

Synthesis, crystal structure and magnetic properties of a three-dimensional cyano-bridged heterometallic complex $\{\text{Ni}^{\text{II}}(\text{Me}_6\text{-[14]ane-N}_4)\}_2[\text{W}^{\text{IV}}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$

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Abstract

Self-assembly of $[\text{W}(\text{CN})_8]^{4-}$ and $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}^{2+}$ ($\text{Me}_6\text{-[14]ane-N}_4 = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$) leads to a novel three-dimensional cyano-bridged complex $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}_2[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$ (**1**), which was characterized by IR, elemental analysis, ICP, TGA and SC-XRD. Magnetic behavior of the complex shows a characteristic of combination of zero-field splitting of Ni^{2+} in an axially distorted octahedral surrounding and a weak antiferromagnetic interaction between Ni^{2+} ions through the diamagnetic $[\text{W}(\text{CN})_8]^{4-}$ bridges.

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Recently, multidimensional extended systems based on octacyanometalate $[\text{M}(\text{CN})_8]^{3-/4-}$ ($\text{M} = \text{Mo}, \text{W}$ and Nb) building blocks have attracted much attention because of their unique structures and physicochemical properties. Among them, the bimetallic assemblies built by $\text{Mn}(\text{II}, \text{III})$, $\text{Cu}(\text{II})$ and $\text{Co}(\text{III})$ complexes with octacyanometalate anions have been surveyed extensively [1–3]. However, just a few bimetallic assemblies based on $\text{Ni}(\text{II})$ and $\text{M}(\text{IV}, \text{V})$ ($\text{M} = \text{Mo}, \text{W}$ and Nb) building blocks have been investigated, including isolated clusters [4–6], one-dimensional [7,8] and two-dimensional [4,7] structures. Although the preparations, infrared and magnetic studies of the compounds $\text{M}_2^{\text{II}}[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot n\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Zn}, \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}, \text{Mn}$; $n = 2\text{--}9$) [9] have been reported for more than thirty years, the structures of $\text{M}_2^{\text{II}}[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot$

$8\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Co}, \text{Mn}, \text{Fe}$) were resolved recently [10,11]. All of them have similar three-dimensional nanoporous structures. To our knowledge, however, no three-dimensional $\text{Ni}(\text{II})\text{-M}(\text{IV}, \text{V})$ ($\text{M} = \text{Mo}, \text{W}$ and Nb) polymers have been characterized by single-crystal X-ray analysis to date. In recent years, the three-dimensional octacyano-based coordination assemblies have attracted considerable interest from the viewpoint of the construction and their potential application as spin carriers in molecular spintronics. In the present paper, we report the synthesis, structure and magnetic properties of a new cyano-bridged complex $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}_2[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$ ($\text{Me}_6\text{-[14]ane-N}_4 = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$) (**1**) with a distorted diamond network, which is the first three-dimensional structural motif found in the bimetallic assembly based on Ni^{2+} complex and $[\text{M}(\text{CN})_8]^{3-/4-}$ ($\text{M} = \text{Mo}, \text{W}$ and Nb).

Pale yellow crystals of complex **1** suitable for X-ray single-crystal structure determination were grown at room

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temperature by slow diffusion of a DMF solution (15 cm³) of {Ni(Me₆-[14]ane-N₄)}(ClO₄)₂ [12] (0.3 mmol) and an aqueous solution (15 cm³) of K₄[W(CN)₈]·2H₂O [13] (0.15 mmol) in a U-shaped tube containing agar for three months. Anal. Calc. for C₄₀H₈₄N₁₆Ni₂O₆W: C, 40.49; H, 7.14; N, 18.89; Ni 9.89; W, 15.49; Found: C, 40.46; H, 7.13; N, 18.90; Ni, 9.87; W, 15.51%.

The IR spectrum of complex **1** exhibits two main peaks at 2111 cm⁻¹ and 2145 cm⁻¹. Terminal cyano ligands in [M(CN)₈]⁴⁻ (M = Mo, W) generally exhibit sharp, very intense bands in the region 2070–2130 cm⁻¹, while bridged cyano ligands shift to higher frequencies [2]. Therefore, a very strong band at 2111 cm⁻¹ is reasonably assigned to the terminal cyano stretching vibration. The strong peak at 2145 cm⁻¹ confirms the presence of bridging cyano groups.

Thermogravimetric analysis were carried out under a He atmosphere in the temperature range 20–600 °C with a heating rate of 10 °C/min. Thermal analysis shows that there were two well-pronounced weight loss steps when the temperature was increased for complex **1**. The two steps can be determined by inflection points at 50 °C and 290 °C. The first weight loss step of 9.13% corresponds to the loss of crystal lattice water molecules located in the channels (calcd. 9.10%). At temperatures above 290 °C framework decomposition occurred.

The asymmetric units of the structure [14] for complex **1** consist of two halves of {Ni(Me₆-[14]ane-N₄)}²⁺ cations, half a [W(CN)₈]⁴⁻ anion and three H₂O molecules (Fig. 1). In the [W(CN)₈]⁴⁻ fragment, each W atom has four bridging and four terminal cyano ligands arranged in a slightly distorted square antiprismatic geometry. The mean W–C and C–N distances are 2.158 Å and 1.138 Å, respectively. The bridging CN ligands exhibit almost linear W–C–N units with the angles ranging from 172.8(4)°

to 179.0(5)° and significantly bent Ni–N–C sequences (151.3(4)° and 158.4(4)° for Ni1–N1–C1 and Ni2–N2–C2, respectively, which are typical for cyano-bridged octacyanides [16–21]).

In the {Ni(Me₆-[14]ane-N₄)}²⁺ unit, each Ni atom is hexacoordinate and presents a distorted octahedral geometry in which the four N atoms from the macrocyclic ligand Me₆-[14]ane-N₄ constitute the basal plane while the apical positions are occupied by the N atoms from cyanide groups. The mean distance of basal Ni–N bonds is 2.076 Å (2.068(5) Å for Ni1–N5, 2.087(5) Å for Ni1–N6, 2.072(5) Å for Ni2–N7 and 2.078(4) Å for Ni2–N8), which are slightly shorter than the mean distance 2.127 Å of the apical Ni–N bonds (2.125(4) Å for Ni1–N1 and 2.128(4) Å for Ni2–N2). The bonding parameters of the macrocyclic ligand Me₆-[14]ane-N₄ are close to those found in related complexes reported previously [22,23].

Through the four bridging cyanide groups of the [W(CN)₈] unit, W and Ni atoms acting as basic components are connected by W–CN–Ni–NC–W linkage to form a three-dimensional structure (Fig. 2). The distances of adjacent W1–Ni1, W1–Ni2, Ni1···Ni2, Ni1···Ni1 and Ni2···Ni2 are 5.227 Å, 5.279 Å, 8.314 Å, 9.711 Å and 9.082 Å, respectively. From a topological standpoint, each [W(CN)₈] unit is a tetrahedral four-connecting node. These nodes are linked to four adjacent [W(CN)₈] units by the Ni(Me₆-[14]ane-N₄) units, acting as linear two-connectors. The result is a distorted diamond network (see Fig. 3).

The temperature dependent magnetic susceptibility of **1** was measured with an applied field $H = 2$ kOe in the temperature range 1.8–300 K. Plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T are given in Fig. 4. At room temperature, the $\chi_M T$ per Ni₂W unit is 2.1 emu K mol⁻¹ (4.1 μ_B), which is consistent with the spin-only value of 2.0 emu K mol⁻¹ (4.0 μ_B) expected for an uncoupled spin system (two $S_{Ni} = 1$, one

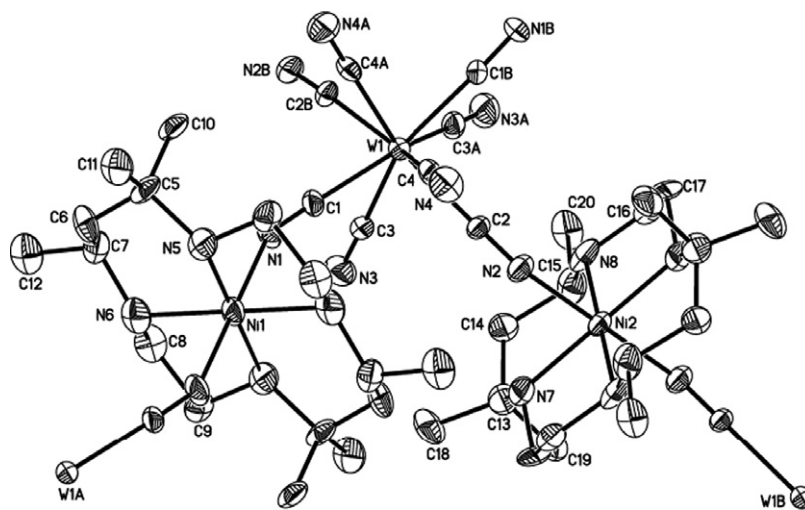


Fig. 1. Asymmetric structural unit of complex **1**. Selected bond lengths (Å) and angles (°): W1–C1 2.146(5), W1–C2 2.152(4), W1–C3 2.154(5), W1–C4 2.178(5), C1–W1 2.146(5), C2–W1 2.152(4), C3–W1 2.154(5), C4–W1 2.178(5), N1–Ni1 2.125(4), N2–Ni2 2.128(4), N5–Ni1 2.068(5), N6–Ni1 2.087(5), N7–Ni2 2.072(5), N8–Ni2 2.076(9), N1–C1–W1 177.4(4), N2–C2–W1 172.8(4), N3–C3–W1 176.7(6), N4–C4–W1 179.0(5), C1–N1–Ni1 151.3(4), C2–N2–Ni2 158.4(4).

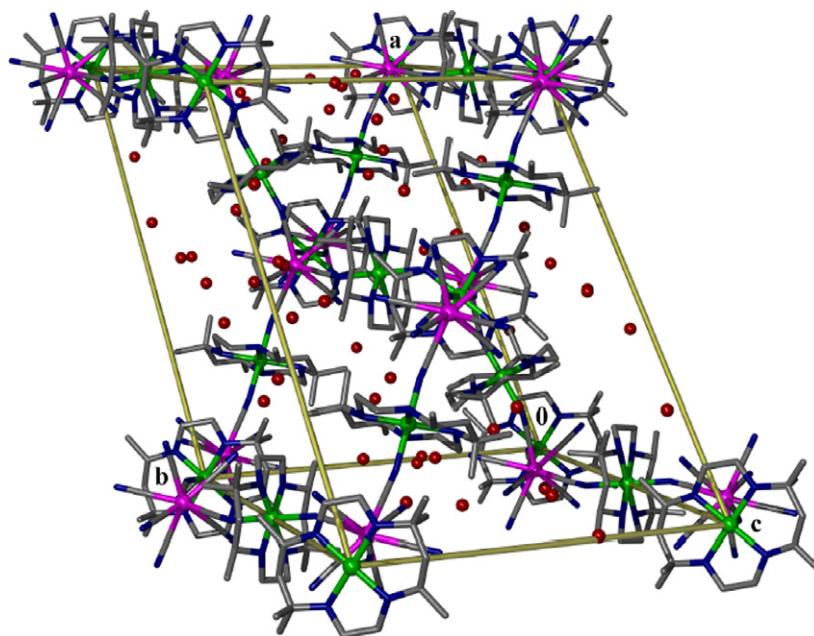


Fig. 2. Packing diagram of complex **1** viewed from the *c*-axis.

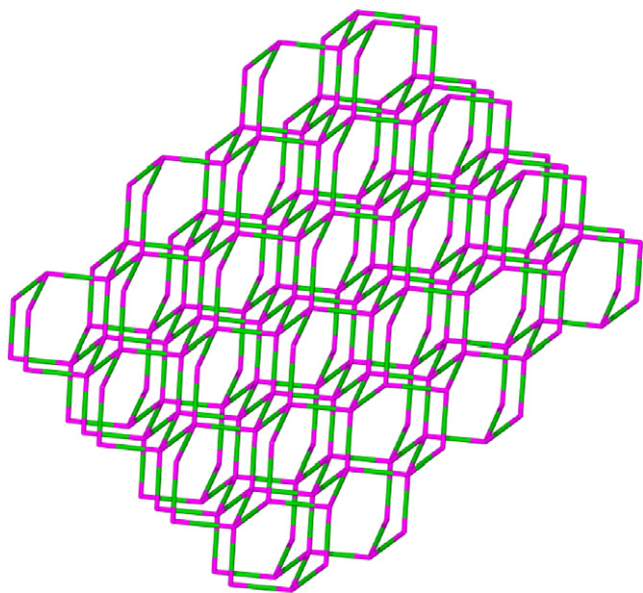


Fig. 3. Topological depiction of complex **1**, where the W nodes and the Ni connectors are shown in pink and green, respectively.

$S_W = 0$) with $g = 2.0$. On lowering the temperature, the $\chi_M T$ value decreases first gradually to $1.92 \text{ emu K mol}^{-1}$ ($3.92 \mu_B$) at 10 K, then sharply with further decreasing temperature to $1.30 \text{ emu K mol}^{-1}$ ($3.23 \mu_B$) at 1.8 K. The plot of $1/\chi_M$ vs. T obeys the Curie–Weiss law with a negative Weiss constant $\theta = -2.1 \text{ K}$. Such magnetic behavior is characteristic of combination of zero-field splitting of Ni^{2+} in an axially distorted octahedral surrounding and a weak antiferromagnetic interaction between Ni^{2+} ions through the diamagnetic $[\text{W}(\text{CN})_8]^{4-}$ bridges.

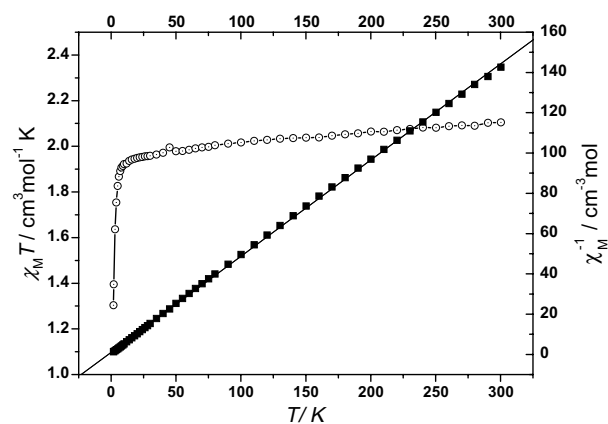


Fig. 4. Temperature dependence of $\chi_M T$ (■) and $1/\chi_M$ (○) for complex **1** measured at 2 kOe. The solid line represents the fit obtained by the Curie–Weiss law (see text).

Supplementary material

CCDC 635742 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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