Grid-Type Two-Dimensional Magnetic Multinuclear Metal Complex: Strands of {[Cu^{II}(μ-4,4'-bpy)]$^{2+}$}$_n$ Cross-Linked by Octacyanotungstate(V) Ions

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Reaction of the preorganized strands of {[Cu^{II}(μ-4,4'-bpy)]$^{2+}$}$_n$ (4,4'-bpy = 4,4'-bipyridine) with [W^V(CN)$_8$]$^{3-}$ leads to a novel cyano-bridged Cu$^{II}_3$W$^V_2$ complex [Cu(μ-4,4'-bpy)(DMF)$_2$][Cu(μ-4,4'-bpy)-(DMF)]$_2$[W^V(CN)$_8$]$_2$·2DMF· 2H$_2$O **1**. The structure of **1** consists of the expected 2-dimensional grid-type network which is built of infinite {[Cu^{II}(μ-4,4'-bpy)]$^{2+}$}$_n$ chains cross-linked by octacyano-tungstate units. The Cu^{II}–NC–W^V–CN–Cu^{II} linkage exhibits the topology of a 3,2-chain. The skeleton of the layer is additionally stabilized by a hydrogen bond network formed by terminal cyano ligands of the [W(CN)$_8$]$^{3-}$ moiety and water molecules. The distance between the adjacent Cu$_3^{II}$W$_2^V$ chains within the layer is 11.12 Å along the *a* axis. The layers are connected by H-bonds of NCN–NDMF−NCN linkages into 3-D supramolecular architecture. The magnetic properties correspond to a dominant ferromagnetic coupling within the Cu$^{II}_3$W$^V_2$ pentamer units (J = +35(4) cm^{-1}) and much weaker effective AF interunit coupling which include both intra- and inter-3,2-chain interactions between pentamers (J' = −0.05(1) cm^{-1}).

The application of octacyanometalate [M(CN)$_8$]$^{n-}$ (M = Mo, W, and Nb) and 3d transition metal molecular precursors in design and construction of new crystalline materials[1] with potentially adjustable magnetic properties[1b,e,g,j–l,2] has developed recently into an area of intense research. In the design of new solid state architectures, the strategy of self-assembly through the formation of coordinate M−CN−M′ bonds between mononuclear molecular precursors accompanied by weaker $\pi-\pi$ stacking, hydrogen bonding, and electrostatic interactions has been widely employed. A logical extension of the building-block approach is to combine the preorganized multinuclear supramolecular coordination compound

formed by 3d metal centers bridged by organic *spacer* ligands with an octacyanometalate moiety. In order to explore this idea we have chosen the predictable coordination polymer network of 1-dimensional chains that are generated from the metal ions coordinated to linear bifunctional ligands such as 4,4'-bipyridine (4,4'-bpy).[3] These polymeric strands are usually cross-linked by hydrogen-bonded bridging 4,4'-bpy ligands. The new strategy consists of the cross-linking of

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$\{[M^{II}(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ chains by $[M(CN)_8]^{3-/4-}$ *spacers*. Herein, we report the synthesis and magnetic properties of $[Cu(\mu\text{-}4,4'\text{-bpy})(DMF)_2][Cu(\mu\text{-}4,4'\text{-bpy})(DMF)]_2[W^V(CN)_8]_2 \cdot 2DMF \cdot 2H_2O$ **1**.

Compound **1** was obtained in 62% yield in a two step process. In the first step the dropwise addition of a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (37.1 mg, 0.1 mmol, 10 mL) in MeOH/MeCN 2:1 to a stirred solution of 4,4'-bipyridine (15.6 mg, 0.1 mmol, 10 mL) in MeOH/MeCN 2:1 gave a violet suspension. DMF (12 mL) was added to dissolve the suspension, resulting in a pale-blue solution. In the second step the resulting solution was slowly added to a 50 mL solution of $(NBu_4)_3[W^V(CN)_8]$ (111.9 mg, 0.1 mmol) in MeCN. The small amount of greenish-blue precipitate immediately formed was filtered off, and the filtrate was subject to crystallization by the slow evaporation method. After 1 week light blue needle-shaped X-ray quality crystals were formed in a very low yield precluding CHN analysis. The composition of **1** was established by X-ray analysis. The ν_{CN} IR spectrum of **1**[4] shows sharp absorptions at 2188m, 2171m, and 2143sh, consistent with maintaining the W^V site and the presence of bridging cyano groups.[1f]

X-ray analysis[5] revealed that the compound consists of the expected 2-dimensional sheet structure which is built of infinite $\{[Cu^{II}(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ chains cross-linked by octa-cyanotungstate units (Figure 1a). The $Cu^{II}-NC-W^V-CN-Cu^{II}$ linkage thus formed exhibits the topology of a 3,2-chain[1h,6] assured by the electroneutrality of **1** (Figure 1b). Relevant bond distances and angles are given in Table 1. The W^V site exhibits a distorted square antiprism coordination geometry with metric parameters typical for a $[W(CN)_8]^{3-}$ building unit.[1f] Three of the cyano groups of $[W(CN)_8]^{3-}$ are linked to Cu^{II} sites. $[Cu(3)(\mu\text{-}4,4'\text{-bpy})(DMF)(NC)_2]$ moieties of compressed square pyramidal geometry occupy the alternate corners of $Cu_2^{II}W_2^V$ squares, whereas $[Cu(2)\text{-}(\mu\text{-}4,4'\text{-bpy})(DMF)_2(NC)_2]$ of elongated octahedral geometry acts as a linker between the two squares in the chain. The
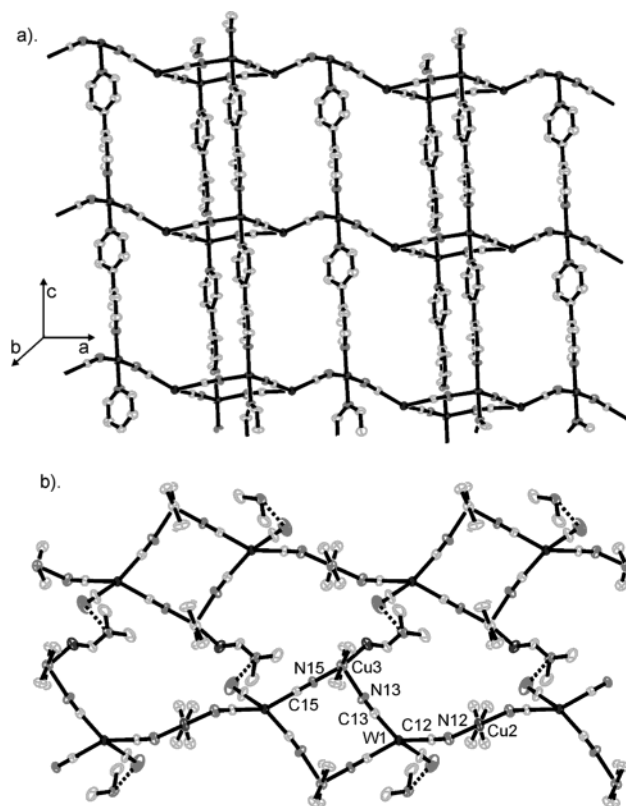
(4) IR spectrum of **1**: ν(O−H) 3511s, 3452s, 3381sh; ν(ArC−H) 3145w, 3104w, 3084w, 3058w, 3018w; ν(C−H) 2962sh, 2928s; ν(H−C≡O) 2873m, 2856m, 2814w; ν(C≡N) 2188s, 2171s, 2143sh; ν(ArC≡C), ν(C=O) 1649vs, 1610vs, 1532m, 1489m, 1433s, 1414s; ν(C−C, C−N), γ(O−H, C−C, C−O, ArC−H in-plane) 1386s, 1366s, 1326sh, 1298sh, 1247m, 1217m, 1148w, 1118w, 1099m, 1070m, 1052sh, 1012w, 977sh, 953sh; γ(ArC−H out-of-plane) 866w, 814s, 728m 688m, 660sh, 646sh; ν(W−C, Cu−N) 573w, 521w, 483m, 454m.

(5) Crystal and refinement parameters: **1** $C_{64}H_{70}Cu_3N_{28}O_8W_2$, $T = 295$ K, $P2_12_12$, $Z = 2$, $a = 17.6167(1)$ Å, $b = 19.0794(3)$ Å, $c = 11.1204(4)$ Å, $V = 3737.75(15)$ Å^3, $d_{calc} = 1.704$ g/cm^3, R1 = 0.0273, wR2 = 0.0822. Data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation and were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods using SIR-92 (Altomare et al.) and refined against all data using SHELXL-97 (Sheldrick). The crystal of **1** exhibited racemic twinning described by the twin matrix −1 0 0/0 −1 0/0 0 −1, and the twin component factor was refined to 0.146(9). The positions of H atoms (except those of water molecules) were calculated using geometrical constraints and included in the refinement using riding model.

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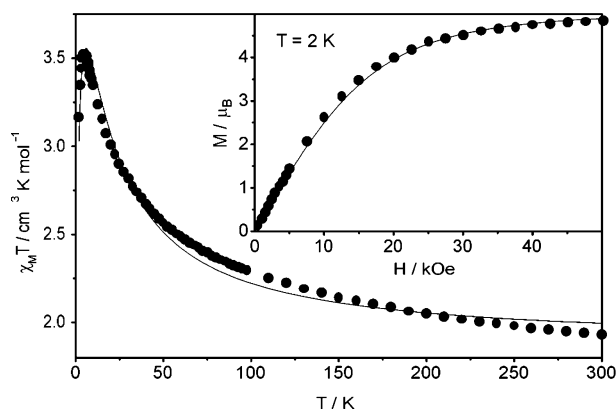
Figure 1. The crystal structure of $[Cu(\mu\text{-}4,4'\text{-bpy})(DMF)_2][Cu(\mu\text{-}4,4'\text{-bpy})\text{-}(DMF)]_2[W^V(CN)_8]_2 \cdot 2DMF \cdot 2H_2O$. Atoms not involved in bridging are omitted for clarity. (a) Side view of 2-D layer. (b) 3-D H-bonding network of **1** in [001] direction with relevant atomic numbering scheme.

Table 1. Relevant Bond Lengths (Å) and Angles (deg) for **1**

$[W(CN)_8]^{3-}$	
W1−C range/average	2.162(7)−2.192(7)/2.173(11)
C−N range/average	1.105(9)−1.140(8)/1.131(11)
W1−C−N range/average	174.4(5)−179.7(6)/177.7(1.6)
$Cu2(bpy)_2(NC)_2(DMF)_2$	
Cu2−N12	2.007(5)
Cu2−N12−C12	151.1(6)
$Cu3(bpy)_2(NC)_2(DMF)$	
Cu3−N13	2.297(5)
Cu3−N13−C13	174.3(5)
Cu3−N15	1.992(5)
Cu3−N15−C15	177.9(5)

structure of the layer is additionally stabilized by a hydrogen bond network formed by terminal cyano ligands of the $[W(CN)_8]^{3-}$ moiety and water molecules. The distance between the adjacent $Cu^{II}_3W^V_2$ chains within the layer is 11.12 Å along the *a* axis. The layers are connected by H-bonds of $N_{CN}-N_{DMF}-N_{CN}$ linkages into 3-D supramolecular architecture.

Magnetic measurements were performed using a Quantum Design SQUID magnetometer. The temperature dependence of the $\chi_M T$ product is shown in Figure 2. The $\chi_M T$ equals 2.0 cm^3 mol^{-1}K at 300 K and gradually increases with decreasing temperature, reaching a maximum of 3.52 cm^3 mol^{-1} K at 5 K. Zero field cooled and field cooled susceptibility measured at 20 Oe (not shown) does not show any trace of irreversibility nor anomaly down to 2 K, which points to lack of a 3-D magnetic ordering. The field
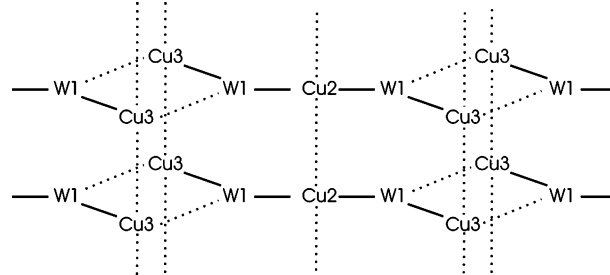
Figure 2. Temperature dependence of $\chi_M T$ value for **1** in the external magnetic field of 1 kOe. Inset: Field dependence of magnetization for **1** at 2 K. Solid lines represent calculated fits to the data.

Scheme 1. The Exchange Interactions in **1** Represented by J (Solid Lines) and J' (Dotted Lines)

dependence of the magnetization measured at 2 K reaches 4.85 μ_B per formula unit at 50 kOe, which is very close to the value expected for five saturated $^1/_2$ spins with $g = 2.0$ (5.0 μ_B). In **1**, there are two copper sites, Cu(2) and Cu(3), and three different [W−CN−Cu] linkages (Scheme S1). The [Cu(2)(bpy)$_2$(NC)$_2$(DMF)$_2$] moiety exhibits symmetrical equatorial cyano bridges in the [W−CN−Cu(2)] linkage. The [Cu(3)(bpy)$_2$(NC)$_2$(DMF)] moiety reveals unsymmetrical equatorial and axial cyano bridges in [W−C15−N15−Cu-(3)] and [W−C13−N13−Cu(3)] linkages, respectively. In the equatorial cyano bridging at Cu(2,3) centers the magnetic orbital of Cu ($3d_{x^2-y^2}$ of σ-symmetry) is orthogonal to the magnetic orbital of W (of π-symmetry, centered on the $5d_{z^2}$ partially delocalized on the π^* orbitals of the cyanide), so that the magnetic interaction is expected to be ferromagnetic (Scheme S2). In contrast, the axial cyano bridging at the Cu(3) center gives rise to the π overlap of the magnetic orbitals of Cu and W, leading to the antiferromagnetic interaction. The magnetic coupling in the Cu^{II}(4,4'-bpy)−Cu^{II} linkage is expected to be weak and antiferromagnetic.[7] On the basis of this qualitative considerations, the magnetic system of **1** can be treated as Cu^{II}$_3$W^V$_2$ pentamer units with identical Cu^{II}···W^V ferromagnetic intrapentamer interactions defined by the parameter J and much weaker effective AF interunit coupling (J'), which includes both intra- and inter-3,2-chain interactions between pentamers (Scheme 1). The Hamiltonian $\mathbf{H}_5 = -J(S_{Cu1}S_{W1} + S_{W1}S_{Cu2} + S_{Cu2}S_{W2} + S_{W2}S_{Cu3}) - g\beta H(S_{Cu1} + S_{W1} + S_{Cu2} + S_{W2} + S_{Cu3})_z$, which represents a chain of five $^1/_2$ spins with the isotropic Heisenberg exchange interaction, was solved numerically. Molar magnetization of the pentamer was calculated as $M_5 = N_A\sum_n(-\partial E_n/\partial H) \exp(-E_n/k_B T)/\sum_n \exp(-E_n/k_B T)$, where E_n denotes eigenvalues of $\mathbf{H}_5$. The low temperature limit of $(\chi_5 T)_{LT}$ (where $\chi_5 = M_5/H$) reaches 4.35 cm^3 mol^{-1} K in this model, which is significantly higher than the experimental value. The difference and the presence of the maximum in the $\chi_M T(T)$ curve was attributed to AF interactions between pentamer units through the cyano- and 4,4'-

bpy bridges (J') and taken into account in the mean field model. At low H fields, where the $M(H)$ dependence is linear, the molar susceptibility was calculated using $\chi_M = \chi_5/(1 - \lambda\chi_5)$ relation where $\lambda = 4J'/N_A g^2\beta^2$. To calculate $M(H)$ at high fields the mean field equation $M = M_5(H + \lambda M)$ was solved numerically. The best agreement with the data was obtained for $J = +35(4)$ cm^{-1}, $J' = -0.05(1)$ cm^{-1}, and fixed $g = 2$. This set of parameters satisfactorily reproduces the $\chi_M T$ product throughout the entire temperature range, and also the magnetization curve at 2 K. The J' value compares favorably with the value estimated for magnetic coupling in the Cu^{II}−(4,4'-bpy)−Cu^{II} linkage ($J_{eff} = -0.052$ cm^{-1}).[7]

In summary, a new assembly based on one-dimensional coordination polymer $\{[Cu(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ and octacyanometalate(V) was designed and constructed: [Cu(μ-4,4'-bpy)-(DMF)$_2$][Cu(μ-4,4'-bpy)(DMF)]$_2$ [W^V(CN)$_8$]$_2$·2DMF·2H$_2$O **1** of magnetic behavior described in a mean field approximation as an assembly of ferromagnetically coupled pentanuclear Cu^{II}$_3$W^V$_2$ units with very weak antiferromagnetic interactions between these units. Further work is being directed toward the construction of multifunctional architectures using 3d metal analogues of $\{[Cu^{II}(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ and related ligands in sequential self-assembly processes. We hope that the new class of magnetic multinuclear metal complexes revealed here represents a step toward supramolecular spintronics.[8]

Supporting Information Available: Crystallographic information file (CIF), Figure S1 (asymmetric unit of **1**), Figure S2 (H-bonded water molecules within the layer of **1**), Scheme S1 (schematic structures of the W−CN−Cu linkages), and Scheme S2 (schemes of magnetic orbitals in **1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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