Crystal structure and magnetic properties of a copper(II)–octacyanotungstate(V) bimetallic complex coordinated with macrocyclic ligand

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ABSTRACT

A new cyanide-bridged heterobimetallic assembly based on octacyanotungstate(V) as building block, $\{[Cu^{II}(L)]_3[W^V(CN)_8]_2\}\cdot[Cu^{II}(L)\cdot 2H_2O]\cdot(ClO_4)_2\cdot 4H_2O$ **1** (L = 3,10-dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane), has been prepared and characterized. X-ray single-crystal analysis reveals that **1** displays a two-dimensional structure with corrugated sheets, in which the 12-membered rings are the basic building units. Magnetic studies reveal that **1** displays a ferromagnetic interaction between Cu^{II} and W^V through cyano bridges.

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1. Introduction

Recently, $[M(CN)_8]^{3-/4-}$ (M = Mo and W) based bimetallic assemblies have attracted much attention due to their intriguing magnetic, photo-magnetic and porous properties as well as potential applications in functional materials and molecular devices [1–4]. Among them, Cu^{II} complexes characterized by the electronic spin $S = 1/2$ along with the different coordination geometries have been widely used as building blocks in design and synthesis of cyano-bridged octacyanometalate-based assemblies [5]. These assemblies assume oligonuclear, one-, two- and three-dimensional structures and exhibit antiferro-, para-, ferro-, ferri-, and photomagnetic behaviors.

For $Cu^{2+}/[M(CN)_8]^{3-/4-}$ (M = Mo and W) bimetallic systems, the magnetic properties are influenced by the overlap between the M $d\pi$ and Cu $d\sigma$ orbits resulting in ferromagnetic interactions caused by orbital orthogonality. To explore the magnetic-exchange properties between paramagnetic centers for the latter in this system, it is necessary to control specific binding sites for bridging units. In view of this point, Cu^{II} complexes containing macrocyclic ligands, in which macrocyclic ligands block partly coordination sites of the metal ions and release their apical ones, can be used to construct cyano-bridged bimetallic complexes with octacyanometalate $[M(CN)_8]^{3-/4-}$ ions. The macrocyclic ligands used to encapsulate the cyanometallates may take part in intermolecular interactions and open up further possibilities to influence the structure and properties of the polymetallic assemblies. To explore structural diversity in octacyanometalate-based systems, we have attempted to design some cyano-bridged bimetallic assemblies with different structural patterns and rich magnetic properties by using macrocyclic ligands [6,7]. For the recent study, we have extended our work to choose $[Cu(L)]^{2+}$ (L = 3,10-dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) as building block to synthesize successfully an octacyanotungstate(V)-based bimetallic complex $\{[Cu^{II}(L)]_3[W^V(CN)_8]_2\}\cdot[Cu^{II}(L)\cdot 2H_2O]\cdot(ClO_4)_2\cdot 4H_2O$ **1**. Herein, we report its preparation, crystal structure and magnetic properties.

2. Experimental

2.1. Physical measurements

Elemental analyses for C, H and N were performed at a Perkin–Elmer 240C analyzer. Cu and W analyses were made on a Jarrell-Ash 1100 + 2000 inductively coupled plasma quantometer (ICP). Infrared spectra were recorded on a Nicolet FT-17SX spectrometer with KBr pellets in the 4000–400 cm^{-1} region. Thermogravimetric analysis was performed using Perkin–Elmer Diamond TGA instruments under a He atmosphere in the temperature range 30–420 °C with the heating rate of 2 °C min^{-1}. The magnetic measurements for **1** were carried out with a Quantum Design MPMS-5 SQUID magnetometer under an applied magnetic field of 2 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.

2.2. Preparations

All chemicals and solvents in the synthesis were of reagent grade and used as received. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with great care.

2.2.1. {[Cu(L)]₃[W(CN)₈]₂}·[Cu(L)·2H₂O]·(ClO₄)₂·4H₂O **1**.

Well-shaped brown crystals of **1** suitable for X-ray single-crystal structure determination were grown at room temperature by slow diffusion of a DMF solution (15 mL) of [Cu(L)](ClO₄)₂ (0.3 mmol) [8] and an aqueous solution (15 mL) of Cs₃[W(CN)₈]· 2H₂O (0.15 mmol) [9] in a U-shaped tube containing agar for about 2 months. All manipulations were in the dark to avoid photoreduction of Cs₃[W(CN)₈]·2H₂O. The resulting crystals were collected, washed with H₂O and dried in air. Anal. calcd. for C₇₂H₁₄₈Cu₄W₂-N₄₀O₁₄Cl₂: C, 34.71; H, 5.99; N, 22.50; W, 14.76; Cu, 10.20%. Found: C, 34.78; H, 5.92; N, 22.35; W, 14.85; Cu, 10.22%.

IR (KBr): ν(C≡N) 2140, 2214 cm⁻¹. The existence of perchlorate anions is detected as strong multiple peaks in the IR spectra in the range 1128–1064 cm⁻¹. A very strong band at *ca.* 2140 cm⁻¹ is reasonably assigned to the terminal cyano stretching vibration (2130–2170 cm⁻¹) in [W(CN)₈]³⁻ [4]. The strong peak at *ca.* 2214 cm⁻¹ suggests the advent of bridging cyanide in **1**, indicating the formation of Cu^II—CN—W^V bridges.

2.3. Crystallography

Diffraction data for **1** were collected at 291(2) K on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with the ω scan mode. The structures were solved by direct methods and refined by full matrix least-squares techniques based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. The idealized positions of the hydrogen atoms were located by using a riding model and the hydrogen atoms bonded to the water molecule were not found. All computations were carried out using the SHELXTL-PC program package [10]. Selected crystal data collection and refinement parameters are given in Table 1. Selected bond distances and angles are in Table 2.

Table 1
Data collection and structure refinement for **1**.

Formula	C₇₂H₁₄₈Cu₄W₂N₄₀O₁₄Cl₂
F_w	2491.20
Crystal system	Triclinic
Space group	P-1
a (Å)	12.107(3)
b (Å)	14.735(3)
c (Å)	15.801(4)
α (°)	93.91(2)
β (°)	111.41(2)
γ (°)	96.20(2)
V (Å³)	2591.3(11)
Z	6
D_c (gm cm⁻³)	1.5906
μ (Mo Kα) (mm⁻¹)	3.143
Total/unique data	10474/9640
Observed data [$I > 2\sigma(I)$]	4149
R (int)	0.0204
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0331/0.0732
R_1, ωR_2 (all data)	0.0447/0.0753

Table 2
Selected bond distances (Å) and angles (°) for **1**.

W—C(29)	2.152(5)	Cu(1)—N(16)	2.648(5)
W—C(30)	2.181(4)	Cu(2)—N(4)	2.004(4)
W—C(31)	2.159(5	Cu(2)—N(5)	1.996(4)
W—C(32)	2.170(5)	Cu(2)—O(7)	2.596(4)
W—C(33)	2.173(5)	Cu(3)—N(7)	2.002(4)
W—C(34)	2.160(5)	Cu(3)—N(8)	2.009(4)
W—C(35)	2.146(6)	Cu(3)—N(14)	2.654(4)
W—C(36)	2.155(5)	Cu(4)—N(10)	2.000(4)
Cu(1)—N(1)	2.016(4)	Cu(4)—N(11)	2.024(4)
Cu(1)—N(2)	1.997(4)	Cu(4)—N(17)	2.614(4)
C(32)—N(16)—Cu(1)	147.6(4)	N(16)—C(32)—W	175.6(4)
C(30)—N(14)—Cu(3)	145.4(4)	N(17)—C(33)—W	175.6(5)
C(33)—N(17)—Cu(4)	147.2(4)	N(18)—C(34)—W	178.0(4)
N(13)—C(29)—W	178.2(5)	N(19)—C(35)—W	175.6(4)
N(14)—C(30)—W	175.7(4)	N(20)—C(36)—W	177.3(5)
N(15)—C(31)—W	177.4(5)		

3. Results and discussion

3.1. Crystal structure

The crystal structure of **1** consists of neutral {[Cu(L)]₃[W(CN)₈]₂} skeleton, isolated [Cu(L)·2H₂O]²⁺ and perchlorate counter-ions, and four crystallized water molecules (Fig. 1). In the repeating fragment {Cu$_3^{II}$W$_2^V$}$_n$, each W atom has three bridging and five terminal cyano ligands arranged in a slightly distorted square antiprismatic geometry. The W—C bond distances range from 2.146(6) Å to 2.181(4) Å. All of angles W—CN range from 175.6(4)° to 178.2(5)°, which exhibits linear linkages close to 180° and highly delocalized electronic density between W^V ion and CN groups. The coordination environment of [W(CN)₈]³⁻ is typical for the cyano-bridged octacyanotungstates reported previously [11].

In the structure of **1**, there are two different types of Cu^II centers. In Cu1, Cu3 and Cu4 centers, each Cu^II atom is in an elongated octahedral coordination environment, in which four nitrogen atoms from L ligand are located at the equatorial positions with the Cu—N$_{eq}$ bond distances in the range of 1.997–2.024 Å, while the axial sites are occupied by two nitrogen atoms from bridging cyanide groups of [W(CN)₈]³⁻, respectively. The axial Cu—N$_{ax}$ distances (the average value is 2.639 Å) are much longer than those of equatorial ones (the average value is 2.008 Å) due to Jahn–Teller effects. The Cu—NC bridging units appear as significantly bent (the average value is 146.7°). The bonding parameters of [Cu(L)]²⁺ are close to those found in related complexes containing macrocyclic ligand L reported previously [6].

The other copper center Cu2 also displays a distorted octahedral geometry. The Cu2 atom is surrounded by the four nitrogen atoms from L ligand in the equatorial plane and the two oxygen atoms from two coordinate water molecules in the apical direction, respectively. So its coordination environment is different from Cu1, Cu3 and Cu4 centers. The average Cu2—O length is 2.596 Å, which is much longer than those equatorial Cu2—N lengths (the average value is 2.000 Å).

As displayed in Fig. 2, the 12-membered rings are the basic building units of the corrugated two-dimensional sheets. The rings with each offset by 11 Å have dimensions of 11 Å (W1···W1A) × 22 Å (W1···W1D). The sheets contain [Cu(L)(μ-CN)₂]²⁺ and three-connected [W(CN)₅(μ-CN)₃]³⁻ units, which are linked *via* cyanides into 12-membered rings. As seen in Fig. 3, the separation between adjacent corrugated sheets, which are stabilized by isolated [Cu(L)·2H₂O]²⁺, perchlorate counterions, and crystallized water molecules through hydrogen-bonds, is 10 Å (Cu···Cu). The two-dimensional layered structure of **1** is similar to those of octacyanometalate-based bimetallic assemblies [12–15].
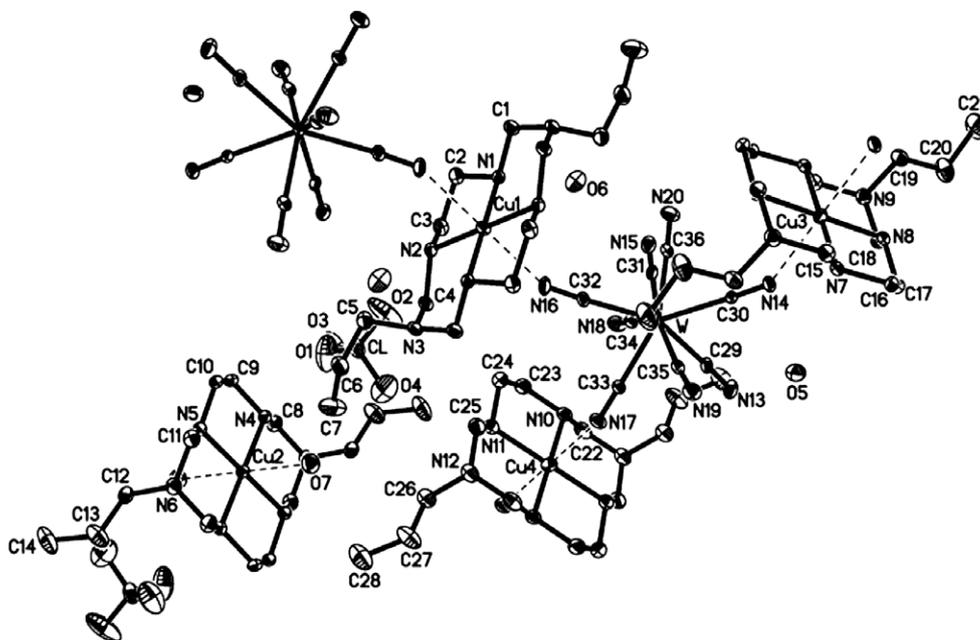
Fig. 1. ORTEP view of **1**, showing the atom labeling. Hydrogen atoms are omitted for clarity and thermal ellipsoids are presented at the 30% probability level.
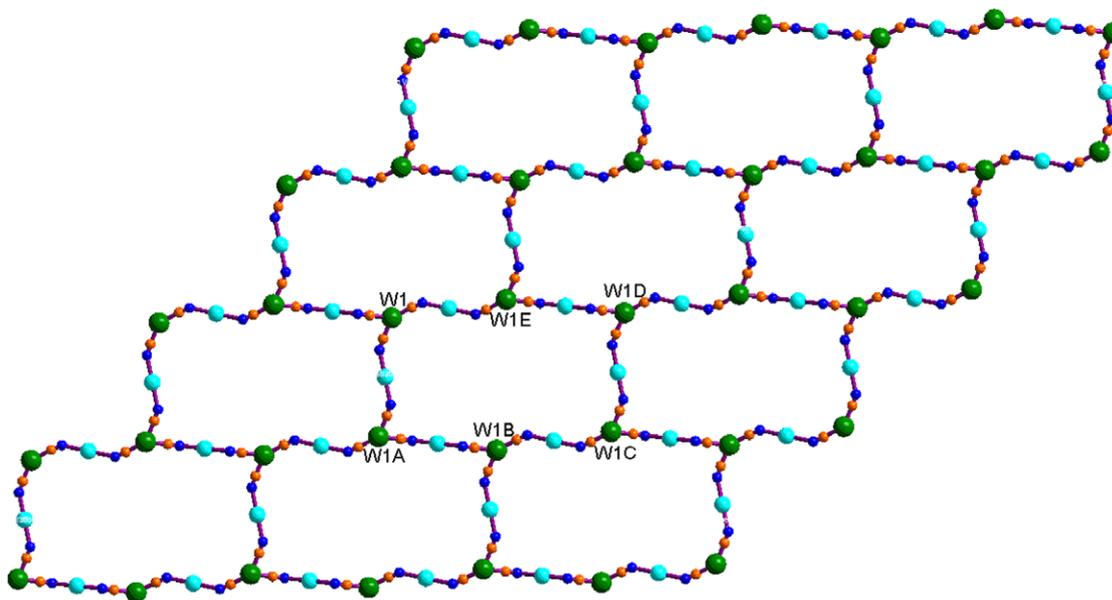

Fig. 2. View of the structure in the *ac* plane of **1**. Isolated [Cu(L)·2H$_2$O]$^{2+}$, perchlorate counterions and water molecules are omitted for clarity.

3.2. Thermal analysis

As mentioned, two water molecules coordinated to Cu2 atom and four crystallized water molecules are contained in the asymmetric unit of **1**. The TGA curve shows the weight loss of 2.87% from 40 to 74 °C, corresponding to the loss of the four crystallized water molecules (calcd. 2.89%). Upon heating to 94 °C, the two coordinated water molecules release with the weight loss of 1.44% (calcd. 1.45%). The remaining complex is heated to 200 °C without any additional weight decrease. At temperatures above 200 °C, framework decomposition occurred.

3.3. Magnetic properties

The magnetic susceptibilities of **1** were measured with an applied field H = 2 kOe in the temperature range 1.8–300 K. The plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T are given in Fig. 4a. At room temperature, the $\chi_M T$ per Cu$_4$W$_2$ unit is 2.35 emu K mol^{-1} (4.34 μ_B), which is slightly higher than the spin-only value of 2.25 emu K mol^{-1} (4.24 μ_B) expected for an uncoupled spin system (four S_{Cu} = 1/2, two S_W = 1/2) with g = 2.0. On lowering the temperature, the $\chi_M T$ value monotonically increases, first gradually down to *ca.* 15 K and then sharply up to a value of 11.36 emu K mol^{-1} (9.53 μ_B) at 1.8 K, which is larger than the value of 6.0 emu K mol^{-1} (6.93 μ_B) for the S_T = 3 state resulting from the ferromagnetic coupling of four Cu(II) ions (S = 1/2) and two W(V) ions (S = 1/2). The plot of $1/\chi_M$ vs. T obeys the Curie–Weiss law with a positive Weiss constant θ = +4.1 K, which also indicates the presence of a ferromagnetic coupling between Cu(II) and W(V) ions. The field dependence of the magnetization measured at 1.8 K is shown in Fig. 4b. The magnetization increases very rapidly in low field and reaches a saturation of magnetization above *ca.* 50 kOe. The
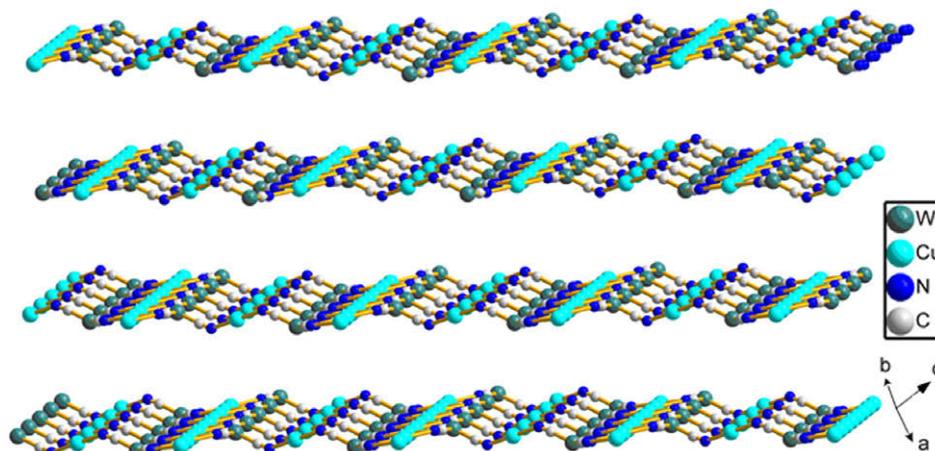
Fig. 3. Topological diagram of **1**, showing two-dimensional corrugated sheets.
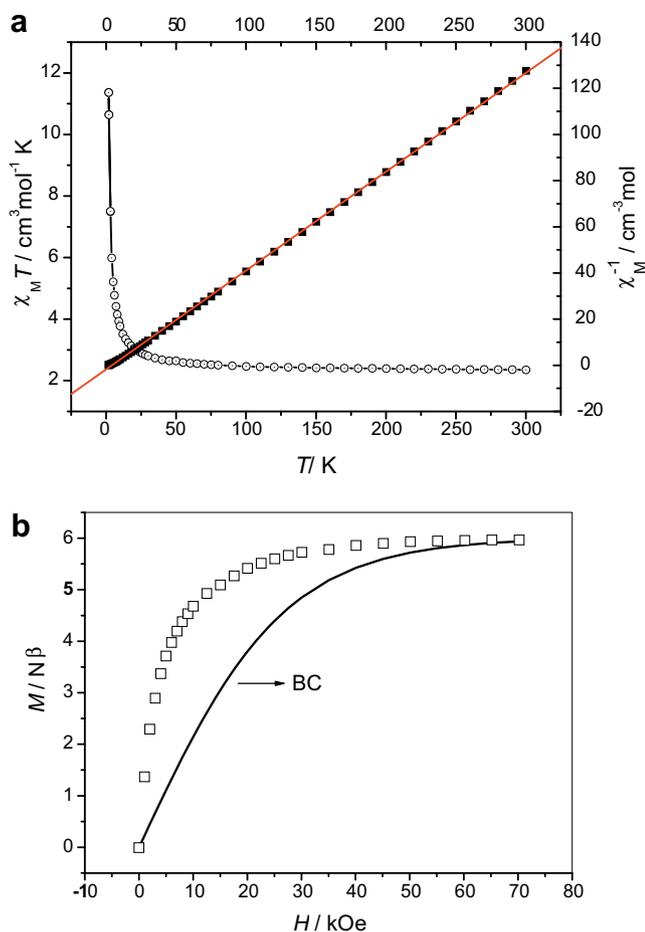

Fig. 4. (a) Temperature dependence of $\chi_M T$ (■) and $1/\chi_M$ (○) for **1** measured at 2 kOe. The solid line represents the fit obtained by the Curie–Weiss law (see text). (b) Field dependence of the magnetization for **1** at 1.8 K. The Brillouin curve (BC) for the independent four Cu(II) and two W(V) ions is given at 1.8 K.

saturation magnetization M_s = 5.96 $N\beta$ is close to the expected S = 3 value of 6 $N\beta$ for the ferromagnetic Cu_4W_2 system. The experimental curve at 1.8 K is always higher than that derived from the Brillouin function, confirming further ferromagnetic coupling between the adjacent Cu(II) and W(V) ions. The ferromagnetic interaction between the Cu(II) and W(V) can be rationalized in terms of the strict orthogonality of the magnetic orbits of these ions.

4. Conclusion

In the present paper, a new copper(II)-octacyanotungstate(V) bimetallic complex, $\{[Cu(L)]_3[W(CN)_8]_2\}\cdot[Cu(L)\cdot2H_2O]\cdot(ClO_4)_2\cdot4H_2O$ (**1**), using macrocyclic ligand has been synthesized and structurally characterized. X-ray crystallography reveals that **1** displays a two-dimensional structure with corrugated sheets, in which the 12-membered rings are the basic building units. Magnetic studies reveal that **1** displays a ferromagnetic interaction between Cu^{II} and W^V through cyano bridges.

5. Supplementary materials

CCDC 624451 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).

Acknowledgment

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