

Synthesis, crystal structure and magnetic properties of an octacyanometallate-based 3-D $\text{Cu}^{\text{II}}\text{--W}^{\text{IV}}$ bimetallic assembly

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Abstract

The three-dimensional cyano-bridged bimetallic coordination polymer, $[\text{Cu}(\text{L})_2][\text{W}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ ($L = 3,10$ -diethanol-1,3,5,8,10,12-hexaaza-cyclotetradecane) **1**, has been synthesized and characterized. X-ray study shows that the asymmetric unit of the three-dimensional $\text{Cu}(\text{II})\text{--W}(\text{IV})$ polymeric assembly consists of four crystallized water molecules, two $[\text{Cu}(\text{L})]^{2+}$ cations and one $[\text{W}(\text{CN})_8]^{4-}$ anion. The Cu^{II} centers in compound **1** exhibit elongated octahedral geometries, while the W^{IV} centers adopt distorted square antiprism geometries. Each W^{IV} coordinated via four cyano groups to four Cu^{II} . The structure of compound **1** can be described as an infinite 3-D assembly of $\text{W} \cdots \text{Cu} \cdots \text{W}$ linkage. The thermal and magnetic behavior of this compound has been investigated. Variable-temperature magnetic susceptibility measurements reveal that there is a weak antiferromagnetic interaction between the Cu^{II} centers in compound **1**.

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1. Introduction

In the past decades, hexacyanometalate ions, acting as good building units, have been successfully utilized to obtain a large number of one-, two-, and three-dimensional cyano-bridged assemblies with high magnetic ordering temperature and interesting architectures [1,2]. The highest Curie temperature $T_c = 315$ K of all molecular materials was obtained for V–Cr hexacyanide. Recently, new molecular-based magnets have attracted a great deal of interest based on their diffuse orbitals, various geometrical structures, lower symmetries and rich magnetic exchange couplings using the $[\text{Mo}(\text{CN})_7]^{4-}$ [3], $[\text{M}(\text{CN})_8]^{n-}$ ($M = \text{W}, \text{Mo}; n = 3, 4$) [4] precursors.

The eightfold coordinated diamagnetic building blocks $[\text{M}(\text{CN})_8]^{4-}$ ($M = \text{W}, \text{Mo}$) offering eight bridged cyano ligands potentially being able to form tightly connected architectures, have been extensively exploited in recent years because of the whole range of structural dimensionality, magnetic and photomagnetic properties [5]. Among these, Cu^{II} complexes characterized by the electronic spin $S = 1/2$ along with the different coordination geometries were widely used as building blocks owing to their effective in design and synthesis of magnetic and photomagnetic cyano-bridged octacyanometalate-based assemblies. For example, discrete $[\text{Cu}^{\text{II}}(\text{bpy})_2]_2[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ [5a] and $\{\text{Mo}^{\text{IV}}(\text{CN})_2[\text{CNCu}^{\text{II}}(\text{tren})]_6\}(\text{ClO}_4)_8$ [6] photomagnetic molecules have been reported. 1-D chain topology is featured by $\{\text{Cu}_2^{\text{II}}(\text{NH}_3)_8[\text{Mo}^{\text{IV}}(\text{CN})_8]\}_n$ [7] whereas $\{[\text{Cu}(\text{cyclam})]_2[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 0.5\text{H}_2\text{O}\}$ [8] exhibits a 2-D structure. 3-D architecture is realized in $\{[\text{Cu}(\text{en})_2][\text{Cu}(\text{en})][\text{W}^{\text{IV}}(\text{CN})_8] \cdot \text{H}_2\text{O}\}_n$ [9] and $\{\text{Cu}_2^{\text{II}}[\text{Mo}^{\text{IV}}(\text{CN})_8]\} \cdot x\text{H}_2\text{O}$ [10] has photomagnetic properties. In addition, the macrocyclic ligands are potentially able to block part equatorial

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positions of the metal ion M^b and release apical coordination sites. A net-based approach to framework construction may theoretically predict the structural dimensionality of molecular assemblies based on the connection and the number of molecular nodes [8].

In order to better elucidate the role of coordination bridging geometry and 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-metal or by alternating different terminal ligands on the metal ions. For the recent study, we chose $[Cu(L)]^{2+}$ (the macrocyclic ligand L is 3,10-diethanol-1,3,5,8,10,12-hexaaza-cyclotetradecane) and $[W(CN)_8]^{4-}$ as building blocks to synthesize successfully a novel 3-D framework compound: $[Cu(L)]_2[W(CN)_8] \cdot 4H_2O$. In this paper, we report its preparation, X-ray single-crystal structure, thermogravimetric and magnetic properties.

2. Experimental

2.1. Physical 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 Nicolet FT-IR 170 SX spectrometer using KBr pellets. The magnetic measurements were carried out with a Quantum Design MPMS-5 SQUID magnetometer under an applied magnetic field of 10 kOe in the temperature range 1.8–300 K. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for the sample holder. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(X_M T)^{1/2}$, where X_M is the molar magnetic susceptibility corrected for the diamagnetism of the constituting atoms. Thermogravimetry (TG) analysis was performed using PerkinElmer Diamond TG/DTG instruments under helium atmosphere from 18 °C to 700 °C at a heating rate of 10 °C min^{-1} .

2.2. Preparations

Unless otherwise noted, all chemicals are commercially available, and reagent grade products were used without purification. $Cu(L)(ClO_4)_4$ and $K_4[W(CN)_8] \cdot 2H_2O$ are prepared according to the literatures [11,12].

$[Cu(L)]_2[W(CN)_8] \cdot 4H_2O$ (1). Well-shaped brown square prismatic crystals were grown in the dark at room temperature by slow diffusion of a DMF solution of $Cu(L)(ClO_4)_2$ (0.2 mol) and an aqueous solution of $K_4[W(CN)_8]$ (0.1 mol) in a U-shaped tube containing agar for two months. The resulting crystals were collected, washed with H_2O and dries in air. Calcd for $C_{32}H_{68}Cu_2WN_{20}O_8$: C, 32.76; H, 5.80; N, 23.90; W, 15.69; Cu, 10.48%. Found: C, 32.68; H, 5.96; N, 23.96; W, 15.71; Cu, 10.87.

IR (cm^{-1}): 2094.69, 2129.01 cm^{-1} . The infrared C–N stretch (2129.01 cm^{-1}) is shifted toward higher frequencies

from those of $K_4[W(CN)_8] \cdot 2H_2O$ (2096.09 cm^{-1} , 2125.65 cm^{-1}) clearly showing a coordination of a few CN groups to copper ions. The stretches observed at 2094.69 (sh, s) cm^{-1} show that free CN groups are also present in this compound. The IR feature is confirmed by the X-ray crystallographic analysis.

2.3. Crystallography

A single crystal of compound **1** was selected for lattice parameter determination and collection of intensity data at 293(2)K on a Bruker SMART APEX CCD area detector diffractometer with graphite monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω – 2θ scan mode to a maximum 2θ value of 52.0°. The intensity data were corrected for Lorentz and polarization effects during data reduction. The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically. The sites of hydrogen atoms were placed by the geometry. The contributions of these hydrogen atoms were included in the structure factor calculations. All computations were carried out using the SHELXTL-PC program package [13]. Analytical anomalous dispersion corrections were incorporated. The maximum and minimum residual densities in the final difference Fourier map were 0.70 and $-0.83 e/\text{\AA}^3$, respectively.

Crystal data for **1**: $C_{32}H_{68}Cu_2WN_{20}O_8$, $M = 1171.99$, tetragonal, space group $I4(1)/a$, $a = b = 20.0629(17) \text{ \AA}$, $c = 15.4502(15) \text{ \AA}$, $V = 6219.0(10) \text{ \AA}^3$, $Z = 4$, $D_c = 1.252 \text{ g/cm}^3$, $F(000) = 2384$, $\mu = 2.574 \text{ mm}^{-1}$. 16,436 reflections measured, 3058 unique ($R_{int} = 0.058$). $S = 0.97$. The final $R_1 = 0.0451$ and $wR_2 = 0.1095$ for 2461 observed reflections [$I > 2\sigma(I)$] and 153 parameters.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the ORTEP drawing of the asymmetric unit of compound **1**, which consists of a $[W(CN)_8]^{4-}$ ion, two $[Cu(L)]^{2+}$ cations and four crystallized water molecules. Projection of $[W(CN)_8]^{4-}$ moiety coordinates via four cyano bridged to four $Cu(L)$ fragments, respectively, and the four other cyano groups being terminal. The projections of compound **1** along c -axis and a -axis are shown in Figs. 2 and 3, respectively. Selected bond lengths and bond angles are listed in Table 1. Hydrogen bonding scheme lengths and angles are list in Table 2.

As expected, the W site in $[W(CN)_8]^{4-}$ building block adopts a square antiprism geometry (D_{4h}) changed from the dodecahedral one in the starting compound $K_4[W(CN)_8]$, in which the average angle between the W–CN and the quasi-8-axis is 56.5°. The average value of edge lengths of the basal plane ranges from 2.556 Å to 2.615 Å and is 1.1959 times that of all W–CN bond lengths changed from 2.129 Å to 2.195 Å, comparable with those

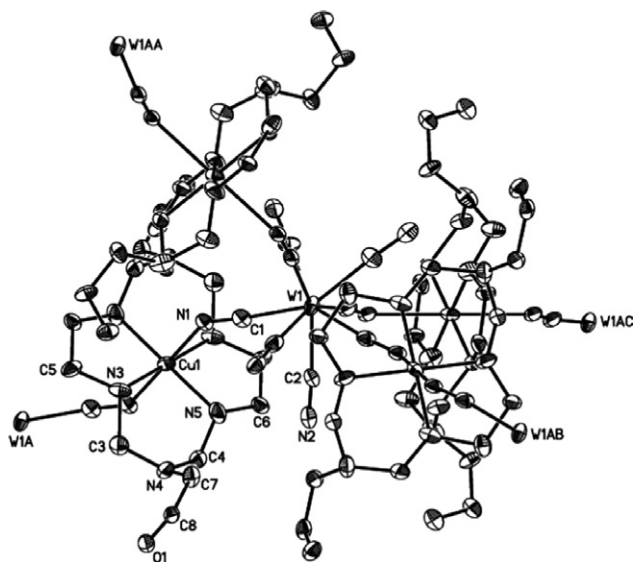


Fig. 1. The ORTEP drawing of compound 1 (omitting hydrogen atoms).

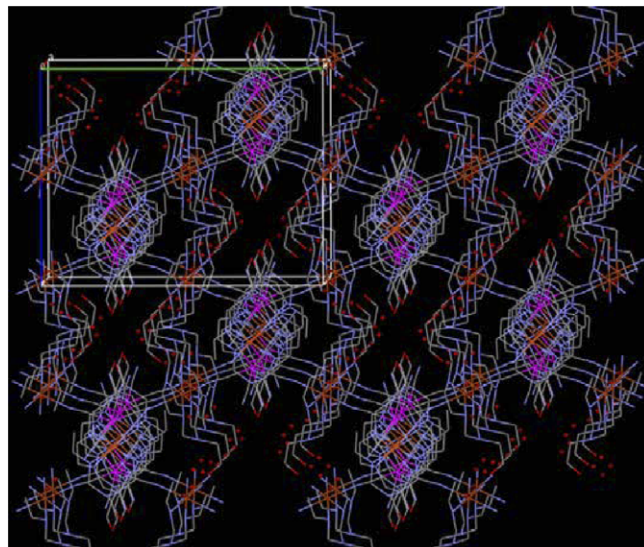
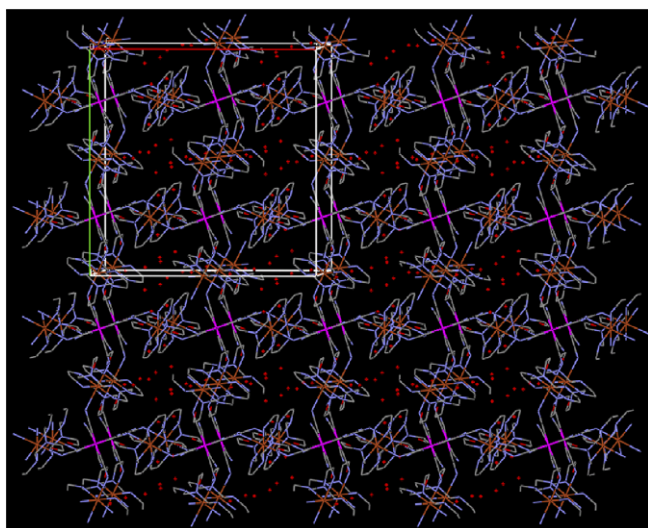
Fig. 3. Projection of compound 1 along *a*-axis.Fig. 2. Projection of compound 1 along *c*-axis.

Table 1

Selected bond distances (Å) and bond angles (°) for the compound 1

Atom	Distance	Atom	Distance
W1–C1	2.129(4)	N3–C5	1.500(7)
W1–C2	2.195(5)	N4–C3	1.493(7)
Cu1–N1	2.468(4)	N4–C7	1.480(6)
Cu1–N3	2.052(4)	N4–C4	1.532(7)
Cu1–N5	2.026(4)	N5–C6	1.464(7)
N1–C1	1.146(6)	N5–C4	1.460(7)
N2–C2	1.241(7)	C7–C8	1.507(8)
N3–C3	1.603(6)	O1–C8	1.282(6)
Atom	Angle	Atom	Angle
C1–W1–C2	74.4(2)	Cu1–N3–C3	110.6(3)
W1–C1–N1	174.6(4)	Cu1–N3–C5	113.2(3)
W1–C2–N2	174.5(5)	Cu1–N5–C4	113.5(3)
N1–Cu1–N3	86.71(14)	Cu1–N5–C6	115.6(3)
N1–Cu1–N5	89.87(14)	C3–N3–C5	113.9(4)
N3–Cu1–N5	97.58(16)	C3–N4–C7	125.1(4)
N3–C3–N4	117.4(4)	C3–N4–C4	109.4(4)
N4–C4–N5	118.7(4)	C4–N4–C7	114.6(4)
N4–C7–C8	114.2(4)	C4–N5–C6	119.5(4)
Cu1–N1–C1	138.1(4)	O1–C8–C7	112.7(4)

of the most favorable polyhedron (MFP) of square antiprism (57.1° and 1.2156 times) [14].

The W atom is surrounded by eight cyano groups in a distorted square antiprism, with W–C distance ranging from 2.129(5) Å to 2.164(5) Å. All of angles N–C–W are $174.6(4)^\circ$, which exhibits linear linkages closed 180° and highly delocalized electronic density between W^{IV} and CN groups. Each Cu^{II} is in an elongated octahedral coordination environment, in which four nitrogen atoms (N3, N5, N3₁ and N5₁) from L are located at the equatorial positions with the Cu–N_{eq} bond distances in the range of 2.027(5)–2.052(4) Å, while the axial sites are occupied by two nitrogen atoms (N1 and N1₁) from the bridging cyanide groups on $[W(CN)_8]^{4-}$ anion. The Cu–N cyanide interactions at the apical positions are occurring to each Cu^{II} atom. The axial Cu–N_{ax} bonds for Cu1

(Cu1–N1 = 2.468(4) Å) are much longer than the equatorial Cu–N_{eq} bonds (mean value is 2.040 Å). But all linkages between Cu^{II} ions and CN groups are not linear like those between W and CN. All angles of Cu–N–C are $138.2(4)^\circ$, which are similar to those in other complexes of this type of system [4f,8,15]. It is indicative of the flexibility of W–CN–Cu linkages in Cu^{II} – $W^{IV}(CN)_8$ system that may lead to the versatile structures of bimetallic octacyanides.

Through the four bridging cyano groups of $[W(CN)_8]$ unit, W and Cu atoms are linked by W–CN–Cu zigzag linkage to construct an infinite plane structure along *c* axis (see Fig. 2). The distance of adjacent $W \cdots Cu$ is 5.375 Å. Meanwhile, along *a* axis, the plane is also connected together by W–CN–Cu linkages to form 3-D porous network structure, as depicted in Fig. 3. The crystallized water

Table 2
Hydrogen bonding scheme lengths (Å) and angles (°) for compound 1

D–H···A bond	D–H distance	H···A distance	D···A distance	Angle of D–H···A
O1–H1C···O2	0.8500	2.3000	2.989(8)	138.00
N5–H5···N2	0.9100	2.4700	3.168(6)	134.00
C6–H6B···N2	0.9700	2.2300	3.040(6)	140.00

molecules reside in the porous cavities formed by the 3-D structure. Lattice water molecules themselves form a O1–H1C···O2 H-bond with the distance 2.989(8) Å of O1···O2. Hydrogen bonding scheme lengths and angles is list in Table 2.

3.2. Thermal analysis

Thermogravimetric analysis revealed that there were two well-pronounced weight loss steps with the temperature was increased. The two steps can be determined by inflection points at 55 and 190 °C. The first weight loss step having weight loss of 23.3% corresponds with the loss of crystallized water molecules located in the channels. The reason that the weight loss is bigger than theoretic one (6.1%) is that the samples are not dried before test. At a temperature above 190 °C, decomposition of the original structure occurs (see Fig. 4).

3.3. Magnetic properties

The magnetic data of compound 1 were recorded with an applied field $H = 2$ kOe in the temperature range 1.8–300 K (Fig. 5). At the room temperature, $\chi_M T$ is $0.738 \text{ emu K mol}^{-1}$ ($2.43 \mu_B$) per Cu_2W , which is in good agreement with the expected spin-only value ($0.750 \text{ emu K mol}^{-1}$, $2.45 \mu_B$ per Cu_2W) for two Cu^{II} ($S_{\text{Cu}} = 1/2$) and one W^{IV} ions ($S = 0$) center ($g = 2.0$). As the temperature is lowered, the complex exhibits Curie-like behavior and the Weiss constant obtained from the Curie–Weiss fitting is -5.2 K, which indicates the presence of

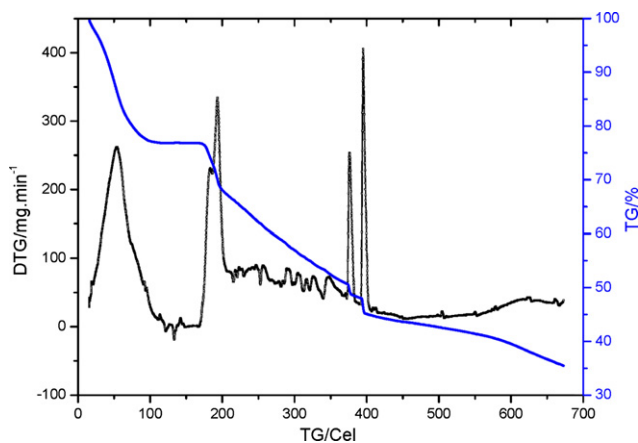


Fig. 4. Thermal analysis curve of compound 1.

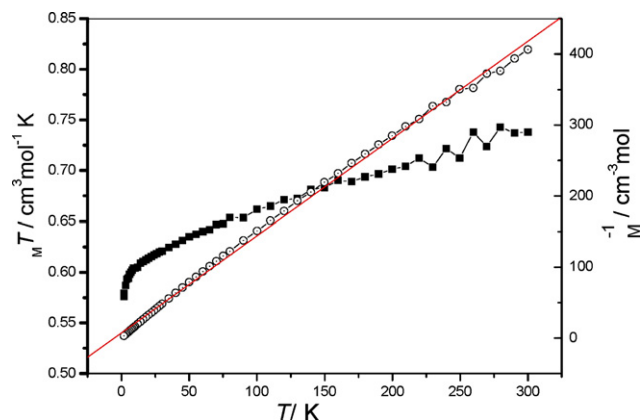


Fig. 5. Plots of $\chi_M T$ (○) and $1/\chi_M$ (■) of compound 1 versus T .

weak antiferromagnetic interaction between the adjacent paramagnetic Cu^{II} ions through the diamagnetic NC–W(IV)–CN bridge in the complex (see Fig. 5).

4. Conclusion

A novel cyano-bridged bimetallic coordination polymer, $[\text{Cu}(\text{L})_2][\text{W}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$, has been characterized structurally, thermally and magnetically. The complex shows a 3-D framework structure, in which W^{IV} centers adopt a distorted square antiprism geometry. Variable-temperature magnetic susceptibility measurements reveal that there is weak antiferromagnetic interaction between the Cu^{II} centers in the compound.

5. Supplementary material

CCDC 618421 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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