

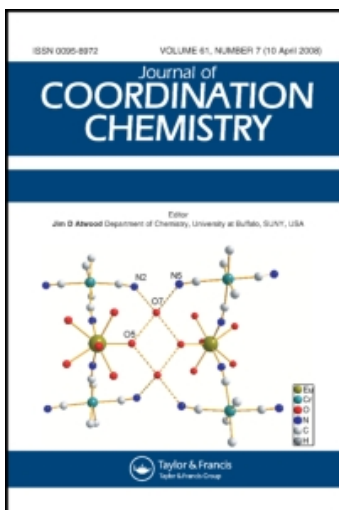
This article was downloaded by: [2007-2008-2009 Seoul National University]

On: 17 October 2009

Access details: Access Details: [subscription number 907490176]

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713455674>

Synthesis, crystal structure, and magnetic properties of an octacyanometallate-based Ni/Mo bimetallic complex with the diamond topological network

Aihua Yuan ^a; Wenyan Liu ^a; Hu Zhou ^a; Suyan Qian ^a

^a School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, P. R. China

First Published: November 2009

To cite this Article Yuan, Aihua, Liu, Wenyan, Zhou, Hu and Qian, Suyan (2009) 'Synthesis, crystal structure, and magnetic properties of an octacyanometallate-based Ni/Mo bimetallic complex with the diamond topological network', *Journal of Coordination Chemistry*, 62:22, 3592 — 3598

To link to this Article: DOI: 10.1080/00958970903121297

URL: <http://dx.doi.org/10.1080/00958970903121297>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis, crystal structure, and magnetic properties of an octacyanometallate-based Ni/Mo bimetallic complex with the diamond topological network

AIHUA YUAN*, WENYAN LIU, HU ZHOU and SUYAN QIAN

School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, P. R. China

(Received 13 February 2009; in final form 28 April 2009)

Reaction of $[\text{NiL}]^{2+}$ ($L = 3,10$ -diethyl-1,3,5,8,10,12-hexaazacyclotetradecane) with $[\text{Mo}(\text{CN})_8]^{4-}$ leads to a new Ni_2Mo complex $[\text{Ni}(\text{L})_2][\text{Mo}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ (**1**), which displays a 3-D diamond topological network. Magnetic study indicates a combination of zero-field splitting of Ni^{2+} in an axially distorted octahedral coordination and weak antiferromagnetic interactions between Ni^{2+} centers through diamagnetic $[\text{Mo}(\text{CN})_8]^{4-}$ bridges.

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

1. Introduction

Octacyanometallates $[\text{M}(\text{CN})_8]^{3-/4-}$ ($M = \text{Mo}, \text{W}$ and Nb), a versatile class of building blocks, can adopt three structures (e.g., square antiprism, dodecahedron or bicapped trigonal prism) depending on the external environments such as the surrounding ligands. For this reason, numerous octacyanometallate-based complexes have been characterized [1–4], which display various structures spanning from 0-D discrete molecules, 1-D chains, 2-D layers to 3-D frameworks.

Several bimetallic assemblies built by $\text{Ni}(\text{II})$ complexes with octacyanometallate anions have been reported [5–18]. Despite a much smaller number compared to $M^{\text{II}}/M^{\text{IV/V}}$ ($M' = \text{Cu}, \text{Co}, \text{Mn}$; $M = \text{Mo}, \text{W}, \text{Nb}$) systems, these bimetallic complexes exhibit excellent magnetic properties, for example, photo-magnetic properties [9], higher ground-state spins [6, 7, 11, 16, 17], slow relaxation of the magnetization [16], and single molecule magnetic (SMM) behavior [11].

To get more insight into structural and magnetic variations of $M^{\text{II}}/M^{\text{IV/V}}$ ($M' = \text{transition metals}$) systems, especially $\text{Ni}^{\text{II}}/M^{\text{IV/V}}$, we [8, 10] and other groups [15, 18–22] have attempted to design bimetallic assemblies by using macrocyclic ligands which may take part in intermolecular interactions and open up further possibilities for structure and properties of the polymeric assemblies. Recently, our study extended

*Corresponding author. Email: aihuayuan@163.com

the Ni^{II}/M^{IV/V} system with the tetradentate macrocyclic ligand (L = 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane), which is only slightly altered in the pendant group (e.g., Et for Me, iso-prop, or iso-but). Our effort is to seek a correlation between adjusted structural parameters and resulting magnetic character by modulating molecular structures that rest on changing side groups on macrocycles. Herein, we report the synthesis, structural, and magnetic characterizations of a new complex [Ni(L)]₂[Mo(CN)₈]·8H₂O (**1**).

2. Experimental

2.1. General considerations

Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240C analyzer. Fourier-transform IR (FT-IR) spectra were recorded in KBr pellets on a Nicolet FT-IR 17SX. Variable-temperature magnetic susceptibility measurements of **1** on crystalline samples were performed using a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer from 300 to 3 K under an applied field of 2 kOe.

2.2. Synthesis of **1**

Well-shaped yellow 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 [Ni(L)](ClO₄)₂ (0.30 mmol) [23] and a DMF solution (15 mL) of K₄[Mo(CN)₈] (0.15 mmol) [24]. The resulting crystals were collected, washed with H₂O, and dried in air. Yield: 50 mg, 31%. Anal. Calcd for C₃₆H₈₀MoN₁₆Ni₂O₈: C, 40.09; H, 7.48; N, 20.78; Mo, 8.90; Ni, 10.88%. Found: C, 39.78; H, 7.52; N, 20.35; Mo, 8.85; Ni, 10.82%. IR (KBr): $\nu_{\text{C}\equiv\text{N}}$ 2102, 2127 cm⁻¹.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with great care.

2.3. X-ray crystallography

Single crystal X-ray diffraction measurement for **1** was carried out on a Bruker APEX II diffractometer equipped with MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation. Diffraction data analysis and reduction were performed with SMART and SAINT+ [25]. Correction for Lorentz polarization, and absorption effects were performed with SADABS [26]. Structures were solved using the Patterson method within SHELXL-97 and refined using SHELXL-97 [27]. All nonhydrogen atoms were refined with anisotropic thermal parameters. The idealized positions of the hydrogens were located by using a riding model. The crystal data and structure refinement for **1** are summarized in table 1. Selected bond lengths and angles for **1** are listed in table 2.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C ₃₆ H ₈₀ MoN ₁₆ Ni ₂ O ₈
Formula weight	1078.52
Crystal system	Tetragonal
Space group	<i>I</i> 41/ <i>amd</i>
Unit cell dimensions (Å, °)	
<i>a</i>	19.586(3)
<i>b</i>	19.586(3)
<i>c</i>	15.481(4)
α	90.00
β	90.00
γ	90.00
Volume (Å ³), <i>Z</i>	5939(2), 4
Calculated density (g cm ⁻³)	1.206
Absorption coefficient (MoK α) (mm ⁻¹)	0.888
Total/unique	22079/1555
Observed [<i>I</i> > 2 σ (<i>I</i>)]	1409
Independent reflection	0.056
Goodness-of-fit on <i>F</i> ²	1.087
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0372, <i>wR</i> ₂ = 0.1131
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0436, <i>wR</i> ₂ = 0.1170

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

Mo1–C1	2.079(3)	C2–N2	1.157(5)	Ni1–N2	2.014(3)
Mo1–C2	2.106(4)	C1–N1	1.196(4)	Ni1–N3	2.072(2)
N1–C1–Mo1	179.1(3)	N2–C2–Mo1	179.0(4)	Ni1–N2–C2	173.0(3)

3. Results and discussion

3.1. Crystal structure of **1**

Single crystal X-ray diffraction reveals that **1** is made up of two [Ni(L)]²⁺ cations, one [Mo(CN)₈]⁴⁻ anion and eight waters of crystallization. The coordination geometries of the [Mo(CN)₈]⁴⁻ and [NiL]²⁺ centers are described as distorted square antiprismatic and axially elongated octahedral, respectively (figure 1). The Mo is surrounded by eight cyano groups with Mo–C distance ranging from 2.079 to 2.105 Å. The first square C1–C2–C1^{viii}–C2^{viii} slightly distorted (symmetry code: (viii) 0.75 – *y*, 0.75 – *x*, 0.25 – *z*; C...C distance in the range from 2.405 to 2.569 Å), with angles in the range from 77.63 to 97.53°, is compared to the second square C1^v–C2^v–C1^{ix}–C2^{ix} (symmetry codes: (v) 1 – *x*, 0.5 – *y*, *z*; (ix) 0.25 + *y*, *x* – 0.25, 0.25 – *z*; C...C distance and angles are the same to the first square). Furthermore, the two distorted squares are twisted with an angle of about 45°. As a result, **1** presents a 3D diamond topological network (figure 2), where Mo and Ni atoms act as linkers and connectors, respectively. The distances of adjacent Mo...Ni, Mo...Mo, and Ni...Ni are 5.265, 10.530, and 9.793 Å, respectively. The topological structure of **1** is close to that seen for related Ni₂^{II}M^{IV} compounds reported previously [8, 10], although tetradentate macrocyclic ligands chelated in these complexes have different pendant groups.

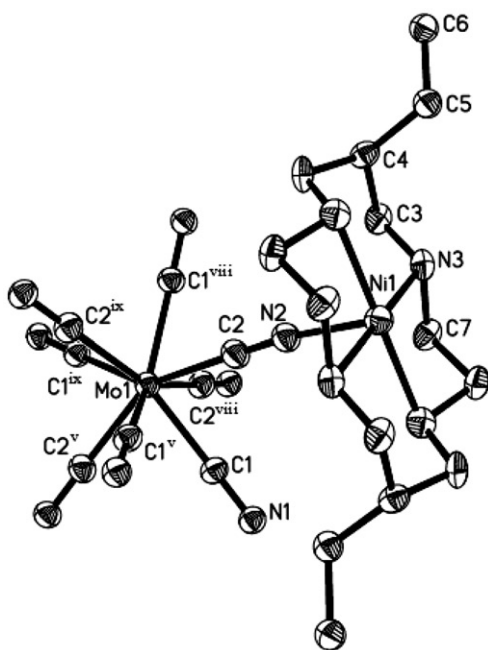


Figure 1. ORTEP diagram of **1** showing the 30% probability thermal motion ellipsoid. Water molecules and hydrogen atoms have been omitted for clarity. Symmetry codes: (v) $1-x, 0.5-y, z$; (viii) $0.75-y, 0.75-x, 0.25-z$; (ix) $0.25+y, x-0.25, 0.25-z$.

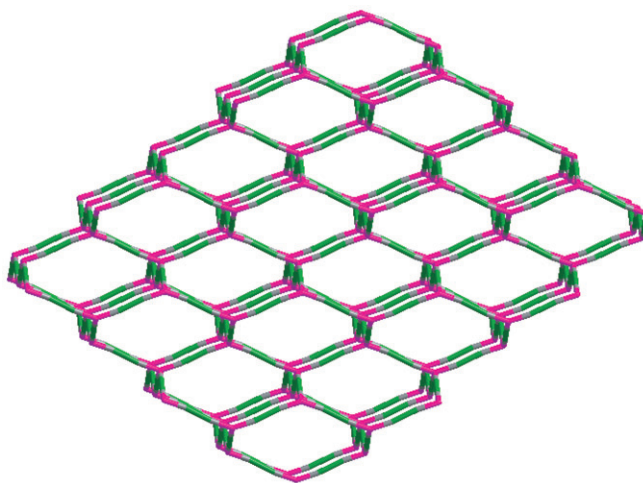


Figure 2. Topological depiction of **1**, where the Mo nodes and the Ni connectors are shown in pink and green, respectively.

3.2. Thermal analysis of **1**

Thermogravimetric analyses (TGA) were carried out on a TA Instrument Perkin-Elmer Diamond analyzer to determine the thermal stability of **1**. The temperature was ramped at $1^{\circ}\text{C min}^{-1}$ from 30 to 650°C under nitrogen. The TG curve shows

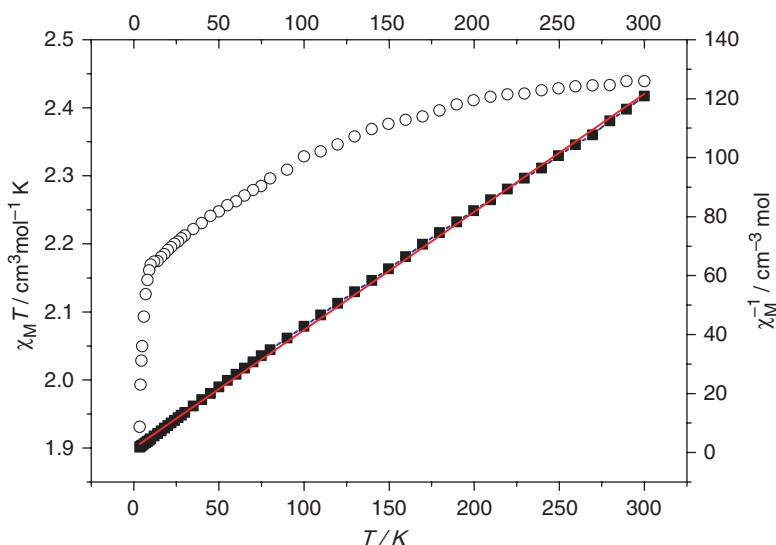


Figure 3. Temperature dependence of $\chi_M T$ (○) and χ_M^{-1} (■) measured at 2 kOe in the temperature 3.5–300 K for **1**. The solid red line represents the fit obtained by the Curie–Weiss law.

two well-pronounced weight loss steps with inflection points at 70 and 180°C, respectively. The first weight loss of 13.05% is consistent with loss of the eight waters of crystallization (Calcd 13.36%), while the second corresponds to decomposition of framework.

3.3. Magnetic properties of **1**

Magnetic measurements of **1** were carried out with a Quantum Design MPMS-5 SQUID magnetometer. Plots of $\chi_M T$ versus T and χ_M^{-1} versus T are given in figure 3. The $\chi_M T$ value per Ni_2Mo unit of $2.4 \text{ emu K mol}^{-1}$ ($4.4 \mu_B$) at 300 K is slightly higher than the spin-only value of $2.0 \text{ emu K mol}^{-1}$ ($4.0 \mu_B$) expected for an uncoupled spin system (two $S_{\text{Ni}}=1$, one $S_{\text{Mo}}=0$) with $g=2.0$. Upon cooling from 300 to 10 K, the $\chi_M T$ value shows a slight decrease. Below 10 K, the $\chi_M T$ value decreases rapidly to $1.9 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ($3.9 \mu_B$) at 3.5 K. The plot of χ_M^{-1} versus T obeys the Curie–Weiss equation $\chi_M = C/(T-\theta)$ with $C = 2.5 \text{ cm}^{-3} \text{ K mol}^{-1}$ and $\theta = -3.7 \text{ K}$. Such magnetic behavior is characteristic of combination of zero-field splitting of Ni^{2+} in an axially distorted octahedron and weak antiferromagnetic interactions between Ni^{2+} centers through diamagnetic $[\text{Mo}(\text{CN})_8]^{4-}$ bridges.

4. Conclusion

An octacyanommetallate-based bimetallic complex has been synthesized and structurally characterized. X-ray crystallography reveals that **1** displays a 3-D diamond topological network. Magnetism indicates a combination of zero-field splitting of Ni^{2+} in axially

distorted octahedral coordination and weak antiferromagnetic interactions between Ni^{2+} centers through the diamagnetic $[\text{Mo}(\text{CN})_8]^{4-}$ bridges.

Supplementary material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-711540. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223 336-033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgment

This work was supported by the University Natural Science Foundation of Jiangsu Province (No. 07KJB150030).

References

- [1] P. Przychodzeń, T. Korzeniak, R. Podgajny, B. Sieklucka. *Coord. Chem. Rev.*, **250**, 2234 (2006).
- [2] B. Sieklucka, R. Podgajny, P. Przychodzeń, T. Korzeniak. *Coord. Chem. Rev.*, **249**, 2203 (2005).
- [3] J. Larionova, S. Willemin, B. Donnadiou, B. Henner, C. Guérin, B. Gillon, A. Goujon. *J. Phys. Chem. Solids*, **65**, 677 (2004).
- [4] B. Sieklucka, R. Podgajny, P. Przychodzeń, R. Kania. *C. R. Chim.*, **5**, 639 (2002).
- [5] T.S. Venkatakrisnan, C. Desplanches, R. Rajamani, Ph. Guionneau, L. Ducasse, S. Ramasesha, J.P. Sutter. *Inorg. Chem.*, **47**, 4854 (2008).
- [6] J.H. Lim, H.S. Yoo, J.H. Yoon, E.K. Koh, H.C. Kim, C.S. Hong. *Polyhedron*, **27**, 299 (2008).
- [7] J.H. Lim, H.S. Yoo, J.I. Kim, J.H. Yoon, N. Yang, E.K. Koh, J.G. Park, C.S. Hong. *Eur. J. Inorg. Chem.*, 3428 (2008).
- [8] H. Zhou, Y.Y. Chen, A.H. Yuan, X.P. Shen. *Inorg. Chem. Commun.*, **11**, 363 (2008).
- [9] T. Korzeniak, C. Mathonière, A. Kaiba, Ph. Guionneau, M. Koziel, B. Sieklucka. *Inorg. Chim. Acta*, **361**, 3500 (2008).
- [10] H. Zhou, A.H. Yuan, X.P. Shen, Y.Y. Chen, D.J. Price, C.J. Kepert. *Inorg. Chem. Commun.*, **10**, 940 (2007).
- [11] J.H. Lim, J.H. Yoon, H.C. Kim, C.S. Hong. *Angew. Chem. Int. Ed.*, **45**, 7424 (2006).
- [12] D. Visinescu, C. Desplanches, I. Imaz, V. Bahers, R. Pradhan, F.A. Villamena, P. Guionneau, J.P. Sutter. *J. Am. Chem. Soc.*, **128**, 10202 (2006).
- [13] J.R. Withers, C. Ruschmann, P. Bojang, S. Parkin, S.M. Holmes. *Inorg. Chem.*, **44**, 352 (2005).
- [14] J.R. Withers, C. Ruschman, S. Parkin, S.M. Holmes. *Polyhedron*, **24**, 1845 (2005).
- [15] R. Pradhan, C. Desplanches, Ph. Guionneau, J.P. Sutter. *Inorg. Chem.*, **42**, 6607 (2003).
- [16] F. Bonadio, M. Gross, H. Stoeckli-Evans, S. Decurtins. *Inorg. Chem.*, **41**, 5891 (2002).
- [17] F. Chang, H.L. Sun, H.Z. Kou, S. Gao. *Inorg. Chem. Commun.*, **5**, 660 (2002).
- [18] B. Mowicka, M. Rams, K. Stadnicka, B. Sieklucka. *Inorg. Chem.*, **46**, 8123 (2007).
- [19] Y.S. You, D. Kim, Y. Do, S.J. Oh, C.S. Hong. *Inorg. Chem.*, **43**, 6899 (2004).
- [20] Y.S. You, J.H. Yoon, J.H. Lim, H.C. Kim, C.S. Hong. *Inorg. Chem.*, **44**, 7063 (2005).
- [21] J.H. Lim, J.S. Kang, H.C. Kim, E.K. Koh, C.S. Hong. *Inorg. Chem.*, **45**, 7821 (2006).
- [22] J.H. Lim, Y.S. You, H.S. Yoo, J.H. Yoon, J.I. Kim, E.K. Koh, C.S. Hong. *Inorg. Chem.*, **46**, 10578 (2007).
- [23] M.P. Suh, S.G. Kang. *Inorg. Chem.*, **27**, 2544 (1988).
- [24] J.G. Leipoldt, L.D. Bok, P.J. Cilliers. *Z. Anorg. Allg. Chem.*, **409**, 343 (1974).

- [25] SMART, SAINT and XPREP. *Area detector and data integration and reduction software*, Bruker Analytical Instruments Inc., Madison, WI (1995).
- [26] G.M. Sheldrick. *SADABS. Empirical adsorption correction program for area detector data*, University of Göttingen: Göttingen, Germany (1996).
- [27] G.M. Sheldrick. *SHELXL-97. Program for crystal structural solution and refinement*, Bruker Analytical Instruments Inc., Madison, WI (1997).