

A novel three-dimensional Cu^{II}–Mo^{IV} bimetallic complex: Synthesis, crystal structure, and magnetic properties

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Received 25 February 2006; received in revised form 26 April 2006; accepted 26 April 2006

Available online 19 June 2006

Abstract

The reaction between $K_4[Mo^{IV}(CN)_8] \cdot 2H_2O$ and $[Cu(L)](ClO_4)_2$ ($L = 3,10$ -dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) gives a novel three-dimensional cyano-bridged coordination compound $[Cu(L)_2][Mo(CN)_8] \cdot 2.5H_2O$ (**1**). The thermal and magnetic behaviors of compound **1** have been investigated. X-ray single-crystal structure determinations reveal that the Mo^{IV} centers in **1** adopt a distorted square antiprism geometry, while the Cu^{II} centers in **1** adopt an elongated octahedral geometry. Each Mo^{IV} coordinated via four cyano groups to four Cu^{II} . Variable-temperature magnetic susceptibility measurements reveal that there is negligible magnetic interaction between the Cu^{II} centers in compound **1**.

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Keywords: Octacyanotungstate(IV); Copper complex; Cyano-bridged complex; Crystal structure; Magnetic properties

1. Introduction

To design and synthesis complexes having unlimited extended-structure is one of the main challenges in the field of molecular science [1–3]. The eightfold coordinated network structures based on octacyanometalates $[M(CN)_8]^{3-/4-}$ ($M = Mo, W$ and Nb) have been one of the attractive subjects in crystal engineering of coordination polymers owing to their lower symmetry, interesting structural features, rich magnetic, and photomagnetic properties [4]. In recent years, a lot of structurally characterized coordination polymers have been obtained by the self-assembly of the systems containing $[W^{IV}(CN)_8]^{4-}$, $[W^V(CN)_8]^{3-}$ as building blocks [5,6]. Moreover, to our knowledge, structural reports of cyano-bridged bimetallic compounds based on $[Mo(CN)_8]^{3-/4-}$ are very recent and have mostly low-dimensional structures [7]. In order

to obtain more 3D-structural compounds and better understand the magnetostructural correlation of these complexes, it is important to synthesize and structurally characterize new compounds. We have reported that the reaction of $[Cu(L)]^{2+}$ ($L = 3,10$ -dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) with $[Cr(CN)_6]^{3-}$ has led to a 3D coordination polymer [8]. For the recent study, we chose $[Cu(L)]^{2+}$ and $[Mo(CN)_8]^{4-}$ as building blocks to synthesize successfully a novel 3D framework compound: $[Cu(L)_2][Mo(CN)_8] \cdot 2.5H_2O$ (**1**). Herein we report its preparation, structure and properties.

2. Experimental

2.1. Physical measurements

Elemental analysis for C, H, and N was determined with a Perkin-Elmer 240C elemental analyzer. The IR spectra was recorded in the 4000 – 400 cm^{-1} region on a Nicolet FT-IR 170 SX spectrometer using KBr pellets. Thermogravimetric (TG) analysis was performed using Perkin-Elmer Diamond TG/DTA instruments under

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helium atmosphere from 18 to 1200 °C at a heating rate of 10 °C min⁻¹. Magnetic susceptibility data on crystalline samples were measured with a Quantum Design MPMS-5 SQUID magneto under an applied magnetic field of 10 kOe in the temperature range 4.8–299 K. The data were corrected for the sample holder and the diamagnetism contributions were calculated from the Pascal's constants. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the molar magnetic susceptibility corrected for the diamagnetism of the constituting atoms.

2.2. Preparations

[Cu(L)](ClO₄)₂ [9] and K₄[Mo(CN)₈]·2H₂O [10] were synthesized as described in the literature. The other reagents were of analytical grade from commercial sources and were used without any further purification.

2.2.1. [Cu(L)]₂[Mo(CN)₈]·2.5H₂O (1)

Well-shaped reddish brown crystals of the title compound were grown at room temperature by slow diffusion of a DMF solution (15 cm³) of [Cu(L)](ClO₄)₂ (0.3 mmol) and an aqueous solution (15 cm³) of K₄[Mo(CN)₈]·2H₂O (0.15 mmol) in a U-shaped tube containing agar. The resulting crystals were collected, washed with H₂O and dried in air. Calcd for C₇₂H₁₅₄Cu₄Mo₂N₄₀O₅: C, 41.02; H, 7.31; N, 26.59; Mo, 9.12; Cu, 12.57. Found: C, 41.08; H, 7.29; N, 26.67; Mo, 9.08; Cu, 12.57%. IR (cm⁻¹): 2101.91, 2125.87 ($\nu_{\text{C}\equiv\text{N}}$).

2.3. Crystallography

A single crystal of the title complex was selected for lattice parameter determination and collection of intensity data at 293(2) K on a Bruker SMART APEX CCD area detector diffractometer with graphite monochromatic MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -2 θ scan mode to a maximum 2 θ value of 52.0°. The intensity data were corrected for Lorentz and polarization effects during data reduction. The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically. The sites of hydrogen atoms were placed by the geometry. The contributions of these hydrogen atoms were included in the structure factor calculations. All computations were carried out using the SHELXTL-PC program package. Analytical anomalous dispersion corrections were incorporated. The maximum and minimum residual densities in the final difference Fourier map were 0.35 and -0.45 e/\AA^3 , respectively.

Crystal data for **1**: C₃₆H₇₈Cu₂MoN₂₀O₅, $M = 1094.04$, orthorhombic, space group *Fddd*, $a = 18.420(2)$, $b = 29.833(2)$, $c = 42.962(2) \text{ \AA}$, $U = 23,609(5) \text{ \AA}^3$, $Z = 8$, $D_c = 1.181 \text{ g/cm}^3$, $F(000) = 8784$, $\mu = 0.969 \text{ mm}^{-1}$, 30,727 reflections measured, 5819 unique ($R_{\text{int}} = 0.065$). The final $R_1 = 0.0570$ and $wR_2 = 0.1218$ for 4228 observed reflections [$I > 2\sigma(I)$] and 306 parameters.

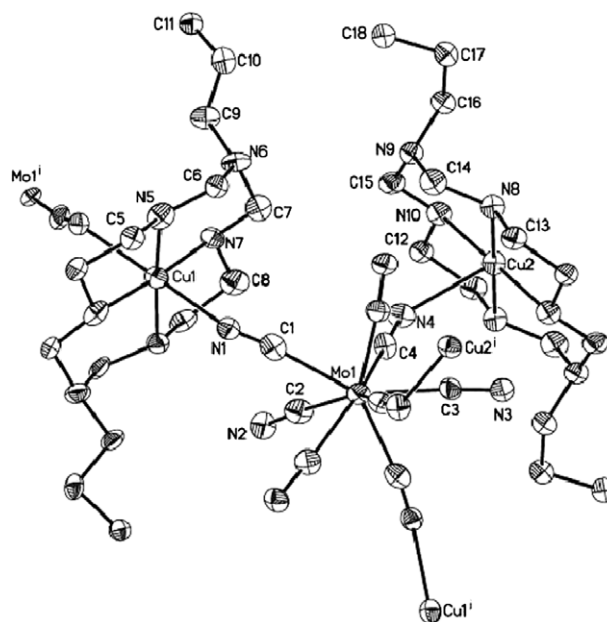


Fig. 1. ORTEP drawing of compound 1.

3. Results and discussion

3.1. IR spectrum

The infrared C—N stretch ($2125.87 \text{ (sh, m) cm}^{-1}$) is shifted toward higher frequencies from those of K₄[Mo(CN)₈]·2H₂O ($2101 \text{ (s), } 2120 \text{ (s) cm}^{-1}$) clearly showing a coordination of a few CN groups to copper ions. The stretches observed at $2101.91 \text{ (sh, s) cm}^{-1}$ show that free CN groups are also present in this compound. The IR feature is confirmed by the X-ray crystallographic analysis.

3.2. Crystal structure

The compound contains two copper sites and Mo atom localized at the special equivalent position. An ORTEP drawing of [Cu(L)]₂[Mo(CN)₈]·2.5H₂O is shown in Fig. 1 and Projection of compound **1** along *a*-axis is shown in Fig. 2. Selected bond lengths and angles are listed in Table 1. The asymmetric unit of the structure consists of one octacyanotungstate [Mo(CN)₈]⁴⁻ moiety coordinated via four cyano bridged to four Cu(L) fragments, the four other cyano groups being terminal. (Fig. 1)

The molybdenum atom is surrounded by eight cyano groups in a distorted square antiprism (D_{4h}), with Mo—C distance ranging from 2.108 to 2.273 Å (the mean value is 2.183 Å). The first square C1—C2—C3—C4 slightly distorted (C···C distance in the range from 2.509 to 2.645 Å), with angles in the range from 84.23° to 94.82°, which is compared to the second square C1_d—C2_d—C3_d—C4_d (C···C distance and angles are the same to the first square.). Simultaneously, the two squares are twisted with the angle of about 45°. Each Cu^{II} is in an elongated octahedral coordination environment, in which four nitrogen atoms from L ligand are located at the equatorial positions

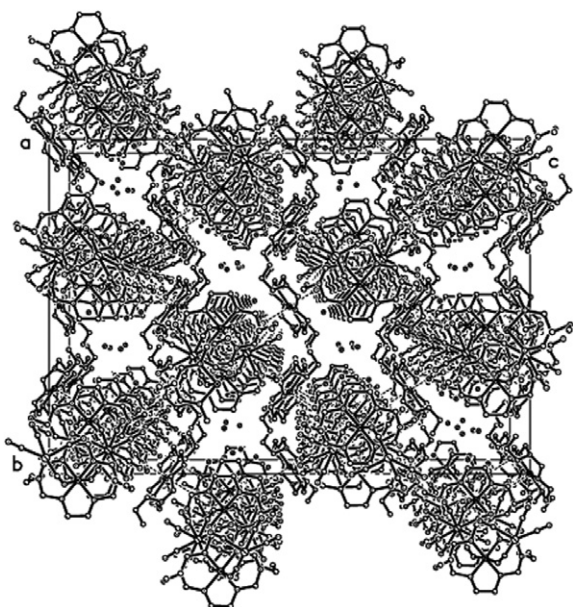


Fig. 2. Projection of compound **1** along *a*-axis (omitting hydrogen atoms).

Table 1
Selected bond lengths (Å) and bond angles (deg) for compound **1**

Mo1—C1	2.273(3)	Cu2—N4	2.566(2)
Mo1—C2	2.157(3)	Cu2—N8	2.025(2)
Mo1—C3	2.108(3)	Cu2—N10	2.099(2)
Mo1—C4	2.193(3)	N1—C1	1.122(4)
Cu1—N1	2.396(2)	N2—C2	1.196(3)
Cu1—N5	1.999(2)	N3—C3	1.184(3)
Cu1—N7	2.037(2)	N4—C4	1.192(3)
Mo1—C1—N1	172.6(2)	Mo1—C4—N4	173.5(2)
Mo1—C2—N2	172.7(2)	N4—Cu2—N4	180.00
Mo1—C3—N3	175.3(2)	Cu1—N1—C1	137.8(2)

with the Cu—N_{eq} bond distances in the range of 1.999(2)–2.099(2) Å, while the axial sites are occupied by two nitrogen atoms from the bridging cyanide groups on [Mo(CN)₈]⁴⁻ anion. Owing to the Jahn-Teller effects occurring to each copper atom, the Cu—N_{cyanide} interactions at the apical positions are observably different. The axial Cu—N_{ax} bonds for Cu1 and Cu2 [Cu1—N1 = 2.396(2) Å, Cu2—N4 = 2.566(2) Å] are slightly longer than the equatorial Cu—N_{eq} bonds (mean value is 2.040 Å). In addition, the apical C1—N1—Cu1—N1_d—C1_d and C4—N4—Cu2—N4_d—C4_d are closed to equal 180°, respectively.

It is notice that the C—N—Cu bond angles are far from linearity with the angles ranging from 137.8(2)° to 138.88(19)°, although the Mo—C—N angles are almost linear, ranging from 172.6(2)° to 175.3(2)° and highly delocalized electronic density between Mo^{IV} ions and CN group, which are similar to those in other complexes: [M^{II}(H₂O)₂][Mo^{IV}(CN)₈]₂·4H₂O (M = Mn, Co) [11], [Fe^{II}(H₂O)₂][Mo^{IV}(CN)₈] [12], {[Cu(en)₂]₃[W(CN)₈]₂·H₂O} [13], and Mn^{II}₂(H₂O)₂(CH₃COO)₂[W^V(CN)₈]₂·2H₂O [14].

It is indicative that the flexibility of Mo—C—N—Cu linkage in Cu^{II}—Mo^{IV}(CN)₈ system may lead to the versatile structures of bimetallic octacyanides. The structure

of compound **1** can be described as an infinite 3D assembly of Mo...Cu...Mo linkage and the Mo...Mo separations along the Mo—CN—Cu—NC—Mo linkage varying from 10.005 to 11.114 Å. (Fig. 2). The different structure between compound **1** and the two-dimensional compound [Cu(cyclam)]₂[Mo(CN)₈]·10.5H₂O [15] is mainly due to the different spatial steric hindrance effect of the macrocyclic ligand L. This arrangement results in channels running along the *a*-axis occupied by crystallized water molecules.

3.3. TGI/DTG analysis

The thermal analysis effectuated under an helium atmosphere from room temperature up to 1200 °C exhibits two well-pronounced weight loss steps as the temperature was increased (Fig. 3). The two steps can be determined by inflection points at 70 and 189 °C corresponding to weight losses of 14.4% and 23.0%, respectively. The first weight loss step corresponds well with the loss of 2.5 crystallized water molecules located in the channels. The second step corresponds with the decomposition of the original structure.

3.4. Magnetic properties

The temperature dependence of $\chi_M T$ and $1/\chi_M$ for a polycrystalline sample of compound **1** is presented in Fig. 4. The μ_{eff} per Cu₂Mo unit at room temperature, 2.4 μ_B , is consistent with the value of 2.45 μ_B expected for the magnetically dilute spin ions. On lowering the temperature, the μ_{eff} value almost remains constant, which shows weak interaction between paramagnetic Cu²⁺ ions (*S* = 1/2). The magnetic susceptibility obeys the Curie–Weiss law with a positive Weiss constant $\theta = 0.73$ K and a Curie constant $C = 0.728$ emu K mol⁻¹. These results indicate further that there is negligible magnetic interaction between the Cu²⁺ ions through the diamagnetic NC—Mo(IV)—CN bridge.

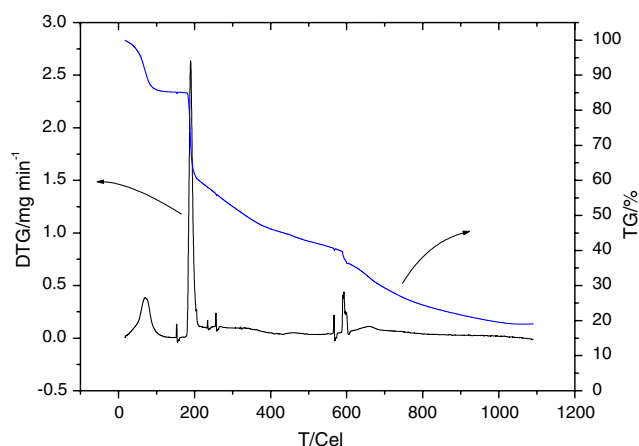


Fig. 3. Thermal analysis curve of compound **1**.

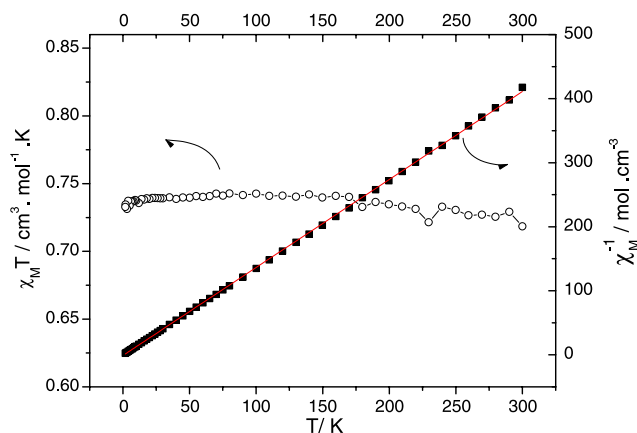


Fig. 4. Plots of $\chi_M T$ (○) and $1/\chi_M$ (■) of the compound **1** versus T .

4. Conclusion

It should be noted that structurally characterized polynuclear compounds based on the use of $[\text{Mo}(\text{CN})_8]^{4-}$ as a building block are still rare. A new three-dimensional compound $[\text{Cu}(\text{L})_2][\text{Mo}(\text{CN})_8] \cdot 2.5\text{H}_2\text{O}$ (**1**) with the use of a macrocyclic ligand **L** has been crystallized, structurally and magnetically characterized. The Mo^{IV} centers in **1** adopt a distorted square antiprism geometry, while the Cu^{II} centers in **1** adopt an elongated octahedral geometry. Variable-temperature magnetic susceptibility measurements reveal that there is negligible magnetic interaction between the Cu^{II} centers in compound **1**. Additionally, given that the diamagnetic Mo^{IV} ion is photooxidized to paramagnetic Mo^{V} ion, this compound may also exhibit interesting photomagnetic properties.

5. Supplementary materials

CCDC 294055 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).

Acknowledgement

The work is supported by the Natural Science Foundation of Jiangsu Province (No. BK2005056).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2006.04.051](https://doi.org/10.1016/j.molstruc.2006.04.051).

References

- [1] M. Ohba, H. Okawa, *Coord. Chem. Rev.* 198 (2000) 313.
- [2] J. Larionova, S. Willemin, B. Donnadieu, B. Henner, C. Guérin, B. Gillon, A. Goujon, *J. Phys. Chem. Solids* 65 (2004) 677.
- [3] (a) A.H. Yuan, J.Z. Zou, B.L. Li, Z.G. Zha, C.Y. Duan, Y.J. Liu, Z. Xu, S. Keizer, *Chem. Commun.* (2000) 1297; (b) A.H. Yuan, X.P. Shen, Q.J. Wu, Z.X. Huang, Z. Xu, *J. Coord. Chem.* 55 (2002) 411.
- [4] (a) R. Podgajny, T. Korzeniak, K. Stadnicka, Y. Dromzée, N.W. Alcock, W. Errington, K. Kruczala, M. Balanda, T.J. Kemp, M. Verdaguier, B. Sieklucka, *Dalton Trans.* (2003) 3458; (b) P. Przychodzeń, K. Lewiński, M. Balanda, R. Pelka, M. Rams, T. Wasiutyński, C. Guyard-Duhayon, B. Sieklucka, *Inorg. Chem.* 43 (2004) 2967; (c) T. Korzeniak, R. Podgajny, N.W. Alcock, K. Lewiński, M. Balanda, T. Wasiutyński, B. Sieklucka, *Polyhedron* 22 (2003) 2183; (d) W. Dong, Y.Q. Sun, L.N. Zhu, D.Z. Liao, Z.H. Jiang, S.P. Yan, P. Cheng, *New J. Chem.* 27 (2003) 1760.
- [5] (a) G. Rombaut, C. Mathoniere, P. Guionneau, S. Golhen, L. Ouahab, M. Verelst, P. Lecante, *Inorg. Chim. Acta* 326 (2001) 27; (b) R. Kania, K. Lewiński, B. Sieklucka, *Dalton Trans.* (2003) 1033; (c) F.T. Chen, D.F. Li, S. Gao, X.Y. Wang, Y.Z. Li, L.M. Zheng, W.X. Tang, *Dalton Trans.* (2003) 3283.
- [6] (a) D.F. Li, L.M. Zheng, X.Y. Wang, J. Huang, S. Gao, W.X. Tang, *Chem. Mater.* 15 (2003) 2094; (b) Y. Arimoto, S.I. Ohkoshi, Z.J. Zhong, H. Seino, Y. Mizobe, K. Hashimoto, *Chem. Lett.* (2002) 832; (c) D.F. Li, L.M. Zheng, Y.Z. Zhang, J. Huang, S. Gao, W.X. Tang, *Inorg. Chem.* 42 (2003) 6123; (d) D.F. Li, S. Gao, L.M. Zheng, K.B. Yu, W.X. Tang, *New J. Chem.* 26 (2002) 1190.
- [7] (a) C. Mathoniere, R. Podgajny, P. Guionneau, C. Labrugere, B. Sieklucka, *Chem. Mater.* 17 (2005) 44; (b) Y.S. You, D. Kim, Y. Do, S.J. Oh, C.S. Hong, *Inorg. Chem.* 43 (2004) 6899; (c) D. Kim, Y. Do, S.J. Oh, C.S. Hong, *Inorg. Chem.* 43 (2004) 6899; (d) K. Lewiński, M. Balanda, T. Wasiutyński, B. Sieklucka, *Polyhedron* 22 (2003) 2183; (e) F. Tuna, S. Golhen, L. Ouahab, J.P. Sutter, *Comptes Rendus Chimie* 6 (2003) 377; (f) S. Willemin, J. Larionova, R. Clerac, B. Donnadieu, B. Henner, X. Le Goff, C. Guerin, *Eur. J. Inorg. Chem.* 10 (2003) 1866; (g) R. Eckhardt, H. Hanika-Heidl, R.D. Fischer, *Chemistry* 9 (2003) 1795; (h) S. Si, X. Liu, D.Z. Liao, S.P. Yan, Z.H. Jiang, P. Cheng, *J. Coord. Chem.* 56 (2003) 337; (i) B. Sieklucka, R. Podgajny, T. Korzeniak, P. Przychodzen, R. Kania, *Comptes Rendus Chimie* 5 (2002) 639; (j) F. Chang, H.L. Sun, H.Z. Kou, S. Gao, *Inorg. Chem. Commun.* 5 (2002) 660; (k) D.F. Li, S. Gao, L.M. Zheng, W.X. Tang, *J. Chem. Soc. Dalton Trans.* (2002) 2805; (l) T. Korzeniak, R. Podgajny, N.W. Alcock, D.F. Li, S. Gao, L.M. Zheng, W.X. Tang, *J. Chem. Soc. Dalton Trans.* 14 (2002) 2805; (m) G. Rombaut, C. Mathoniere, P. Guionneau, S. Golhen, L. Ouahab, M. Verelst, P. Lecante, *Inorg. Chim. Acta* 326 (2001) 27; (n) G. Rombaut, S. Golhen, L. Ouahab, C. Mathoniere, O. Kahn, *Dalton* 20 (2000) 3609; (o) A.K. Sra, G. Rombaut, F. Lahit, S. Golhen, L. Ouahab, C. Mathoniere, J.V. Yakhmi, O. Kahn, *New J. Chem.* 24 (2000) 871; (p) G. Rombaut, S. Golhen, L. Ouahab, C. Mathoniere, O.J. Kahn, *Chem. Soc. Dalton Trans.* (2000) 3609; (q) A.K. Sra, M. Andruh, O. Kahn, S. Golhen, L. Ouahab, J.V. Yakhmi, *Angew. Chem., Int. Ed.* 38 (1999) 2606; (r) B. Nowicka, M. Hagiwara, Y. Wakatsuki, H. Kisch, *Bull. Chem. Soc. Jpn* 72 (1999) 441.
- [8] X.P. Shen, S. Gao, G. Yin, K.B. Yu, Z. Xu, *New J. Chem.* 28 (2004) 996.
- [9] M.P. Suh, S.G. Kang, *Inorg. Chem.* 27 (1988) 2544.

- [10] A. Samotus, *Pol. J. Chem.* 47 (1973) 265.
- [11] S. Willemin, J. Larionova, R. Clérac, B. Donnadien, B. Henner, X.F. Le Goff, C. Guérin, *Eur. J. Inorg. Chem.* (2003) 1866.
- [12] Z.J. Zhong, H. Seino, Y. Mizobe, M. Hidai, M. Verdaguar, S.I. Ohkoshi, K. Hashimoto, *Inorg. Chem.* 39 (2000) 5095.
- [13] D.F. Li, S. Gao, et al., *New J. Chem.* 26 (2002) 485.
- [14] Y. Song, S.I. Ohkoshi, Y. Arimoto, H. Seino, Y. Mizobe, K. Hashimoto, *Inorg. Chem.* 42 (2003) 1848.
- [15] J. Larionova, R. Clérac, B. Donnadien, S. Willemin, C. Guérin, *Cryst. Growth Des.* 3 (2003) 267.