Synthesis, crystal structure and magnetic properties of a new three-dimensional cyano-bridged Ni(II)–Mo(IV) complex

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Abstract

The reaction of \([\text{Mo(CN)}_8]^{4-}\) with \([\text{Ni(Me}_6-\text{[14]ane-N}_4])^{2+}\) (\(\text{Me}_6-\text{[14]ane-N}_4 = 5,7,7,12,14,14\text{-hexamethyl-1, 4,8,11-tetraazacyclotetradecane}\)) led to a new three-dimensional cyano-bridged bimetallic assembly \([\text{Ni(Me}_6-\text{[14]ane-N}_4])^{2+}[\text{Mo(CN)}_8]^{4-}\) \(12\text{H}_2\text{O}\) (1), which was characterized by IR, elemental analysis, ICP, TGA and SC-XRD. Magnetic behavior of complex 1 showed a weak antiferromagnetic interaction between Ni\(^{2+}\) ions through the diamagnetic \([\text{W(CN)}_8]^{4-}\) bridges.

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The rational design of the cyanometallate networks and clusters has been seen a dramatic resurgence of activity in recent years [1]. Cyanometallate anions have various geometries, for example, linear, as in \([\text{M(CN)}_2]^{2-}\) (\(\text{M} = \text{Au and Ag}\)) [2,3], trigonal, as in \([\text{Cu(CN)}_3]^{2-}\) [4], tetrahedral, as in \([\text{Cd(CN)}_4]^{2-}\) [5], square planar, as in \([\text{M(CN)}_4]^{2-}\) (\(\text{M} = \text{Fe, Co, Cr and Mn}\)) [9–12], and pentagonal bipyramidal, as in \([\text{M(CN)}_5]^0\) [13]. The octacyanometallates, \([\text{M(CN)}_8]^{n-}\) (\(\text{M} = \text{Mo and W}; n = 3 \text{ and } 4\)) generally adopt square antiprismatic, bicapped trigonal prismatic, or dodecahedral structures and are able to form up to eight cyanide bridges to adjacent metal centers. The structural diversity suggests \([\text{M(CN)}_8]^{n-}\) building blocks for constructing polynuclear complexes and networks that exhibit markedly different properties (e.g. photomagnetism, magnetism, and so on [13,14]) compared with known 3d hexa-cyanometallate analogues [15]. Coordination complexes of this system generally contain two central components, connector and linker. Transition-metal cations are often utilized as versatile connectors while \([\text{M(CN)}_8]^{n-}\) anions as linkers in the construction of octacyanometallates. Among them, the bimetallic assemblies built by \(\text{Mn(II, III), Cu(II), Co(II, III), and Pt(II)}\) complexes with octacyanometallate anions have been surveyed extensively [13,14]. Although the first examples of lattices containing octacyanometallate anions, \(\text{M}^{II}[\text{Mo}^{IV}(\text{CN})_8] \cdot n\text{H}_2\text{O} (\text{M}^{II} = \text{Zn, Cu, Ni, Co, Fe, Mn}; n = 2–9) [16]\) were reported in 1973, the structures of \(\text{M}^{II}[\text{Mo}^{IV}(\text{CN})_8] \cdot 8\text{H}_2\text{O} (\text{M}^{II} = \text{Co, Fe and Mn})\) were resolved recently [17]. In recent years, octacyanometallates with high dimensional structures have attracted considerable interest from the viewpoint of the construction and their potential application as spin carriers in molecular spintronics. But it should be noted that structurally characterized three-dimensional polynuclear complexes based on \(\text{Ni(II)}\) and \([\text{M(CN)}_8]^{3-/4-}\) (\(\text{M} = \text{Mo and W}\)) building blocks are still rare. To our knowledge, only one example has been characterized by single-crystal X-ray analysis up to date [18]. So it is urgent to synthesize and structurally characterize more new three-dimensional complexes in order to better understand the magneto-structural correlation of this system.

In this paper, \(\text{Me}_6-\text{[14]ane-N}_4\) is chosen as ligand coordinated to transition metal ion \(\text{Ni(II)}\) based on the advantage that macrocyclic ligands can block partly

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coordinate sites of the metal ion and release its apical ones. Herein, we report the synthesis, crystal structure and magnetic properties of a new cyano-bridged complex \(\text{[Ni(Me}_6\text{-[14]ane-N}_4\text{]_2[Mo(CN)_8]}\cdot12\text{H}_2\text{O}}\) \((\text{Me}_6\text{-[14]ane-N}_4 = 5.7, 7, 12, 14, 14\text{-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecan})\) (1) with a distorted diamond network containing \(\text{Ni}^{2+}\) and octacyanomolybde \(\text{[Mo(CN)_8]}^{4-}\) precursors.

Pale yellow crystals of complex 1 suitable for X-ray single-crystal structure determination were grown at room temperature by slow diffusion of a DMF solution (15 cm\(^3\)) of \([\text{Ni(Me}_6\text{-[14]ane-N}_4\text{]}(\text{ClO}_4)_2\] [19] (0.3 mmol) and an aqueous solution (15 cm\(^3\)) of \(\text{K}_4\text{[Mo(CN)_8]}\cdot2\text{H}_2\text{O}\) [20] (0.15 mmol) in a U-shaped tube containing agar for three months. Anal. Calc. for \(\text{C}_{10}\text{H}_{24}\text{Mo}_{0.25}\text{N}_4\text{Ni}_{0.5}\text{O}_3\): C, 39.81; H, 8.19; N, 18.57; Ni, 9.73; Mo, 7.95. Found: C, 39.78; H, 8.18; N, 9.74; Mo, 7.96. Infrared spectra of complex 1 exhibit two sharp and strong peaks at ca. 2111 cm\(^{-1}\) and 2141 cm\(^{-1}\) in the range 2100–2200 cm\(^{-1}\), assigned to terminal and bridging CN\(^-\) ions, respectively. The higher frequency band at 2141 cm\(^{-1}\) was blue-shifted from the \(\nu(C\equiv N)\) stretching frequency of \(\text{[M(CN)_8]}^{4-}\) \((M = \text{Mo and W})\) to the strongly bent Ni–N–C unit (160.9(16)) \(^\circ\) indicating the presence of bridging cyanide in complex 1. A very strong band at 2111 cm\(^{-1}\) is reasonably assigned to the terminal cyano stretching vibration. The IR feature is confirmed by the X-ray crystallographic analysis.

Thermogravimetric analysis were carried out under an He atmosphere in the temperature range 20–610 \(^\circ\)C with a heating rate of 10 \(^\circ\)C/min. Thermal analysis for complex 1 shows that there were two well-pronounced weight loss steps when the temperature was increased. Inflection points can determine the two steps at 55 and 260 \(^\circ\)C, respectively. Water molecules and hydrogen atoms are omitted for clarity.

In the \(\text{Ni(Me}_6\text{-[14]ane-N}_4\text{]}\) \(^{2+}\) unit, the geometry around Ni atom can be described as axially elongated octahedral (Fig. 2). The four N atoms from \(\text{Ni(Me}_6\text{-[14]ane-N}_4\text{]}\) constitute the basal while the apical positions are occupied by the N atoms from CN groups. The mean distance of basal Ni–N is 2.074 \(\text{Å}\), Ni2–N is 2.074 \(\text{Å}\), Ni1–N is 2.076 \(\text{Å}\), which are in the normal range of cyano-bridged octacyanides [18,22].

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bond angles are nearly linear while the NMe6-[14]ane-N4–Ni–
Ncyanide bond angles are nearly 90°. The bonding parameters of the macrocyclic ligand Me6-[14]ane-N4 are reminiscent of those found in related complexes reported previously [18,23].

As displayed in Fig. 3, Mo and Ni atoms acting as center components (linker and connector, respectively) are connected by Mo–CN–Ni–NC–Mo linkage to form a three-dimensional structure. The network is composed of \{Ni(Me6-[14]ane-N4)\}2+ unit that is linked via cyanides to adjacent four-connected [MoIV(CN)8(μ-CN)4]4− centers. The adjacent Mo···Mo, Mo···Ni1, Mo···Ni2, Ni1···Ni1, Ni1···Ni2 and Ni2···Ni2 are 10.508 Å, 5.254 Å, 5.224 Å, 9.378 Å, 8.328 Å and 10.039 Å, respectively. From a topological viewpoint, each Ni(Me6-[14]ane-N4) unit is a linear two-connecting node while each [Mo(CN)8] unit is a tetrahedral four-connecting one. These nodes of [Mo(CN)8] units are linked to four adjacent [Mo(CN)8] units by the Ni(Me6-[14]ane-N4) units. As a result, complex I displays a distorted diamond network (Fig. 4), which is similar to the octacyanometalate based bimetallic complex reported previously [18].

The magnetic susceptibilities of complex I were measured with an applied field \( H = 2 \text{ kOe} \) 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. 5. At room temperature, the \( \chi_M T \) per Ni2Mo unit is 2.46 emu K mol\(^{-1}\) (4.4 \( \mu_B \)), which is slightly bigger than the spin-only value of 2.0 emu K mol\(^{-1}\) (4.0 \( \mu_B \)) expected for an uncoupled spin system (two \( S_{Ni} = 1 \), one \( S_{Mo} = 0 \)) with \( g = 2.0 \). This is likely due to the orbital contribution to the magnetic moment of the Ni(II) due to the spin-orbital coupling. On lowering the temperature, the \( \chi_M T \) value decreases first gradually to 2.1 emu K mol\(^{-1}\) (4.1 \( \mu_B \)) at 6.0 K, then sharply with further decreasing temperature to 1.55 emu K mol\(^{-1}\) (3.5 \( \mu_B \)) at 1.8 K. The plot of \( 1/\chi_M \) vs. \( T \) obeys the Curie–Weiss law with a negative Weiss constant \( \theta = -3.2 \text{ K} \). These results indicate the presence of a weak antiferromagnetic interaction in complex I, which can be attributed to antiferromagnetic coupling between Ni(II) ions through the diamagnetic [Mo(CN)8]4− bridges.

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Appendix A. Supplementary material

CCDC 664607 contains the supplementary crystallographic data for this paper. These data can be obtained free...

References