the small increase at the lowest temperatures is indicative of a paramagnetic impurity arising from monomeric Cu^{II} species. For the solvent-free complex **2**, $\chi_M T$ also decreases upon cooling, dropping to a value of 0.02 cm³ K mol⁻¹ at 5 K, consistent with an $S = 0$ ground state and negligible signs of 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, should derive from a combination of the different Cu^{II} environments and differences in the metric parameters (*i.e.* Cu–OR–Cu angles and Cu–O–N–Cu torsion angles), among others. Fitting of the $\chi_M T$ vs. T data, as well as detailed DFT studies, are required to make conclusions about the exact strength of the constituent exchange parameters, J . This work is in progress and the results will be reported in an upcoming full paper. Note, however, that the very small $\chi_M T$ values at 300 K (relative to that expected for 10 non-interacting Cu^{II} atoms), particularly for **1**, indicate very strong antiferromagnetic interactions between the Cu^{II} atoms in these wheels.

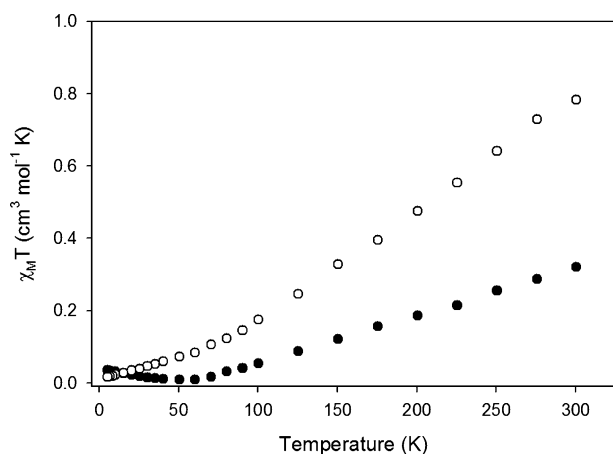


Fig. 3 Plot of $\chi_M T$ vs. T for complexes 1·3DMF·2H₂O (●) and **2** (○).

In conclusion, the initial use of α -benzoin oxime (bzoxH₂) in 3d-metal chemistry has afforded a beautiful new family of decametallate Cu^{II} clusters with a single-strand wheel or loop topology. These prototype products suggest that reactions of this ligand with other paramagnetic metal ions promises to deliver many new and exciting clusters.

Acknowledgements

This work was supported by the National Science Foundation (CHE-0414555 to G.C.), and the Operational and Vocational Training II (EPEAEK II) and particularly the program PYTHAGORAS (Grant b.365.037 to S.P.P.).

Notes and references

‡ Vacuum-dried samples of both compounds analysed as 1·3DMF·2H₂O and **2**. Calcd. (found) for 1·3DMF·2H₂O: C, 56.29 (56.15); H, 4.78 (4.62); N, 6.93 (7.07%). Calcd. (found) for **2**: C, 58.23 (58.02); H, 3.84 (3.76); N, 4.85 (4.97%).

§ Crystal data for 1·12DMF·2H₂O: C₁₈₈H₂₂₆Cu₁₀N₂₆O₃₈, $M_w = 4093.35$, triclinic, space group $P\bar{1}$ with $a = 17.6557(3)$, $b = 17.9324(3)$, $c = 18.0189(3)$ Å, $\alpha = 67.520(1)$, $\beta = 85.575(1)$, $\gamma = 65.977(1)^\circ$, $V = 4793.97(14)$ Å³, $T = 180(2)$ K, $Z = 1$, $D_c = 1.418$ g cm⁻³, 64 335 reflections collected, 15 673 unique ($R_{int} = 0.0754$), $R1 [I > 2\sigma(I)] = 0.0765$, $wR_2 = 0.2178$ (F^2 , all data). Crystal data for 2·8CH₂Cl₂·2Et₂O: C₁₃₆H₁₄₆Cu₁₀Cl₁₆N₁₀O₂₂, $M_w = 3715.43$, monoclinic, space group $P2_1/n$ with $a = 16.940(1)$, $b = 27.976(2)$, $c = 16.991(1)$ Å, $\beta = 91.464(1)^\circ$, $V = 8049.5(9)$ Å³, $T = 173(2)$ K, $Z = 2$, $D_c = 1.533$ g cm⁻³, 53 932 reflections collected, 18 359 unique ($R_{int} = 0.0753$), $R1 [I > 2\sigma(I)] = 0.0297$, $wR_2 = 0.0765$ (F^2 , all data). CCDC 717731 and 717732. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b901990a

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