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Eicosanuclear Cluster [$Cu_{13}W_7$] of Copper-Octacyanotungstate Bimetallic Assembly: Synthesis, Structure, and Magnetic Properties

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Octacyanotungstate(V) reacts with $Cu(NO_3)_2 \cdot 2H_2O$ and 1,4,7-trimethyl-1,4,7-triazacyclononane in methanol, resulting in an eicosanuclear cluster [$Cu_{13}W_7$], which shows a diamondoid shape with a Tolkowsky cut and bears intracluster ferromagnetic coupling.

In the past few years, cyanide-bridged bimetallic systems have attracted special attention in the field of molecular magnetism because cyanide is an efficient linear bridge mediating strong magnetic coupling interaction between spin carriers.[1] Many recently reported works indicate that the octacyanometalate group, $[M^{IV(V)}(CN)_8]^{4-(3-)}$ (M = Mo and W), is a very promising building block for the design and synthesis of molecule-based magnets because of its versatile spatial configurations [e.g., square antiprism (D_{4d}), dodecahedron (D_{2d}), and bicapped trigonal prism (C_{2v})],[2−5] compared to the extensively investigated hexacyanometalates. Especially, $[M(CN)_8]$ coordinates to 3d metal ions easily to form $M'_9[M(CN)_8]_6$ (M′ = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}) clusters[5] with high spins, and some of them show single-molecule-magnet properties.[5c,e] Cu^{II} ions usually ferromagnetically couple to octacyanometalate via a cyanide group,[6] but rare clusters based on Cu^{II} ions have been reported,[6f,l] which is undoubtedly ascribed to the different coordination environments between Cu^{II} and other metal ions. The Jahn−Teller effect leads to Cu^{II} ions adopting D_{4h} or C_{4v} rather than O_h symmetry. Reported works show that the divalent 3d cations with O_h symmetry stabilize the structure of $M'_9[M(CN)_8]_6$.[5]

We used octacyanotungstate as the building block coordinating to Cu^{II} ions to obtain the largest octacyano cluster to

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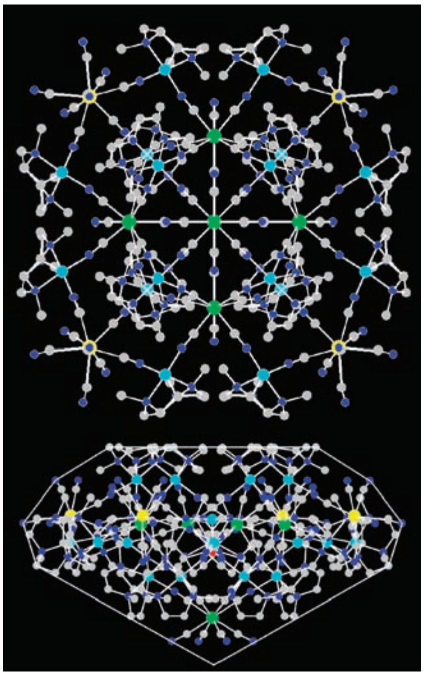

Figure 1. Eicosanuclear cluster in **1** showing a diamondoid shape with a Tolkowsky cut: top view from the *ab* plane and side view in the *bc* plane. Cu, W1 (W2), W3, C, N, and O atoms are represented as cyan, bright green, yellow, dark gray, blue, and red, respectively. Solvated molecules and H atoms are omitted for clarity.

date, $[Cu(H_2O)\{Cu(Me_3tacn)\}_{12}\{W^V(CN)_8\}_2\{W^{IV}(CN)_8\}_5]\cdot 24H_2O$ (**1**, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), in which Me_3tacn caps Cu^{II} ions to prevent the formation of extended structures. Herein, the corresponding synthesis, structure, and magnetic properties are reported.

$Cu(NO_3)_2\cdot 2H_2O$ reacting with $(Bu_3NH)_3[W(CN)_8]\cdot 4H_2O$ (Bu_3N = tributylamine) in the presence of Me_3tacn readily yielded blue block crystals after 2 days.[7] Single-crystal X-ray diffraction[8] reveals that complex **1** features a neutral eicosanuclear cluster, consisting of four crystallographically independent Cu^{II}, two W^{IV}, and one W^V atoms (Figures 1 and S1 in the Supporting Information). Though the phenomenon of partial reduction of W^V to W^{IV} is rare, three more such octacyanometallate copper-containing complexes have been reported elsewhere.[6d,e,l]

The neutral cyano-bridged eicosanuclear cluster in **1** exhibits an interesting spatial structure. This cluster looks like a nanosized diamond with a Tolkowsky cut (Figure1), of which the diameters of the table and waist are 15.102 and 27.237 Å, respectively, and the height is 13.406 Å. However, in crystallography, we generalize the eicosanuclear cluster as a winged opening molecular cage. The opening cage contains nine Cu^{II} ions constructing a body-centered cube, illustrated by a dashed line as shown in Figure 1. With reminiscence of the structure of the cluster $M'_9[M(CN)_8]_6$,[5] a body-centered regular cubic or slightly distorted cubic M'_9 structure is found with each face capped by an $M(CN)_8$ unit, from which the central M′ ion is coordinated by six corresponding cyano groups. In **1**, because of the Jahn–Teller effect, the axial elongation of the central Cu^{II} ion makes the rigid face-capped body-centered-cubic structure hard to form, resulting in a five-capped body-centered cube of opening-cage structure. A water molecule replaces the cyano group of the top $W(CN)_8$ and coordinates to the central Cu^{II} ion along axis, and the top $W(CN)_8$ (W2) has four terminal cyano groups. Thus, the opening cage can be regarded as a capped frustum of a square pyramid rather than a cube, where the sizes of the top and bottom squares are 6.917 × 6.917 and 8.200 × 8.200 $Å^2$, respectively. Other $W(CN)_8$ units of the open cage further connect two wings of trinuclear $Cu_2W(CN)_8$ with half-occupancy, and each remains two terminal cyano groups. Four $[Cu_2W(CN)_8]_{0.5}$ fragments surround the opening cage, with W2, O1, and Cu1 lying on a 4-fold axis, which is fashioned into a diamondoid shape with a Tolkowsky cut (Figure 2). In the wing, the $W(CN)_8$ unit provides three bridging cyano groups to connect Cu^{II} ions. All $W(CN)_8$ groups in **1** adopt a square-antiprism configuration but have three independent coordination environments. W2 is on the 4-fold axis, so the $W(CN)_8$ group of W2 shows a regular square-antiprism geometry but the other two $W(CN)_8$ groups are distorted. The W–CN bond lengths range from 2.123(8) to 2.192(17) Å and the C–N ones from 1.129(9) to 1.192(14) Å, and the W–C–N linkages are almost linear from 170.5(10)° to 180(2)°. All bond lengths and angles based on $W(CN)_8$ in **1** are comparable with those reported in the literature.[3–6]

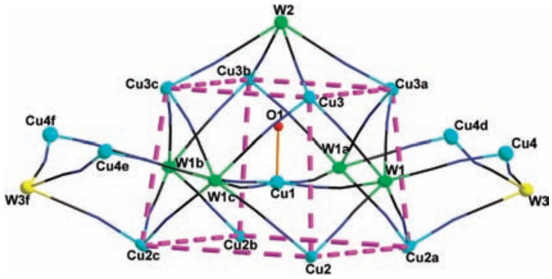

Figure 2. Topology of the winged opening molecular cage constructed by the metallic ions and bridging cyano ligand (symmetry codes: a, $-y, x, z$; b, $-x, -y, z$; c, $y, -x, z$; d, $-y, -x, z$; e, y, x, z; f, $-x, -y, z$).

The central Cu^{II} ion (Cu1) is five-coordinated and takes a regular square-pyramidal geometry, consisting of four equatorial N donors from four equivalent $W1(CN)_8$ units (Figure 2) with a Cu–N length of 1.947(19) Å and one axial O1 atom of H_2O with a Cu–O length of 2.366(16) Å. Cu2 is five- or six-coordinated because of the disordered $W(CN)_8$ groups in the wings. When Cu2 is five-coordinated, three N atoms are from the Me_3tacn ligand and the other two N atoms from the CN ligands of the $W(CN)_8$ units, N2C2–W1 and N2eC2e–W1c, in which N2N2eN13N13e constructs the basic plane and N14 is at the apical position, leading to a distorted square-pyramidal geometry around Cu2. When Cu2 is six-coordinated, an additional CN ligand from W-$(CN)_8$ of W3 coordinates to Cu2 along the axis to complete the octahedral geometry. The Cu–N lengths in the basic plane are 1.969(6) and 2.047(6) Å, and the ones along the axis are 2.249(19) and 2.292(11) Å, respectively.

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(7) To prepare complex **1**, a solution of $Cu(NO_3)_2\cdot 2H_2O$ (11.18 mg, 0.05 mmol) in methanol (5 mL) was added to a solution of Me_3tacn (8.56 mg, 0.05 mmol) in methanol (5 mL) with gentle stirring. The subsequent addition of a solution of $(Bu_3NH)_3[W(CN)_8]\cdot 4H_2O$ (25.60 mg, 0.025 mmol) in methanol (3 mL) resulted in a blue solution. The solution was placed in the dark, and light-blue blocks formed after 2 days (ca. 5.1 mg, 23.5% yield). Elem anal. Calcd for **1** ($C_{164}H_{302}Cu_{13}N_{92}O_{25}W_7$): C, 32.42; H, 5.01; N, 21.21. Found: C, 32.26; H, 4.92; N, 21.12. IR data (KBr, cm^{-1}): 2128 and 2144 (μ-CN) correspond to two different valences of tungstate(V/IV), respectively.

(8) Crystal data for **1**: $C_{164}H_{302}Cu_{13}N_{92}O_{25}W_7$, M_r = 6076.01, tetragonal, space group *I*4*mm*, a = 31.2762(12) Å, b = 31.2762(12) Å, c = 16.1133(18) Å, V = 15762(2) $Å^3$, Z = 2, ρ_{calcd} = 1.280 g cm^{-3}, R1 = 0.0532, wR2 = 0.1097, μ = 3.454 mm^{-1}, S = 1.014.

Cu3 is located in a distorted octahedral environment with six N atoms from Me_3tacn and three CN ligands of the $W(CN)_8$ units of W1 (N3C3−W1 and N3eC3e−W1e) and W2 (N6C6−W2). Two N atoms (N16 and N16e) of Me_3tacn, N3 and N3e, form the equatorial plane, while the residual N atom (N15) of Me_3tacn and N6 coordinate to Cu3 by the axis. The Cu−N bonds in the equatorial plane range from 2.000(6) to 2.133(6) Å, and the axial bonds are 2.251(19) and 2.297(10) Å. The coordination environment around Cu4 is similar to the five-coordinated Cu2. N17 and N19 from Me_3tacn, N4 from $W1(CN)_8$, and N8 from $W3(CN)_8$ form the basic plane, while N18 from Me_3tacn occupies the axial position.

In **1**, the oxidation state of all Cu ions is 2+ because of the five- or six-coordinated environments, deducing to two $[W(CN)_8]^{3-}$ and five $[W(CN)_8]^{4-}$ groups in one cluster unit. There are three independent sites of the $[W(CN)_8]$ group in the asymmetry unit, W1, W2, and W3 (Figure S1 in the Supporting Information). After a symmetrical operation forming the cluster, W1 leads to four equivalent sites (Figure 2), giving an affirmative result that W1 is not in $[W(CN)_8]^{3-}$ but in the $[W(CN)_8]^{4-}$ group. W3 has two equivalent sites and W2 is in one site, just corresponding to the residual three sites including two $[W(CN)_8]^{3-}$ and one $[W(CN)_8]^{4-}$ groups, respectively.

Complex **1** was crystallized in a polar point group, *I*4*mm*, so all cluster molecules orient along the *c* axis from the bottom to the table in the Tolkowsky-cut diamond (Figure S2 in the Supporting Information). The water molecules fill in the lattice. The shortest intercluster distance between the metal ions is 8.069 Å, and the central Cu^{II} distance of the neighboring clusters is 23.537 Å.

Magnetic measurements were performed on polycrystalline samples of **1** in the range of 1.8−300 K in the forms of $\chi_M T$ and χ_M vs T (Figures 3 and S4 in the Supporting Information). At room temperature, the $\chi_M T$ value is 5.89 cm^3 K mol^{-1}, which is slightly larger than the spin-only value of 5.63 cm^3 K mol^{-1} for the spin-diluted $W^{IV}{}_5W^V{}_2Cu^{II}{}_{13}$ ($S_{Cu^{II}} = S_{W^V} = {}^1/_2$ and $S_{W^{IV}} = 0$, assuming $g_{Cu^{II}} = g_{W^V} = 2.0$) system. As the temperature is decreased, the $\chi_M T$ value monotonously increases and reaches a maximum of 9.57 cm^3 K mol^{-1} at 1.8 K, indicating ferromagnetic coupling between the W^V and Cu^{II} ions. The $\chi_M T$ product at 1.8 K is slightly higher than the theoretical value of 8.625 cm^3 K mol^{-1} of two ferromagnetic coupling $Cu^{II}{}_3W^V$ units and seven isolated Cu^{II} ions with $g = 2.0$. The plot of the field dependence of the magnetization from 0 to 70 kOe at 1.8 K is given in Figure 3, and the saturation magnetization is close to 15.23 $N\mu_B$ at 70 kOe, which is consistent with the predicted value of 15 $N\mu_B$ for the $W^{IV}{}_5W^V{}_2Cu^{II}{}_{13}$ unit. No magnetic anisotropy (zero-field splitting) in the ground state of the cluster is observed because the isofield lines superimpose (Figure S5 in the Supporting Information).

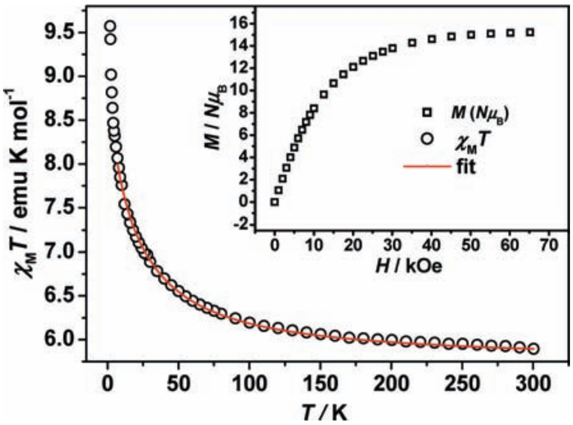

Figure 3. Temperature dependence of the $\chi_M T$ product for **1** at 2 kOe. The inset shows the magnetization versus the applied magnetic field at 1.8 K.

According to the structure of **1**, the eicosanuclear cluster can be regarded as two $Cu^{II}{}_3W^V$ units and seven isolated Cu^{II} ions. In one $Cu^{II}{}_3W^V$ unit, cyano ligands C12N12 and C8N8 bridge between W3 and Cu2 along the axis of Cu2 and between W3 and Cu4 in the basic plane of Cu4, respectively. Thus, the $Cu^{II}{}_3W^V$ unit has two coupling constants and C12N12 mediates a weaker coupling interaction than C8N8. The Hamiltonian of the $Cu^{II}{}_3W^V$ unit indicates that the best fitting of the magnetic properties for complex **1** is given as follows:

$$H = -2J(S_{W3}S_{Cu4} + S_{W3}S_{Cu4'}) - 2J'S_{W3}S_{Cu2}$$

Calculations were performed with the *MAGPACK* package.[9] The fitting results gave $g = 2.02$, $J = 19.80$, and $J' = 3.69$ cm^{-1} with $R = \sum[(\chi_M T)_{calc} - (\chi_M T)_{obs}]^2/\sum(\chi_M T)^2_{obs} = 1.75 \times 10^{-5}$, as shown in the plot of $\chi_M T$ vs T in Figure 3 (solid line).

In summary, we used Me_3tacn as the ligand, obtaining a novel eicosanuclear copper-tungstate cyano-bridged cluster, which is the largest octacyanometallate-based cluster to date and bears intracluster ferromagnetic coupling.

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Supporting Information Available: Physical measurements, X-ray analysis, diagrams and plots relating to the structure, and magnetic properties of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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