A novel Cu(II)-W(V) bimetallic assembly magnet $\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$ (en = ethylenediamine) with cube-like W_8Cu_{12} units from a coordinated anion template self-assembly reaction†

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Received (in Montpellier, France) 1st October 2001, Accepted 20th November 2001
First published as an Advance Article on the web 8th March 2002

A novel molecular-based magnet of three-dimensional (3-D) cyanide-bridged bimetallic assembly, $\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$ (**1**), where en = ethylenediamine, was synthesized and structurally characterized. The assembly has a three-dimensional network structure extended by three kinds of Cu^{II}–NC–W^{V}–CN–Cu^{II} linkages with very long axial Cu–$N_{cyanide}$ interactions due to Jahn–Teller effects. The network is based on a W_8Cu_{12} cube-like unit with eight $[W(CN)_8]^{3-}$ anions at the corners of the distorted cube and twelve $[Cu(en)_2]^{2+}$ cations at the middle of the edges, in which a coordination anion $[W(CN)_8]^{3-}$ acting as template/guest is capsulated in the cavity of the W_8Cu_{12} cube. Magnetic studies reveal that the complex displays 3-D ferromagnetic ordering over the lattice below the Curie temperature at around 2 K.

There is a currently great interest in the construction of molecule-based magnets from molecular precursors. $M(CN)_6^{n-}$ (M = Fe, Cr, Mn, *etc.*) as good building blocks have been extensively studied and a family of assemblies with high Curie or Neel temperatures (T_C or T_N) have been reported in the last decade.[1–29] Very recently, paramagnetic anions $M^{V}(CN)_8^{3-}$ (M = Mo, W) as building blocks for constructing molecule-based magnets have obtained much attention.[30–32] Compared with the octahedral hexacyanometalate species $M(CN)_6^{n-}$, octacyanometalates $M^{V}(CN)_8^{3-}$ may show various geometrical structures (*e.g.*, square antiprism, dodecahedron, bicapped trigonal prism, *etc.*), depending on the external environments.[32] These flexible species may be used as versatile supramolecular synthons to construct a variety of supramolecular architectures or networks with novel topological structures. The diversity of structures may lead to a variety of magnetic behaviors with these architectures. To date, only two Mn^{II}-W^{V} bimetallic assemblies based on $[W(CN)_8]^{3-}$ have been studied structurally and magnetically, by Zhong *et al.*, and they show interesting magnetic properties.[30,32] However, due to the limited examples of octocyanotungstate(V) magnetic species, it is still unclear how to describe the magnetostructural correlation for octocyanotungstate cyanide-bridged bimetallic compounds. Here we present the crystal structure and magnetic properties of the first Cu^{II}-W^{V} three-dimensional ferromagnet $\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$ with cube-like W_8Cu_{12} units, obtained from a one-pot coordinated anion template self-assembly reaction.

† Electronic supplementary information (ESI) available: selected hydrogen bonding parameters in **1** (Table S1) and perspective view showing the three linkages for the title compound (Fig. S1). See http://www.rsc.org/suppdata/nj/b1/b108791f/

Experimental

Measurements

Elemental analysis was determined with a Perkin–Elmer 240C elemental analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region on a Bruker Vector 22 FT-IR instrument using KBr pellets. Magnetic susceptibilities were measured by a Mag Lab^{2000} system. Diamagnetic corrections were made using Pascal's constants. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for the diamagnetism of the constituting atoms.

Preparations

$K_3[W(CN)_8]\cdot H_2O$ was synthesized as described previously in the literature.[33] The other reagents were of analytical grade from commercial sources and were used without any further purification.

$\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$ (1). An aqueous solution of $Cu(ClO_4)_2\cdot 4H_2O$ (29.7 mg, 0.20 mmol) and ethylenediamine (en; 0.001 ml, 0.40 mmol) was added to an aqueous solution of $K_3[W(CN)_8]\cdot H_2O$ (52.7 mg, 0.10 mmol) with stirring to give deep blue solution, which was allowed to stand for several days; dark blue crystals were obtained. All the operations for the synthesis were carried out in the dark to avoid decompositions of $K_3[W(CN)_8]\cdot H_2O$. Yield: 56%. Anal. found: C, 25.12; H, 3.91; N, 29.33, Cu, 14.2%. Calcd. for $C_{28}N_{28}OH_{50}Cu_3W_2$: C, 24.85; H, 3.72; N, 28.98, Cu, 14.06%. IR: ν_{max}/cm^{-1} 2144 and 2097 ($\nu_{C\equiv N}$).

Caution! Perchlorate salts of compounds containing organic ligands are potentially explosive, especially when heated or bumped. Only small quantities of these compounds should be prepared and handled behind suitable protective shields.

X-Ray crystallography

Diffraction data were collected on a Siemens SMART CCD system equipped with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The data integration and empirical absorption corrections were carried out by SAINT[34] and SADABS[35] programs. The structures were solved by direct methods (SHELXS 97) and refined on F^2 by full-matrix least-squares techniques (SHELXL 97).[36] The majority of the non-hydrogen atoms were refined anisotropically. Certain C and N atoms of the en ligands and cyanides around W2 (C9, C12, C14, C19, C20, C25, C26, C27, C28, N9, N11, N13, N14 and N15) in this structure are disordered (S.O.F. = 0.5) and these atoms were refined isotropically. The hydrogen atoms of the water molecule were found from the difference Fourier maps. All other hydrogen atoms were placed in their calculated positions with C–H = 0.96 Å and N–H = 0.90 Å, assigned fixed isotropic thermal parameters (1.2 times those of the atom to which they are attached), and allowed to ride on their respective parent atoms.

Crystal data. $\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$, $C_{28}N_{28}OH_{50}Cu_3W_2$, $M = 1353.28$, triclinic, space group $P\bar{1}$, $a = 10.4759(12)$, $b = 14.7380(16)$, $c = 15.3325(17)$ Å, $\alpha = 87.479(2)$, $\beta = 87.473(2)$, $\gamma = 88.683(2)°$, $U = 2362.1(5)$ Å^3, $Z = 2$, $D_c = 1.903$ g·cm^{-3}, μ(Mo-Kα) = 6.238 mm^{-1}, 10 407 independent ($R_{int} = 0.0334$) with 7139 [$I > 2\sigma(I)$] observed data, $R1 = 0.0508$ and $wR2 = 0.0678$.

CCDC reference number 169196. See http://www.rsc.org/suppdata/nj/b1/b108791f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structure

The perspective view of the asymmetric unit with the atom-numbering scheme is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The asymmetric unit consists of two $[W^V(CN)_8]^{3-}$ anions, one $[Cu(en)_2]^{2+}$ cation and four one-half $[Cu(en)_2]^{2+}$ cations localized at the special equivalent positions (Cu2 0, 1, 1/2; Cu3 0, 1/2, 0; Cu4 0, 1, 0; Cu5 0, 1/2, 1/2). Each Cu^{II} is in an elongated octahedral coordination environment, in which four nitrogen atoms from two en ligands are located at the equatorial positions with the Cu–N_{eq} bond distances in the range of 1.987(8) to 2.031(7) Å (Fig. 1), while the axial sites are occupied by two nitrogen atoms from the bridging cyanide groups on different $[W(CN)_8]^{3-}$ anions. Owing to the Jahn–Teller effects occurring to a different degree for each copper atom, the Cu–$N_{cyanide}$ interactions at the apical positions are observably different. For Cu2, Cu3, Cu4 and Cu5, because they are located on the symmetry elements, the two Cu–$N_{cyanide}$ distances of each are equal, varying from 2.534(7) to 2.731(6) Å, and the N–Cu–N angles are linear (see Table 1). It is noticed that the Cu–$N_{cyanide}$ distances are much longer than those of the reported hexacyanometalate analogs, for example K[Cu(cyclam)]-$[Fe(CN)_6]\cdot 4H_2O$,[28] with Cu–$N_{cyanide} = 2.492(9)$ Å. For Cu1, one of the two axial Cu–$N_{cyanide}$ bond distances is Cu1–N1 = 2.329(6) Å, the other one is rather long with a length of Cu1–N7^{ii} = 2.967(7) Å and the N1–Cu1–N7^{ii} atoms are not in a line, with an angle of 165.9(2)°. In addition, the C–N–Cu bond angles are far from linearity with the angles ranging from 115.7(6) to 143.0(7)°.

In this structure, there are two types $[W(CN)_8]^{3-}$ groups; one anion, coordinated by eight cyanides in a distorted square antiprism environment, bridges the $[Cu(en)_2]^{2+}$ groups to form a three-dimensional network extended by Cu–NC–W–CN–Cu linkages, the other anion fills in the cavity of the 3-D structure [Fig. 2(a)]. It is noticed that there are three kinds of Cu–NC–W–CN–Cu linkages: Cu4–N5–C5–W1–C4–N4–Cu5, Cu2–N3–C3–W1–C8–N8–Cu3 and Cu1–N1–C1–W1–C7–N7–Cu1* (*$x-1$, y, z), see Fig. S1. The former two linkages spread along the *bc* plane to form 2-D sheets with 24-atom macrocyclic $[Cu_4W_4(CN)_8]$ structures, while the latter one extends perpendicularly along the *a* axis, connecting the 2-D sheets to form a 3-D network [see Fig. 2(a)]. The three-dimensional structure of the title complex can be described as an infinite three-dimensional assembly of cube-like W_8Cu_{12} units, in which eight W atoms are located at the corners with the W···W separations along the W–CN–Cu–NC–W linkage varying from 10.29 to 11.06 Å, and twelve $[Cu(en)_2]^{2+}$ units at the edges.

The cavity of the W_8Cu_{12} cube is occupied by a $W(CN)_8{}^{3-}$ anion that is in a distorted bicapped trigonal prism or square antiprism structure [see Fig. 2(b)]. This $W(CN)_8{}^{3-}$ anion is stabilized in the void by the hydrogen bonds that are generated from the $N_{cyanide}$ of the $W(CN)_8{}^{3-}$ with the adjacent –NH_2 groups of the en ligands. For example, N10 as an acceptor forms a hydrogen bond with the N20 atom with N20···N10 = 3.214(12) Å and N20···H20···N10 = 131(5)°. The bond lengths and angles of the hydrogen bonds are summarized in Table S1 in the ESI. Apparently, this $W(CN)_8{}^{3-}$ anion acts as an anion template/guest, playing a very important role in the construction and stabilization of the three-dimensional network [Fig. 2(b)]. It is worth noting that this three-dimensional structure cannot be produced when the en ligand is replaced by 1,3-propanediamine or diethylenetriamine (only the 2-D layer structure is obtained in such cases). This implies that the size, shape and charge of $W(CN)_8{}^{3-}$ are just right to fit the cavity in the $\{W_8[Cu(en)_2]_{12}\}$ cube, and the size of the exogenous ligand en is also a key factor in the formation of this framework. This novel 3-D network is similar to a reported 3-D structure based on a cube formed by 8 $[Fe(CN)_6]^{4-}$ anions at the corners and 12 $[Ni(L)_2]^{2+}$ cations at the edges. However, the void of the Fe_8Ni_{12} cube is filled with two hexafluorophosphate or perchlorate anions.[23] The title complex is the first example to utilize $[W(CN)_8]^{3-}$ acting as coordination anion template to construct a super-coordination complex having a 3-D network.

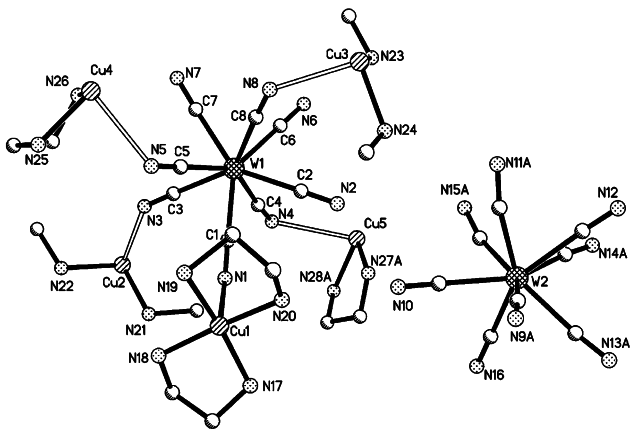

Fig. 1 Molecular structure of the asymmetric unit for $\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$. Only the C and N atoms of the disordered groups labelled A are shown and hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances (Å) and bond angles (deg) in $\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$[a]

Cu1–N1	2.329(6)	Cu1–N7^{ii}	2.967(7)
Cu2–N3	2.534(7)	Cu2–N3^{iii}	2.534(7)
Cu3–N8	2.616(7)	Cu3–N8^{i}	2.616(7)
Cu4^{i}–N5	2.616(7)	Cu4^{i}–N5^{iii}	2.616(7)
Cu5–N4	2.731(6)	Cu5–N4^{iv}	2.731(6)
Cu1–N17	2.029(6)	Cu1–N19	1.997(6)
Cu1–N18	1.989(7)	Cu1–N20	1.991(7)
Cu2–N21	2.021(5)	Cu2–N22	2.021(5)
Cu3–N23	2.004(6)	Cu3–N24	2.005(6)
Cu4–N25	2.031(7)	Cu4–N26	2.007(6)
Cu5–N27A	2.007(9)	Cu5–N28A	1.987(8)
Cu5–N27B	1.994(9)	Cu5–N28B	2.018(9)
W1–C1	2.171(8)	W1–C5	2.159(7)
W1–C2	2.155(8)	W1–C6	2.143(9)
W1–C3	2.203(8)	W1–C7	2.166(7)
W1–C4	2.146(8)	W1–C8	2.153(8)
C1–N1	1.128(8)	C5–N5	1.123(8)
C2–N2	1.128(8)	C6–N6	1.158(9)
C3–N3	1.107(8)	C7–N7	1.137(8)
C4–N4	1.148(8)	C8–N8	1.138(8)
N1–Cu1–N7^{ii}	165.9(2)	N3–Cu2–N3^{iii}	180.0
N8–Cu3–N8^{i}	180.0	N5–Cu4^{i}–N5^{iii}	180.0
N4–Cu5–N4^{iv}	180.0	Cu1–N7^{ii}–C7^{ii}	115.7(6)
Cu1–N1–C1	139.2(6)	Cu2–N3–C3	143.0(7)
Cu3–N8–C8	130.5(6)	Cu4^{i}–N5–C5	120.8(5)
Cu5–N4–C4	122.7(6)	N5–C5–W1	179.3(7)
N1–C1–W1	178.1(7)	N6–C6–W1	177.8(7)
N2–C2–W1	176.9(7)	N7–C7–W1	178.0(8)
N3–C3–W1	178.3(7)	N8–C8–W1	177.1(7)
N4–C4–W1	176.1(8)	N22–Cu2–N22^{v}	180.0
N18–Cu1–N20	174.5(3)	N22–Cu2–N21^{v}	83.8(2)
N18–Cu1–N19	95.1(3)	N22^{v}–Cu2–N21^{v}	96.2(2)
N20–Cu1–N19	85.1(3)	N22–Cu2–N21	96.2(2)
N18–Cu1–N17	83.1(3)	N22^{v}–Cu2–N21	83.8(2)
N20–Cu1–N17	95.7(3)	N21^{v}–Cu2–N21	180.0
N19–Cu1–N17	169.3(3)	N24^{vi}–Cu3–N24	180.0
N18–Cu1–N1	90.1(3)	N24^{vi}–Cu3–N23	83.2(2)
N20–Cu1–N1	95.3(3)	N24–Cu3–N23	96.8(3)
N19–Cu1–N1	94.2(2)	N24^{vi}–Cu3–N23^{vi}	96.8(3)
N17–Cu1–N1	96.3(3)	N24–Cu3–N23^{vi}	83.2(3)
N26–Cu4–N26^{vii}	180.0	N23–Cu3–N23^{vi}	180.0
N26–Cu4–N25	84.6(3)	N28A^{viii}–Cu5–N27A^{viii}	89.7(9)
N26^{vii}–Cu4–N25	95.4(3)	N27A–Cu5–N27A^{viii}	180.0
N26–Cu4–N25^{vii}	95.4(3)	N27B^{viii}–Cu5–N28B^{viii}	80.3(9)
N26^{vii}–Cu4–N25^{vii}	84.6(3)	N27B–Cu5–N28B^{viii}	99.7(9)
N25–Cu4–N25^{vii}	180.0	N27B^{viii}–Cu5–N28B	99.7(9)
N28A–Cu5–N28A^{viii}	180.0	N27B–Cu5–N28B	80.3(9)
N27B^{viii}–Cu5–N27B	180.0	N28B^{viii}–Cu5–N28B	180.0
N28A–Cu5–N27A	89.7(9)	N28A–Cu5–N27A^{viii}	90.3(9)
N28A^{viii}–Cu5–N27A	90.3(9)		

[a] Symmetry transformations used to generate equivalent atoms: *i*: $x, y+1, z$; *ii*: $x+1, y, z$; *iii*: $x, y+2, z+1$; *iv*: $x, y+1, z+1$; *v*: $-x, -y+2, -z+1$; *vi*: $-x, -y+1, -z$; *vii*: $-x, -y, -z$; *viii*: $-x, -y+1, -z+1$.

Magnetic properties

The magnetic data of the title compound were recorded with an applied field $H = 1$ kOe in the temperature range 2–300 K. The cryomagnetic properties of the assembly are shown in Fig. 3. At room temperature, $\chi_M T$ is 1.88 cm^3 mol^{-1} K (3.88 μ_B) per Cu_3W_2, which is in good agreement with the expected spin-only value (1.875 cm^3 mol^{-1} K, 3.87 μ_B per Cu_3W_2) for three Cu(II) ($S = 1/2$) and two W(V) ($S = 1/2$) centers ($g = 2.0$). As the temperature is lowered, the $\chi_M T$ value monotonically increases, first slowly down to around 3 K and then abruptly up to a value of 71.44 cm^3 mol^{-1} K (23.90 μ_B) at 2 K. This value is significantly larger than the value expected (5.92 μ_B) for $S_T = 5/2$ of ferromagnetically coupled Cu_3W_2, and the abrupt increase in $\chi_M T$ around 3 K suggests the onset of a long-range ferromagnetic ordering in the three-dimensional network. In accord with this, the plot of $1/\chi_M$ *vs.* T below 50 K obeys the Curie–Weiss law [based on $1/\chi_M = (T-\theta)/C$] with a positive Weiss constant of $\theta = +1.96$ K (Fig. 3). The zero-field-cooled magnetization (ZFCM) at 100 Oe shows a rapid increase around 2 K [Fig. 4(a)], implying a magnetic phase transition at this point. The ferromagnetic ordering temperature T_c was further estimated to be around 2 K, from the abrupt increase of the zero-field alternating current (ac) susceptibility χ'_M, and the distinct appearance of a nonzero χ''_M, where χ'_M and χ''_M are the in-phase and out-of phase components of the susceptibility, respectively (Fig. 5). The field dependence of the magnetization has also been measured at 1.9 K; it increases very rapidly in low field [Fig. (4b)], reaching a value of 4.8 μ_B (per Cu_3W_2) at 6 T, which is very close to the expected theoretical value of 5 μ_B ($S = 5/2$) at saturation for ferromagnetic coupling. In addition, a very narrow hysteresis loop was observed at 1.9 K in a ± 2000 Oe field, the remnant magnetization and coercive field being *ca.* 0.3 Nβ and 12 Oe, respectively.

The ferromagnetic interaction between the Cu^{II} ($3d^9$) and W^{V} ($5d^1$) can be rationalized in terms of the strict orthogonality of the magnetic orbitals of these ions. According to the crystal structure and ligand-field theory, a copper(II) ion in an axially elongated octahedral surrounding (D_{4h}) has one unpaired

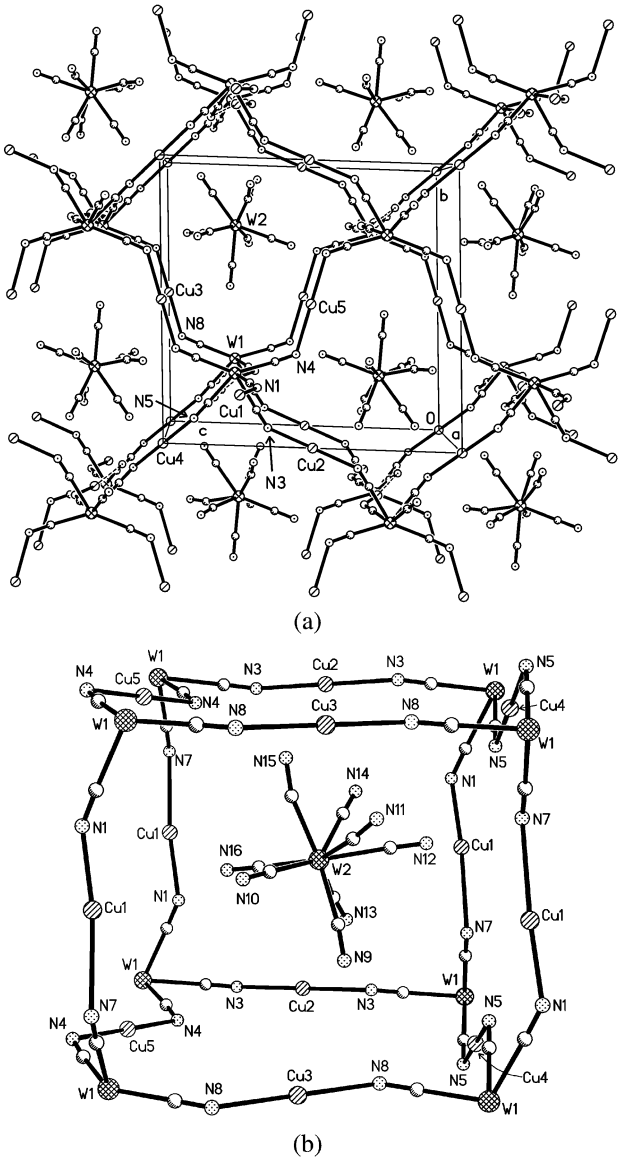

Fig. 2 (a) Projection of the 3-D network of $\{[Cu(en)_2]_3[W(CN)_8]_2{\cdot}H_2O\}_\infty$ in which the $[W(CN)_8]^{3-}$ anions act as templates. Non-bridged cyanides and en ligands are omitted for clarity. (b) Backbone of the W_8Cu_{12} cube-like unit with the $[W(CN)_8]^{3-}$ template.

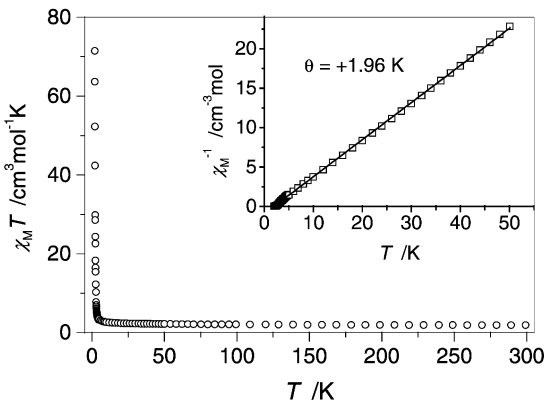

Fig. 3 Plot of $\chi_M T$ *vs.* T in the range of 2–300 K for $\{[Cu(en)_2]_3[W(CN)_8]_2{\cdot}H_2O\}_\infty$. Inset: temperature dependence of $1/\chi_M$ between 2 to 50 K. The solid line indicates the best fit obtained by the Curie–Weiss law (see text).

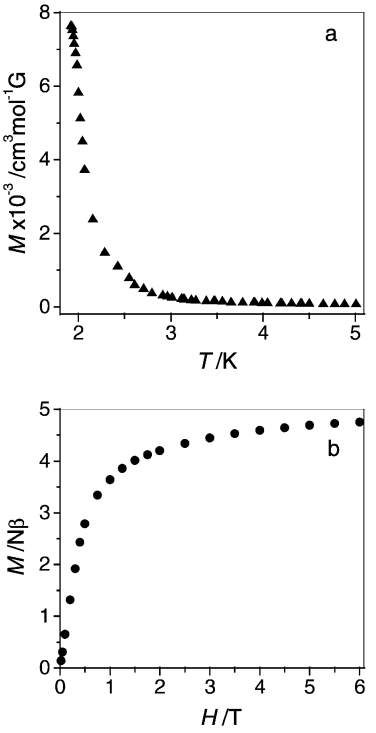

Fig. 4 (a) Temperature dependence of the magnetization M for $\{[Cu(en)_2]_3[W(CN)_8]_2{\cdot}H_2O\}_\infty$ with ZFCM ($H = 100$ Oe). (b) Field dependence of the magnetization M for $\{[Cu(en)_2]_3[W(CN)_8]_2{\cdot}H_2O\}_\infty$ at 1.9 K.

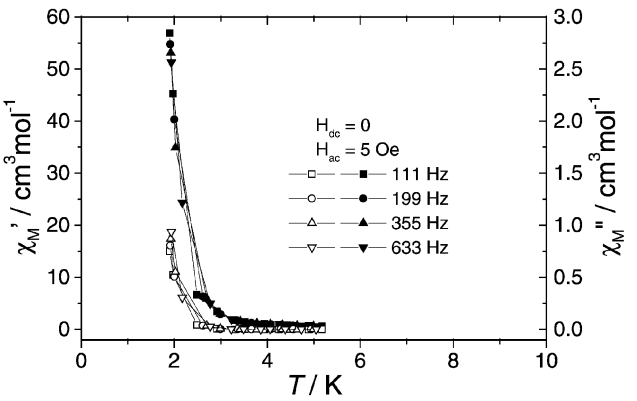

Fig. 5 Temperature dependence of the zero-field ac susceptibility of $\{[Cu(en)_2]_3[W(CN)_8]_2{\cdot}H_2O\}_\infty$, measured in a 5 Oe ac field with frequency 111–633 Hz. The filled symbols are for the in-phase component χ'_M, the open symbols are for the out-of-phase component χ''_M.

electron in a $d_{x^2-y^2}$ orbital (b_{1g}), which interacts with molecular orbitals of the cyano bridge having the same symmetry, producing a magnetic orbital with σ character.[37] A tungstate(v) ion in a square antiprism environment (D_{4d}) has unpaired electron density in the d_{z^2} orbital (a^1),[38,39] which interacts with other molecular orbitals of the same cyano bridge having appropriate symmetry, producing a magnetic orbital with π character. The σ/π interaction would lead to zero overlap and then to a strict orthogonality. However, the magnetic ordering temperature of the title compound is very low. This may be interpreted from the character of the structure of **1**. As discussed in the structural description, the axial Cu–$N_{cyanide}$ bond lengths are very long due to Jahn–Teller effects and the C–N–Cu angles are far from linear. This will markedly weaken the ferromagnetic interactions through the W–C–N–Cu linkages.

Conclusion

A novel cyanide-bridged bimetallic assembly $\{[Cu(en)_2]_3[W(CN)_8]_2\cdot H_2O\}_\infty$ has been obtained and structurally characterized. X-Ray crystallography of the assembly reveals a three-dimensional network structure extended by three kinds of Cu^{II}–CN–W^{V}–CN–Cu^{II} linkages. The network is based on a W_8Cu_{12} cube-like unit with eight W(V) ions at the corners of the cube and twelve Cu(II) ions at the middle of the edges. Interestingly, a coordination ion $[W(CN)_8]^{3-}$ is just capsulated in the cavity formed by the W_8Cu_{12} cube-like unit.

Cryomagnetic property studies show that a three-dimensional magnetic ordering occurs over the crystal lattice, and the T_C of the assembly was determined to be around 2 K. The low T_C of this 3-D complex is due to the long $Cu–N_{cyanide}$ bond lengths and the large Cu–N–C bent angles.

Acknowledgement

This work was supported by the National Natural Science Foundation of China.

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