

Synthesis, crystal structure and magnetic properties of a Cu^{II}–W^{V/IV} bimetallic complex with a novel open framework structure †

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Fabricated by cyano- and alkoxy-bridged groups, a novel three-dimensional structural compound, $\{[\text{Cu}_2(\text{H}_2\text{Tea})_2]_5[\text{W}^{\text{V}}(\text{CN})_8]_2[\text{W}^{\text{IV}}(\text{CN})_8] \cdot x\text{H}_2\text{O}\}_\infty$ (H_3Tea = triethanolamine), has been formed. In the structure, there exist two kinds of W atoms and three types of Cu_2O_2 pairs. The W(1) and W(2) atoms, with oxidation states +5 and +4 respectively, are each linked to the Cu_2O_2 units through two of its eight cyanide ligands, forming two kinds of 1D zigzag chain along the *c*-axis (nominally the W1-chain and the W2-chain). Each W2-chain is connected to four adjacent W1-chains through a third type of Cu_2O_2 unit, leading to the formation of a three-dimensional open framework with channels generated along the [001] direction. The structure may also be viewed as being constructed from W(1) Cu_3 and W(2) Cu_4 clusters, cross-linked by μ -O bridges. The magnetic properties show that the complex displays 3D antiferromagnetic ordering below 2.2 K, although ferromagnetic interactions are present within the W(1) Cu_3 clusters. The dominant antiferromagnetic coupling at low temperature is attributed to the antiferromagnetic exchanges between the W(1) Cu_3 clusters through the alkoxy bridges.

As precursors of molecule-based magnetic materials, the $[\text{M}(\text{CN})_8]^{3-4-}$ ($\text{M} = \text{Mo}, \text{W}$) anions are currently attracting a great deal of interest based on their lower symmetry and rich magnetic exchange coupling. Some special formative complexes have been formed *via* deliberate choices of constituent metal ions at the other end of the CN-bridge.^{1–27} However, examples of such complexes are still limited so far including several cluster compounds possessing a high spin ground state^{1,2,12} and a few polymeric compounds showing three-dimensional ferromagnetic ordering.^{3,7,13,23} In order to better understand the magneto–structural correlation of these complexes, it is important to synthesize and structurally characterize new compounds by selecting second metal ions with appropriate spin-state and oxidation-state or by alternating different terminal ligands on the metal ions. Considering the effect of an ancillary ligand on the geometry of the coordination spheres of the spin carriers and, further, on the assembly of the structure, we chose the tripodal ligand triethanolamine (H_3Tea) as donor to the second metal ion Cu(II). A novel Cu(II)–W(V) complex, $\{[\text{Cu}_2(\text{H}_2\text{Tea})_2]_5[\text{W}^{\text{V}}(\text{CN})_8]_2[\text{W}^{\text{IV}}(\text{CN})_8] \cdot x\text{H}_2\text{O}\}_\infty$ (**1**), is presented here.

Experimental

Materials and general methods

$\text{K}_3[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ was synthesized according to the literature method.²⁸ All other reagents were purchased as reagent grade chemicals and used without further purification. Elemental analyses were performed on a Houres CHNO-Rarid elemental analyzer. IR spectra were measured on a Bruker Vector 22 FT-IR spectrometer with KBr pellets. Thermal analyses were performed in nitrogen with a heating rate of 20 °C min^{-1} on a Perkin-Elmer Pyris 1 thermogravimetric analyzer. The magnetic susceptibilities were measured on polycrystalline samples

in the 2–300 K temperature range using a MagLab System 2000 magnetometer. Pascal's constants were used to determine the diamagnetic contribution.²⁹ Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the molar magnetic susceptibility.

Preparation of $\{[\text{Cu}_2(\text{H}_2\text{Tea})_2]_5[\text{W}^{\text{V}}(\text{CN})_8]_2[\text{W}^{\text{IV}}(\text{CN})_8] \cdot x\text{H}_2\text{O}\}_\infty$ (**1**)

All operations for the syntheses were carried out in the dark to avoid decomposition of $\text{K}_3[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$.

To a stirring aqueous solution (30 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (85 mg, 0.5 mmol) was added H_3Tea (75 mg, 0.5 mmol). The resulting deep blue solution was mixed with $\text{K}_3[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ (79 mg, 0.15 mmol) in water (20 mL), giving an immediate precipitation of grass green microcrystalline **1**. The precipitate was collected and washed with water and ethanol, then dried in air. Yield: 53 mg, 29%. Found: C, 27.17; H, 5.05; N, 12.82%. Anal. Calcd. for $\{[\text{Cu}_2(\text{H}_2\text{Tea})_2]_5[\text{W}^{\text{V}}(\text{CN})_8]_2[\text{W}^{\text{IV}}(\text{CN})_8] \cdot 22\text{H}_2\text{O}\}_\infty$: C, 27.35; H, 5.03; N, 12.91%. Thermal analysis shows a weight loss of 10.6% below 110 °C (Fig. S1†), in agreement with the removal of 22 water molecules (calcd. 10.7%). IR data (KBr, cm^{-1}): 3417s (br), 2971m, 2928m, 2880m, 2184w, 2164s, 2135 (sh), 2125 (sh), 1638w, 1487w, 1461w, 1388w, 1333w, 1264w, 1078s, 1043s, 1023m, 1005w, 905s, 879w, 751w, 631m, 571w, 541w, 501w, 484w, 449w. Selected Raman data (cm^{-1}): 2157s, 2137s. Single crystals of complex **1** suitable for X-ray analysis were grown at room temperature by slow diffusion in a three-compartment tube containing the deep blue aqueous solution (10 mL) of H_3Tea (0.2 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 mmol), a yellow aqueous solution (10 mL) of $\text{K}_3[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ (0.1 mmol) and water (10 mL, in middle tube), respectively.

X-Ray crystallography studies

A single crystal of dimension 0.20 × 0.30 × 0.40 (mm) was mounted on a glass fiber and single-crystal X-ray diffraction was measured on a Bruker Smart Apex CCD diffractometer. The determination of the unit cell and the data collection were performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room

† Electronic supplementary information (ESI) available: thermal analysis, IR spectra, XRD pattern, magnetic susceptibilities and magnetic hysteresis loop for complex **1**. See <http://www.rsc.org/suppdata/dt/b3/b304276f>

Table 1 Crystallographic data for complex **1**

Formula	W ₃ Cu ₁₀ C ₈₄ H ₁₄₀ N ₃₄ O ₃₀ ·5H ₂ O
Formula weight	3383.33
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> /Å	32.349(2)
<i>b</i> /Å	20.892(2)
<i>c</i> /Å	21.162(2)
Volume/Å ³	14302(2)
<i>Z</i>	4
<i>D</i> (calc)/g cm ⁻³	1.571
μ (Mo-K α)/cm ⁻¹	3.928
<i>F</i> (000)	6736
<i>R</i> (int)	0.051
Observed data [<i>I</i> > 2.0 σ (<i>I</i>)]	9910
Total/unique data	80212/15505
<i>R</i> ₁ / <i>wR</i> ₂	0.0435/0.1011

$R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = \sum w(|F_o|^2 - |F_c|^2) / \sum w(F_o)^2$, $w = 1 / [(F_o)^2 + (0.0414P)^2]$, where $P = (F_o^2 + 2F_c^2) / 3$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

W(1)–C(1)	2.207(6)	W(1)–C(2)	2.126(6)
W(1)–C(3)	2.167(6)	W(1)–C(4)	2.170(6)
W(1)–C(5)	2.128(6)	W(1)–C(6)	2.163(6)
W(1)–C(7)	2.108(7)	W(1)–C(8)	2.158(6)
W(2)–C(9)	2.068(6)	W(2)–C(10)	2.062(6)
W(2)–C(11)	2.104(6)	W(2)–C(12)	2.183(6)
Cu(1)–O(1)	1.943(4)	Cu(1)–O(2)	2.406(5)
Cu(1)–O(3)	2.286(5)	Cu(1)–O(4)	1.939(4)
Cu(2)–O(1)	1.961(4)	Cu(2)–O(4)	1.947(4)
Cu(2)–O(5)	2.328(4)	Cu(2)–O(6)	2.390(4)
Cu(3)–O(7)	1.953(4)	Cu(3)–O(8)	2.334(5)
Cu(3)–O(9)	2.398(5)	Cu(3)–O(10)	1.921(4)
Cu(4)–O(7)	1.922(4)	Cu(4)–O(10)	1.973(4)
Cu(4)–O(11)	2.659(5)	Cu(4)–O(12)	2.274(5)
Cu(5)–O(13)	2.807(4)	Cu(5)–O(14)	2.386(4)
Cu(5)–O(15)	2.048(4)	Cu(5)–O(15) ^d	1.856(4)
Cu(1)–Cu(2)	2.908(8)	Cu(3)–Cu(4)	2.916(2)
Cu(5)–Cu(5) ^d	2.912(9)		
N(1)–C(1)–W(1)	177.2(5)	N(2)–C(2)–W(1)	177.8(5)
N(3)–C(3)–W(1)	178.3(5)	N(4)–C(4)–W(1)	174.8(5)
N(5)–C(5)–W(1)	174.2(5)	N(6)–C(6)–W(1)	175.6(6)
N(7)–C(7)–W(1)	177.8(6)	N(8)–C(8)–W(1)	177.0(6)
N(9)–C(9)–W(2)	178.3(6)	N(10)–C(10)–W(2)	168.9(5)
N(11)–C(11)–W(2)	173.0(5)	N(12)–C(12)–W(2)	176.2(6)
Cu(1)–O(1)–Cu(2)	96.35(19)	Cu(1)–O(4)–Cu(2)	96.93(18)
Cu(4)–O(7)–Cu(3)	97.61(19)	Cu(3)–O(10)–Cu(4)	96.99(19)
Cu(5) ^d –O(15)–Cu(5)	96.37(19)		

Symmetry operations: d 1 – *x*, –*y*, 2 – *z*.

temperature (293 K). The structure was solved by direct methods and refined by a full matrix least-squares technique based on *F*² using the SHELXTL program.³⁰ The H-atoms were added theoretically riding on the concerned atoms or found from Fourier maps, and were refined with fixed thermal factors. All non-hydrogen atoms were refined anisotropically. The max./min. residual electron density are 4.95 e Å⁻³ (0.01 Å from W2) and –3.80 e Å⁻³ (0.15 Å from Cu5) respectively. A detailed summary of the crystal data and structure refinement analysis is shown in Table 1. Selected bond distances and angles are listed in Table 2.

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See <http://www.rsc.org/suppdata/dt/b3/b304276f/> for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structure

Fig. 1 shows the building unit of structure **1** with atomic labeling scheme. The asymmetric unit consists of one [W(CN)₈]³⁻, 1/2 [W(CN)₈]⁴⁻ anions and five Cu(H₂Tea) units. There are two

kinds of W site, each of which is coordinated by eight CN ligands with a distorted trigonal dodecahedral environment. The W(1) atom, having an oxidation state of +5, is located in a general position. It links three copper centers [Cu(1), Cu(2), Cu(3)] through three μ -CN bridges, forming W(1)Cu₃ clusters. The W(2) atom, having an oxidation state of +4, occupies a special position and is surrounded by four Cu centers through four μ -CN bridges, forming W(2)Cu₄ clusters. The remaining CN ligands of both W atoms are terminal. The partial reduction of W^v to W^{iv} is unexpected, but a similar phenomenon has been observed in the Cuⁱⁱ–en–[Mo(CN)₈]³⁻ and Cuⁱⁱ–tren–[Feⁱⁱⁱ(CN)₆]³⁻ systems,^{27,31} where [Mo(CN)₈]³⁻ is reduced to [Mo(CN)₈]⁴⁻ and [Feⁱⁱⁱ(CN)₆]³⁻ is reduced to [Feⁱⁱ(CN)₆]⁴⁻.

Five Cu atoms are crystallographically distinct, three [Cu(1), Cu(2), Cu(3)] of which have distorted octahedral geometries. Five coordination sites come from two triethanolamine ligands and one from the nitrogen atom of a cyano-bridge. Their quasi-equatorial basal planes are provided by [N(1A), N(13), O(1), O(4)] for Cu(1), [N(2), N(14), O(1), O(4)] for Cu(2) and [N(3), N(15), O(7), O(10)] for Cu(3), while the axial sites are occupied by [O(2), O(3)] for Cu(1), [O(5), O(6)] for Cu(2) and [O(8), O(9)] for Cu(3), respectively. The axial Cu–O distances [average 2.357(3) Å] are much longer than those of the equatorial ones [average 1.943(7) Å] due to Jahn–Teller effects. The other two copper centers [Cu(4) and Cu(5)] display distorted square pyramidal geometries. The basal sites are placed by [O(7), O(10), N(16), N(9)] for Cu(4) and [O(15), O(15A), N(17), N(10)] for Cu(5), respectively. The average Cu–O length is 1.950(1) Å. The apical sites are occupied by an ethanolic oxygen atom [O(12)] for Cu(4) and [O(14)] for Cu(5), respectively. The average axial Cu–O distance is 2.329(5) Å.

Five crystallographically distinct triethanolamine ligands serve as either tri-dentate [Cu(4), Cu(5)] or tetra-dentate [Cu(1), Cu(2), Cu(3)] ligands to the copper ions. One deprotonated oxygen of each triethanolamine [O(1), O(4), O(7), O(10), O(15)] acts as a μ -O bridge to link two copper ions, thus forming Cu(1)(μ -O)₂Cu(2), Cu(3)(μ -O)₂Cu(4) and Cu(5)(μ -O)₂Cu(5) “dimers” (Fig. 1 and 2). The average Cu–(μ -O) bond length and Cu–Cu distance are 1.946(2) Å and 2.912(7) Å, respectively (Table 2). The Cu–O–Cu angles range from 96.4(2) to 97.6(2)°. The Cu(1)O(1)Cu(2)O(4) and Cu(3)O(7)Cu(4)O(10) cores are non-planar and asymmetric with dihedral angles 25.2° for Cu(1)O(1)Cu(2)O(4) about segment Cu(1)Cu(2) and 28.1° for Cu(3)O(7)Cu(4)O(10) about segment Cu(3)Cu(4).

The three-dimensional network of compound **1** is fabricated by [W(CN)₈]³⁻ and [W(CN)₈]⁴⁻ units *via* three types of Cu–(μ_2 -O)₂Cu pairs. The W(1) and W(2) atoms are each linked to the Cu₂O₂ units through two of its eight cyanide ligands, forming two kinds of 1D zigzag chain along the *c*-axis namely –W(1)–CN–[Cu(1)(μ_2 -O)₂Cu(2)]–CN–W(1)– (W1-chain) and –W(2)–CN–[Cu(5)(μ_2 -O)₂Cu(5)]–CN–W(2)– (W2-chain). The neighboring W1-chains are linked to each other through inter-chain hydrogen bonds, forming a W1-layer in the *bc* plane. Each W2-chain is connected to four adjacent W1-chains between these layers through the third type of Cu(3)(μ_3 -O)₂Cu(4) unit, constituting an open framework structure (Fig. 2 and 3). The non-coordinated OH groups of H₂Tea⁻ point towards the voids of the framework where the lattice water molecules reside. Hydrogen bonds are found among water molecules, nitrogen atoms of terminal CN groups and alcoholic groups of H₂Tea⁻.

Magnetic properties

The variable-temperature (2–300K) magnetic susceptibilities of complex **1** have been measured in a field of 10 kOe. A plot of $\chi_M T$ vs. *T* is shown in Fig. 4, where χ_M is the molar magnetic susceptibility per W₃Cu₁₀ unit. The $\chi_M T$ value (4.63 cm³ K mol⁻¹, 6.09 μ_B) at room temperature is close to the expected value (4.50 cm³ K mol⁻¹, 6.00 μ_B) for the spin-diluted W^{iv}W^vCuⁱⁱ₁₀ system. Upon cooling, the $\chi_M T$ value increases

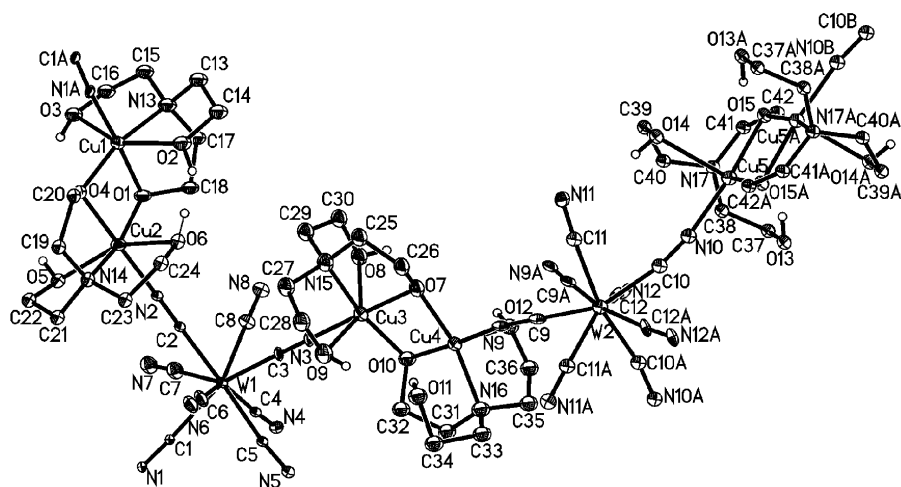


Fig. 1 ORTEP⁴⁷ drawing of compound **1** with thermal ellipsoids at 30% probability. All hydrogen atoms except those attached to oxygens are omitted for clarity.

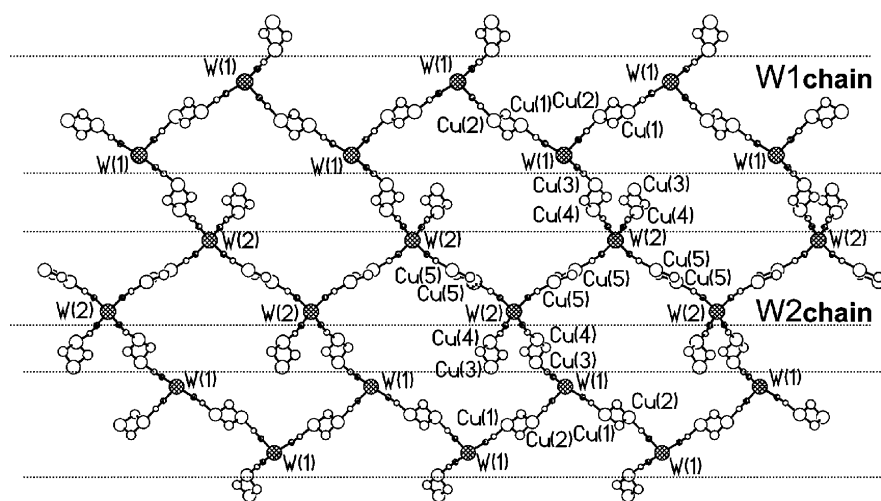


Fig. 2 Projection of complex **1** along the *a* axis showing the 2D honeycomb-like layer. All atoms of the triethanolamine molecules except μ -alkoxy oxygens are omitted for clarity.

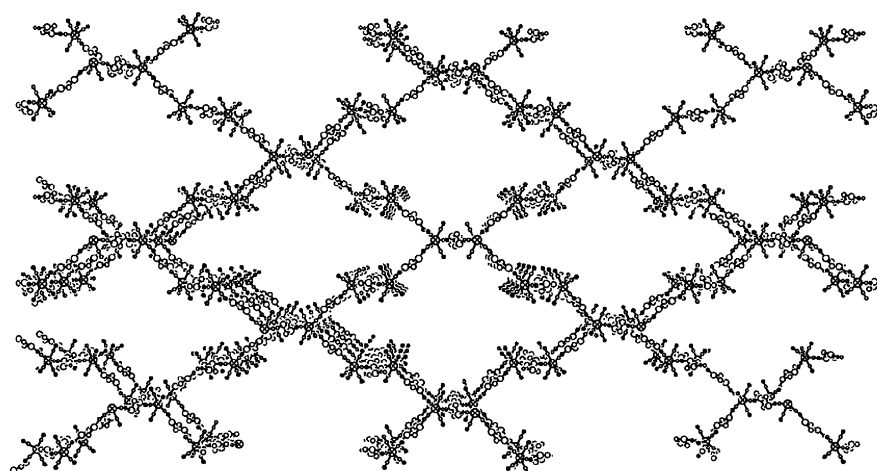


Fig. 3 Packing diagram of complex **1** viewed along the *c*-axis. All triethanolamine and water molecules except the μ -alkoxy oxygens are omitted for clarity.

continuously until reaching a maximum value of $11.87 \text{ cm}^3 \text{ K mol}^{-1}$ ($9.74 \mu_B$) at 5.4 K, suggesting a dominant ferromagnetic coupling between the adjacent metal ions. The ferromagnetic interaction can be rationalized in terms of the strict orthogonality of the magnetic orbitals between the Cu^{II} ($3d^9$) and

$\text{W}^{\text{V}}(3d^1)^{6,23,25,26}$ within the $\text{W}(1)\text{Cu}_3$ clusters. Below 5.4 K, the $\chi_M T$ value decreases rapidly, attributed to the zero-field splitting of the ground state of the clusters and/or the antiferromagnetic interaction between the clusters. The sharp peak appearing in the χ_M versus *T* curve, measured at 200 Oe, suggests an

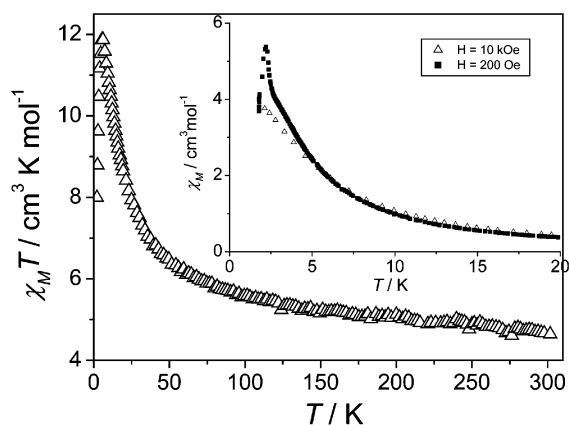


Fig. 4 Plot of $\chi_M T$ versus T for **1** per W_3Cu_{10} unit in a field of 10 kOe. Inset: χ_M versus T curves in applied fields of 200 and 10 kOe for **1**.

antiferromagnetic (AF) ordering below 2.2 K (inset of Fig. 4). The transition to an AF state is proved by the in-phase of the zero-field *ac* magnetic susceptibility $\chi_M'(T)$, which has a peak at *ca.* 2.3 K under $H_{ac} = 2$ Oe and frequencies of 111, 199, 355, 633 and 1111 Hz. No detected out-of-phase signal and frequency dependence was observed, excluding any ferromagnetic contribution (Fig. S4 in ESI†). The antiferromagnetic ground state is derived from the dominant antiferromagnetic interactions between the Cu(II) ions through the alkoxyl bridges as well as the $[W^{IV}(CN)_8]^{4-}$ bridge. It is well known that the exchange couplings involving the alkoxyl bridges are affected by many structural parameters concurrently, such as the bridging angle, coordination bond length, the symmetry of Cu_2O_2 core and so on.^{32–46} Merz and Haase⁴⁶ found an almost linear correlation between the magnitude of the exchange interaction and the Cu–O–Cu bridging angle within the symmetric Cu_2O_2 core of dimeric alkoxo-bridged copper(II) complexes. They concluded that when the Cu–O–Cu angle is greater than 95.8° , the overall magnetic behaviour is antiferromagnetic. Otherwise ferromagnetic coupling is observed. The larger the Cu–O–Cu angle and the smaller the Cu–O distance, the stronger the antiferromagnetic coupling is. In the case of compound **1**, the Cu–O–Cu bond angles are all above 95.8° . Therefore, antiferromagnetic coupling should be expected between the Cu(II) centers. Fig. 5 shows the field dependence of the magnetization at 1.8 K and their differential curve. The magnetization increases very slowly at low field, then rapidly with increasing applied field, suggesting a metamagnetic behavior. When the external field reaches 3 kOe, the antiferromagnetic ground state is switched to a ferromagnetic state. The magnetization at 70 kOe ($11.0 N\beta$) is not saturated compared with the value of $12.0 N\beta$ for a fully ferromagnetically coupled $Cu^{II}_2W^{IV}_2$

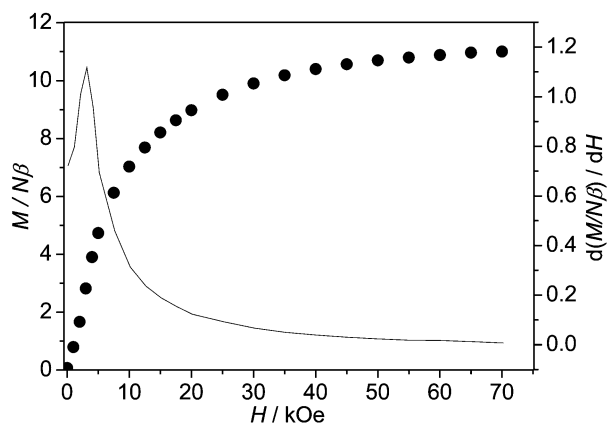


Fig. 5 Magnetization of **1** at 1.8 K (●), and $d(M/N\beta)/dH$ vs. H curve (—).

spin system ($S_T = 6$). The hysteresis loop at 1.8 K displays a small coercive field of 70 Oe and a small remnant magnetization of $0.068 N\beta$, typical for a soft magnet (Fig. S5 in ESI†).

Conclusion

In conclusion, a new copper(II)–tungstate(v) complex namely, $\{[Cu_2(H_2Tea)_2][W^V(CN)_8][W^{IV}(CN)_8] \cdot xH_2O\}_\infty$ ($H_2Tea =$ triethanolamine), has been reported in this paper. It shows a three-dimensional open framework structure in which the $W(1)Cu_3$ and $W(2)Cu_4$ clusters are cross-linked by μ -O bridges between the copper centers. The magnetic properties of the compound reveals a dominant ferromagnetic interaction between the Cu(II) and W(v) centers within the $W(1)Cu_3$ cluster. The weak inter-cluster antiferromagnetic interactions between the Cu atoms through the alkoxyl and $[W^{IV}(CN)_8]^{4-}$ bridges result in a metamagnetic behavior at 1.8 K. When a critical field (3 kOe) is reached, the compound switches from an AF ground state to a ferromagnetic state.

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