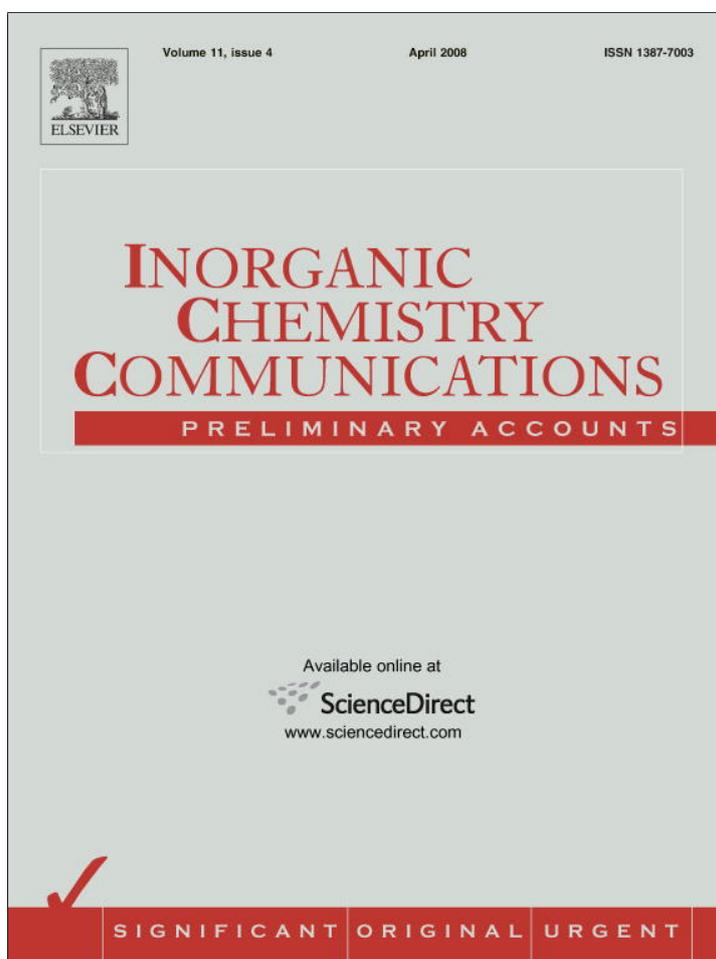


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Synthesis, crystal structure and magnetic properties of a new three-dimensional cyano-bridged Ni(II)–Mo(IV) complex

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Abstract

The reaction of $[\text{Mo}(\text{CN})_8]^{4-}$ with $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}^{2+}$ ($\text{Me}_6\text{-[14]ane-N}_4 = 5,7,7,12,14,14\text{-hexamethyl-1, 4,8,11-tetraazacyclotetradecane}$) led to a new three-dimensional cyano-bridged bimetallic assembly $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}_2[\text{Mo}(\text{CN})_8] \cdot 12\text{H}_2\text{O}$ (**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 $[\text{W}(\text{CN})_8]^{4-}$ bridges.

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Keywords: Octacyanomolybdate; Nickel complex; Crystal structure; Magnetic properties

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 $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Au}$ and Ag) [2,3], trigonal, as in $[\text{Cu}(\text{CN})_3]^{2-}$ [4], tetrahedral, as in $[\text{Cd}(\text{CN})_4]^{2-}$ [5], square planar, as in $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Ni}$, Pd and Pt) [6–8], octahedral, as in $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Fe}$, Co , Cr and Mn) [9–12], and pentagonal bipyramidal, as in $[\text{M}(\text{CN})_7]^{4-}$ [13]. The octacyanomellates, $[\text{M}(\text{CN})_8]^{n-}$ ($\text{M} = \text{Mo}$ and W ; $n = 3$ 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 $[\text{M}(\text{CN})_8]^{n-}$ 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 $[\text{M}(\text{CN})_8]^{n-}$

anions as linkers in the construction of octacyanomellates. Among them, the bimetallic assemblies built by $\text{Mn}(\text{II}, \text{III})$, $\text{Cu}(\text{II})$, $\text{Co}(\text{II}, \text{III})$, and $\text{Pt}(\text{II})$ complexes with octacyanomellate anions have been surveyed extensively [13,14]. Although the first examples of lattices containing octacyanomellate anions, $\text{M}_2^{\text{II}}[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot n\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Zn}$, Cu , Ni , Co , Fe , Mn ; $n = 2\text{--}9$) [16] were reported in 1973, the structures of $\text{M}_2^{\text{II}}[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Co}$, Fe and Mn) were resolved recently [17]. In recent years, octacyanomellates 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 $\text{Ni}(\text{II})$ and $[\text{M}(\text{CN})_8]^{3-/4-}$ ($\text{M} = \text{Mo}$ 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 $\text{Ni}(\text{II})$ based on the advantage that macrocyclic ligands can block partly

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coordination 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 $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}_2[\text{Mo}(\text{CN})_8] \cdot 12\text{H}_2\text{O}$ ($\text{Me}_6\text{-[14]ane-N}_4 = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$) (**1**) with a distorted diamond network containing Ni^{2+} ion and octacyanomolybde $[\text{Mo}(\text{CN})_8]^{4-}$ precursor.

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 $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}(\text{ClO}_4)_2$ [19] (0.3 mmol) and an aqueous solution (15 cm^3) of $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ [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, 18.60; Ni, 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 $2100\text{--}2200\text{ cm}^{-1}$, assigned to terminal and bridging CN^{-1} , respectively. The higher frequency band at 2141 cm^{-1} was blue-shifted from the $\nu(\text{C}\equiv\text{N})$ stretching frequency of $2070\text{--}2130\text{ cm}^{-1}$ in the free $[\text{M}(\text{CN})_8]^{4-}$ ($\text{M} = \text{Mo}$ and W) ion [14b], 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 a He atmosphere in the temperature range $20\text{--}610\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. 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 $55\text{ }^\circ\text{C}$ and $260\text{ }^\circ\text{C}$. The first weight loss step of 18.26% is consistent with the loss of the twelve crystallized water molecules (calcd 18.28%), leading to $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}_2[\text{Mo}(\text{CN})_8]$. After heating at $260\text{ }^\circ\text{C}$ framework decomposition occurred.

Complex **1** crystallizes in the monoclinic ($C2/c$) space group. Each asymmetric unit of the structure [21] for complex **1** is composed of two halves of $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}^{2+}$ cations, half a $[\text{Mo}(\text{CN})_8]^{4-}$ anion and six H_2O molecules (Fig. 1). Among of them, six H_2O molecules are disordered in the structure. The $[\text{Mo}^{\text{IV}}(\text{CN})_8]^{4-}$ moiety has four bridging cyano ligands, leaving four terminal ones as expected from the IR data. Each four-connected $[\text{Mo}(\text{CN})_8]^{4-}$ center adopts a distorted square antiprismatic geometry and forms $\mu\text{-CN}$ linkages to adjacent $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}^{2+}$ units (Fig. 2). The average $\text{Mo}^{\text{IV}}\text{-C}$ and C-N distances are 2.153 \AA and 1.150 \AA , respectively. The bridging $\text{Mo}^{\text{IV}}\text{-C-N}$ angles remain almost linear with the maximum deviation from linearity of 3.0° in opposition to the strongly bent Ni-N-C unit ($160.9(16)^\circ$ and $154.5(14)^\circ$ for Ni1-N5-C17 and Ni2-N8-C20 , respectively), which are in the normal range of cyano-bridged octacyanides [18,22].

In the $\{\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4)\}^{2+}$ unit, the geometry around Ni atom can be described as axially elongated octahedral (Fig. 2). The four N atoms from $\text{Ni}(\text{Me}_6\text{-[14]ane-N}_4$

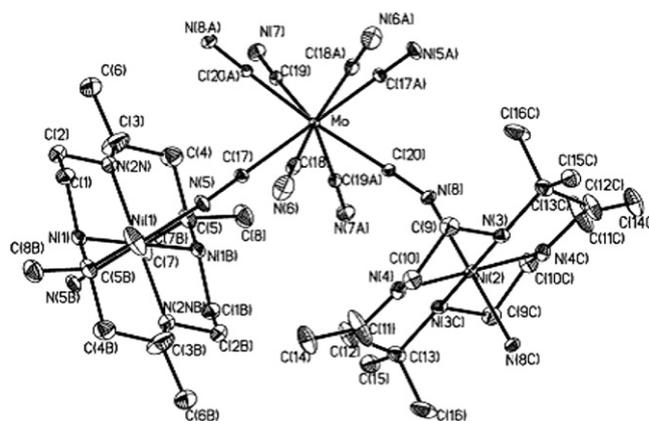


Fig. 1. Asymmetric unit of complex **1**. Thermal ellipsoids are at the 30% level and all hydrogen atoms are removed for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Mo-C17 2.132(17), Mo-C18 2.170(18), Mo-C19 2.173(17), Mo-C20 2.136(16), Ni1-N1 2.095(16), Ni1-N2N 2.053(17), Ni1-N5 2.0593(16), Ni2-N3 2.090(15), Ni2-N4 2.060(15), Ni2-N8 2.073(14), N5-C17 1.142(2), N6-C18 1.153(3), N7-C19 1.155(2), N8-C20 1.150(2), C17-N5-Ni1 160.94(16), C20-N8-Ni2 154.54(14), N5-C17-Mo 178.10(16), N6-C18-Mo 178.40(2), N7-C19-Mo 177.42(16), N8-C20-Mo 177.06(15).

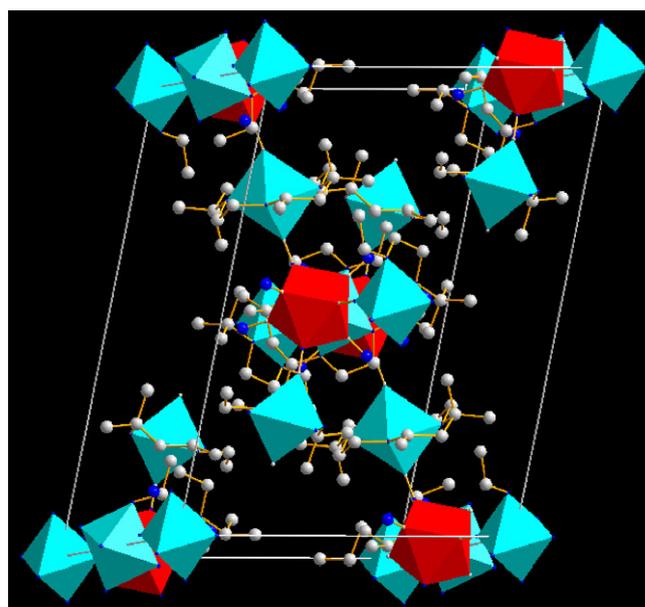


Fig. 2. Three-dimensional crystal structure using polyhedral model for complex **1**. Red and light-blue polyhedrons show MoC_8 and NiN_6 , respectively. Water molecules and hydrogen atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

constitute the basal while the apical positions are occupied by the N atoms from CN groups. The mean distance of basal Ni1-N_{eq} and Ni2-N_{eq} is 2.074 \AA and 2.076 \AA , respectively, ($2.095(16)\text{ \AA}$ for Ni1-N1 , $2.053(17)\text{ \AA}$ for Ni1-N2N , $2.060(15)\text{ \AA}$ for Ni2-N3 and $2.090(15)\text{ \AA}$ for Ni2-N4), which are slightly shorter than the mean distance 2.066 \AA of the apical Ni-N bonds ($2.059(12)\text{ \AA}$ for Ni1-N5 and $2.073(14)\text{ \AA}$ for Ni2-N8). The nickel (II)-nitrile N-Ni-N

bond angles are nearly linear while the $N_{Me_6-[14]ane-N_4}-Ni-N_{cyanide}$ bond angles are nearly 90° . The bonding parameters of the macrocyclic ligand $Me_6-[14]ane-N_4$ are reminiscent of those found in related complexes reported previously [18,23].

As display 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 $\{Ni(Me_6-[14]ane-N_4)\}^{2+}$ unit that is linked via cyanides to adjacent four-connected $[Mo^{IV}(CN)_8(\mu-CN)_4]^{4-}$ centers. The adjacent $Mo \cdots Mo$, $Mo \cdots Ni1$, $Mo \cdots Ni2$, $Ni1 \cdots Ni1$, $Ni1 \cdots Ni2$ and $Ni2 \cdots Ni2$ 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 $Ni(Me_6-[14]ane-N_4)$ 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 $Ni(Me_6-[14]ane-N_4)$ units. As a result, complex **1** displays a distorted diamond network (Fig. 4), which is similar to the octacyanometalate based bimetallic complex reported previously [18].

The magnetic susceptibilities of complex **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. 5. At room temperature, the $\chi_M T$ per Ni_2Mo 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

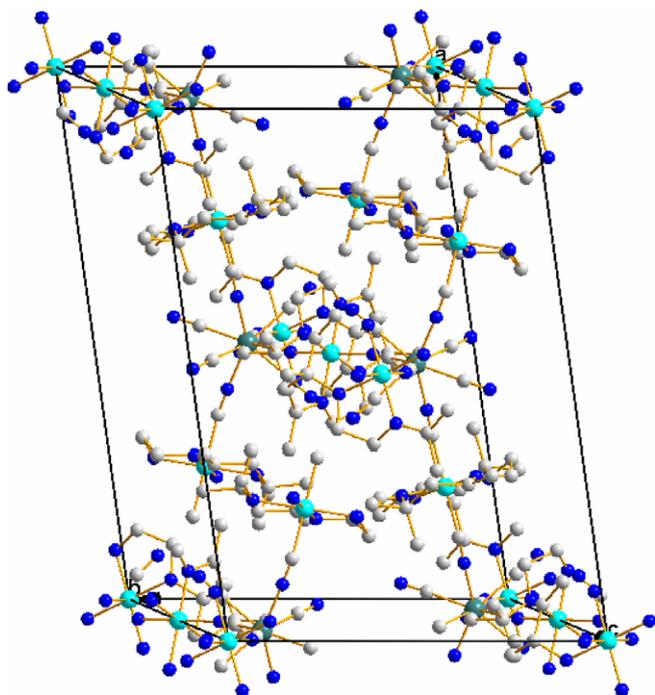


Fig. 3. Packing diagram of complex **1** viewed from the c -axis.

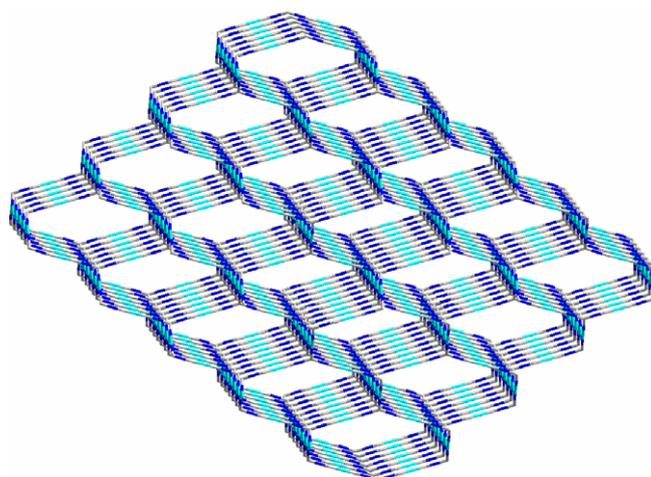


Fig. 4. Topological depiction of complex **1**, where the Mo and Ni atoms are shown in dark blue and light-blue, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

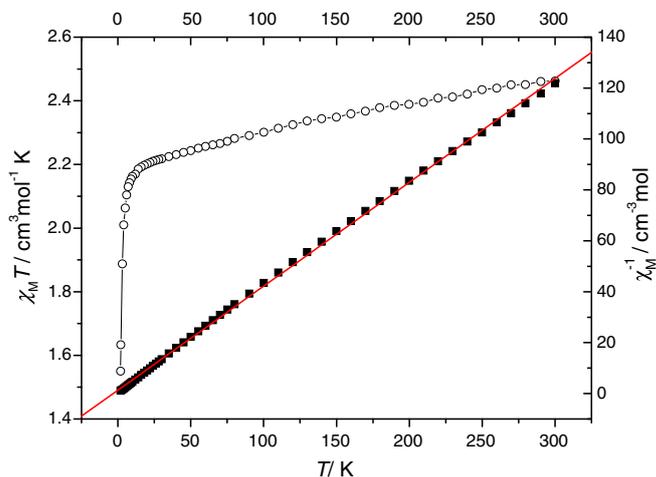


Fig. 5. Temperature dependence of $\chi_M T$ (■) and $1/\chi_M$ (○) for complex **1** measured at 2 kOe. The solid line represents the fit obtained by the Curie–Weiss law.

$\chi_M T$ 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 $\theta = -3.2$ K. These results indicate the presence of a weak antiferromagnetic interaction in complex **1**, 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

of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2007.12.030](https://doi.org/10.1016/j.inoche.2007.12.030).

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