

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

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>

Design, synthesis and magnetic properties of a ladderlike complex constructed by secondary building units

Jin-Ling Lu^a; Xin-Hua Li^a; Hong-Ping Xiao^a; Qian Shi^a

^a College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325027, P.R. China

First published on: 08 February 2010

To cite this Article Lu, Jin-Ling , Li, Xin-Hua , Xiao, Hong-Ping and Shi, Qian(2010) 'Design, synthesis and magnetic properties of a ladderlike complex constructed by secondary building units', *Journal of Coordination Chemistry*, 63: 4, 617 – 624, First published on: 08 February 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970903583819

URL: <http://dx.doi.org/10.1080/00958970903583819>

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.

Design, synthesis and magnetic properties of a ladderlike complex constructed by secondary building units

JIN-LING LU, XIN-HUA LI*,
HONG-PING XIAO and QIAN SHI

College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou,
Zhejiang 325027, P.R. China

(Received 10 April 2009; in final form 23 September 2009)

A secondary building unit (SBU), $[\text{Ni}(2,2'\text{-bipy})(5\text{-npa})(\text{H}_2\text{O})_n]$ [where 2,2'-bipy = 2,2'-bipyridine, 5-npa = 5-nitroisophthalic dianion], was synthesized as starting material of a polystep reaction. A ladderlike complex (LLC) Ni(II) coordination polymer, $\{[\text{Ni}(2,2'\text{-bipy})(5\text{-npa})(4,4'\text{bipy})_{0.5}](\text{H}_2\text{O})_n\}$, was constructed by polystep reaction using this SBU. In LLC, two SBUs were cross-linked by 4,4'-bipy [where 4,4'-bipy = 4,4'-bipyridine] forming a 1-D ladderlike structure. The magnetic properties of the LLC and SBU are discussed.

Keywords: Polystep reaction; Secondary building units (SBUs); Synthesis

1. Introduction

Design and construction of inorganic–organic hybrid coordination complexes is a hot topic due to their fascinating structural features and potential as functional materials in magnetism, gas storage, ion exchange, catalysis, separations, electric conductivity, and molecular recognition [1–4]. Coordination complexes based on self-assembly [5–8] have been studied intensively. Owing to difficult prediction of either composition or structure of the final product [9, 10], designing a target framework was limited. The most effective approach is using secondary building units (SBUs) as the designing material to obtain tailor-made structures with the required structures and properties starting from well-characterized inorganic and organic species (SBUs) [11–14]. Many coordination complexes have been prepared by multiple step reactions [13, 15]; under some reaction conditions, solvent coordinated to metal [16–18]. Replacing the coordinated solvent with a rigid linker could provide a method for synthesis of predictable structures. Thus, coordination complexes with coordinated solvent could act as starting materials for further reactions. By choosing appropriate rigid linkers, target structures with predictable properties could be obtained by polystep

*Corresponding author. Email: lixinhua01@126.com

reactions [19, 20], as those SBUs already had their own geometry conformation and properties. Here, we report the synthesis of a ladderlike Ni(II) coordination polymer, $\{[\text{Ni}(2,2'\text{-bipy})(5\text{-npa})(4,4'\text{-bipy})0.5]\cdot(\text{H}_2\text{O})\}_n$ [where $2,2'\text{-bipy} = 2,2'\text{-bipyridine}$, $4,4'\text{-bipy} = 4,4'\text{-bipyridine}$, $5\text{-npa} = 5\text{-nitroiso phthalic dianion}$], by polystep reactions. $[\text{Ni}(2,2'\text{-bipy})(5\text{-npa})(\text{H}_2\text{O})]_n$ was synthesized for polystep reactions, in which the coordinated water molecule had suitable position to be replaced by $4,4'\text{-bipy}$ (figure 1).

2. Experimental

2.1. General information

Commercially available reagents were used as received without purification. Single-crystal diffraction data were recorded on a Bruker Smart-1000 CCD diffractometer. X-ray powder diffraction measurements were recorded on a Bruker D8 ADVANCE diffractometer. IR spectra (KBr disk) were recorded on an EQUINOX55 (Bruker) spectrophotometer. Temperature-dependent magnetic measurements were determined on a Quantum Design SQUID-XL7 magnetometer. Thermal gravimetric analysis from 40 to 500 °C was carried out under N_2 at a heating rate of 5°C min^{-1} using a TA-Q600 instrument. Carbon, hydrogen, and nitrogen were determined using an EA 1112 elemental analyzer.

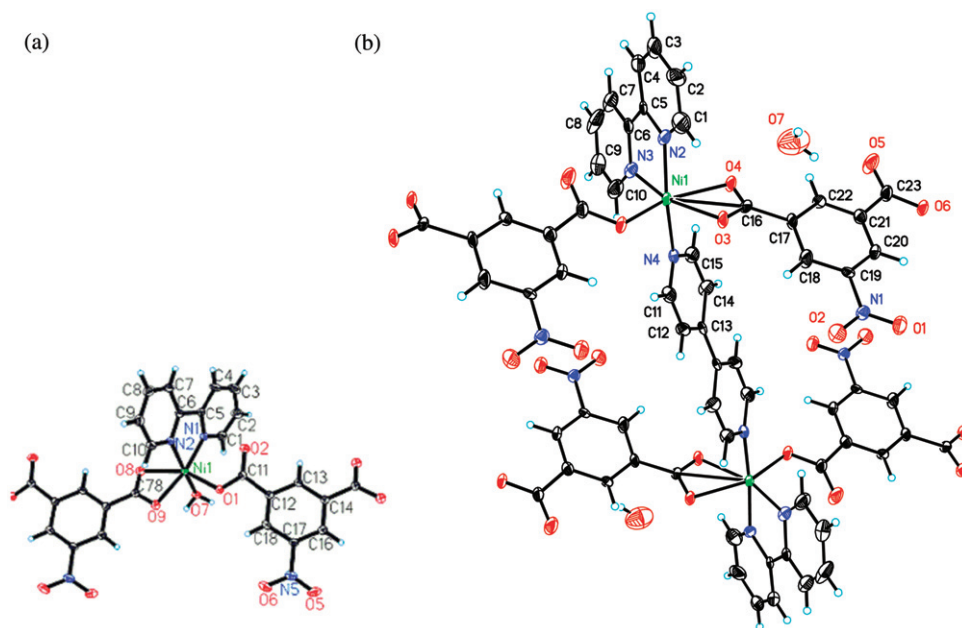


Figure 1. ORTEP plot of the title compounds showing 50% probability displacement ellipsoids. Only the contents of the asymmetric unit are labeled: (a) SBU and (b) LLC.

2.2. Synthesis of secondary building units

A mixture of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (1 mM, 267 mg), 5-npa (1 mM, 215.5 mg), NaOH (200 μL , 10 M), 2,2'-bipy (1 mM, 158 mg), and H_2O (5 mL) was heated in a 25 mL stainless steel reactor with a Teflon liner at 150°C for 48 h. The blue crystalline product was filtered and washed with water. Yield: 75% based on Ni. Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{N}_3\text{NiO}_7$: C, 48.98; H, 2.95; N, 9.52. Found: C, 49.29; H, 2.99; N, 9.74. IR (KBr): 3407, 1721, 1640, 1609, 1541, 1451, 1397, and 1341 cm^{-1} .

2.3. Synthesis of the ladderlike complex

A mixture of SBUs (1 mM, 442 mg), 4,4'-bipy (0.5 mM, 79 mg), and H_2O (10 mL) was heated in a 25 mL stainless steel reactor with a Teflon liner at 150°C for 48 h. Navy blue crystalline product was obtained, then filtered and washed with water. Yield: >90% based on SBUs. Anal. Calcd for $\text{C}_{46}\text{H}_{32}\text{N}_8\text{Ni}_2\text{O}_{13}$: C, 54.05; H, 3.16; N, 10.96. Found: C, 54.16; H, 3.05; N, 11.02. IR (KBr): 3451, 1609, 1570, 1540, 1435, 1400, and 1354 cm^{-1} .

2.4. X-ray crystallographic studies

Intensity data for SBU and LLC were measured on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All empirical absorption corrections were applied using SADABS [21]. The structures for SBU and LLC were solved by direct methods and refined on F^2 by full-matrix least squares using the SHELXL-97 program package [22]. The positions of hydrogens were generated theoretically (C–H fixed at 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbons before the final cycle of refinement. Crystal data and structure determination summaries are summarized in table 1.

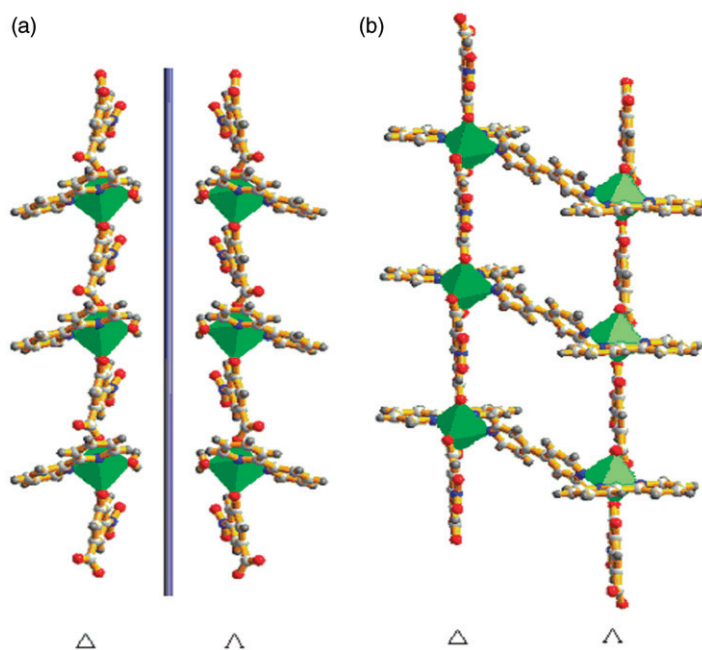
3. Results and discussion

Designing a functional SBU with coordinated solvent was the most important step in this polystep reaction. We chose nickel(II) sulfate hexahydrate, 5-npa, and 2,2'-bipy as reactants. Each Ni(II) was six coordinate with bonding to a water, a 2,2'-bipy, and two 5-npa ligands forming a distorted octahedral geometry (figure 1). This coordination could be found in most Ni coordination compounds [23–28]. 5-npa could coordinate monodentate [29], but simultaneous chelating and monodentate coordination of the same 5-npa led to a 1-D structure. There were strong intermolecular hydrogen bonds and π – π interactions between chains. This coordination of carboxyl is also found in Ni coordination complexes, but leads to a binuclear nickel(II) complex, not a chain [26]. The coordinated water had suitable volume to be replaced by 4,4'-bipy. Chiral chains (Δ - and Λ -chains) existed in neighboring holes, and they were racemic complexes (figure 2). If the coordinated water was replaced by 4,4'-bipy, a ladderlike coordination polymer could be obtained (figure 3). The thermogravimetric analysis of the SBU

Table 1. Crystallographic data and processing parameters for SBUs and LLC.

	SBUs	LLC
Empirical formula	C ₁₈ H ₁₃ N ₃ NiO ₇	C ₂₃ H ₁₇ N ₄ NiO ₇
Formula weight	442.00	520.10
Temperature (K)	298(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions (Å, °)		
<i>a</i>	8.4076(7)	7.439(2)
<i>b</i>	10.0247(11)	9.750(2)
<i>c</i>	12.0437(10)	15.670(4)
α	74.826(2)	78.11(3)
β	72.0690(10)	80.67(4)
γ	65.2300(10)	69.68(3)
Volume (Å ³), <i>Z</i>	866.51(14), 2	1037.9(5), 2
Calculated density (g cm ⁻³)	1.694	1.664
Absorption coefficient (mm ⁻¹)	1.171	0.992
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.0332, <i>wR</i> ₂ = 0.0842	<i>R</i> ₁ = 0.0659, <i>wR</i> ₂ = 0.1469
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0366, <i>wR</i> ₂ = 0.0862	<i>R</i> ₁ = 0.1408, <i>wR</i> ₂ = 0.1770

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

Figure 2. Δ - and Λ -chains of the title compounds: (a) Enantiotopic chains in the neighboring holes of SBUs and (b) Enantiotopic chains in the same ladder of LLC.

(Supplementary material) shows the first step 150–175°C is loss of coordinated water [30] (calculated for a coordinated water 4.07%, found 3.76%), indicating that the coordinated water could be replaced by 4,4'-bipy at hydrothermal conditions; this substitution was successfully achieved in this article, and we obtained the LLC.

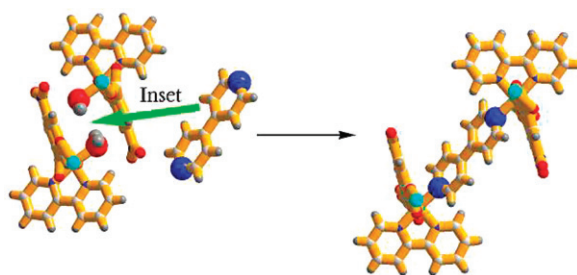


Figure 3. Inserting 4,4'-bipy into the neighboring chains of SBUs.

Each Ni(II) was six coordinate in LLC with bonding to a 4,4'-bipy molecule, a 2,2'-bipy, and two 5-npa ligands; 4,4'-bipy was a bridging ligand (figure 1). Two chains were cross-linked by 4,4'-bipy resulting in one-dimension (1-D) infinite chains adopting a 1-D ladderlike structure motif assembled from edge-sharing rhombic squares [31]. The chains interacted by π - π stacking and hydrogen interactions [32]. There were also some ladderlike coordination polymers of lanthanide [33].

It was difficult to synthesize the LLC starting with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 2,2'-bipy, 4,4'-bipy, and 5-npa, as a difficult to separate mixture was obtained. By preparing the SBU, we obtained pure LLC with high yield. As the SBUs already had its own geometry, the structure of the LLC could be forecast. Cross-linking two chains of SBUs with 4,4'-bipy, we constructed the ladderlike structure.

3.1. IR spectra

The IR spectra of SBUs and LLC were performed as KBr pellets from 4000 to 400 cm^{-1} . These polymers showed asymmetric vibration bands of the carboxylates [34–36] at 1640 – 1540 cm^{-1} for SBUs, 1609 – 1540 cm^{-1} for LLC, and the symmetric vibration bands at 1457 – 1348 cm^{-1} for SBUs, 1430 – 1354 cm^{-1} for LLC. The values $\Delta [\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)] = 89\text{ cm}^{-1}$ for SBUs, 110 cm^{-1} for LLC indicated chelating carboxylate [34–36]. The IR asymmetric and symmetric (CO_2) stretching vibrations at 1541 and 1397 cm^{-1} , 1341 cm^{-1} for SBUs, 1540 , 1400 , and 1354 cm^{-1} for LLC, showed that 5-npa adopted both monodentate and chelating coordination [37]. The stretching vibration at 3407 cm^{-1} for SBUs showed the presence of coordinated water, while at 3451 cm^{-1} for LLC showed the presence of guest water. A strong band at 1571 cm^{-1} in the spectrum of LLC confirmed the presence 2,2'-bipy and 4,4'-bipy ligands, which was consistent with the X-ray analysis.

3.2. Magnetic properties

Magnetic measurements were performed on samples of SBU and LLC. The temperature dependence of magnetic susceptibility of SBUs and LLC in the forms of χ_{M} versus T with $\chi_{\text{M}}T$ versus T plot as an inset, and $1/\chi_{\text{M}}(T)$ versus T are displayed in figures 4 and 5, respectively.

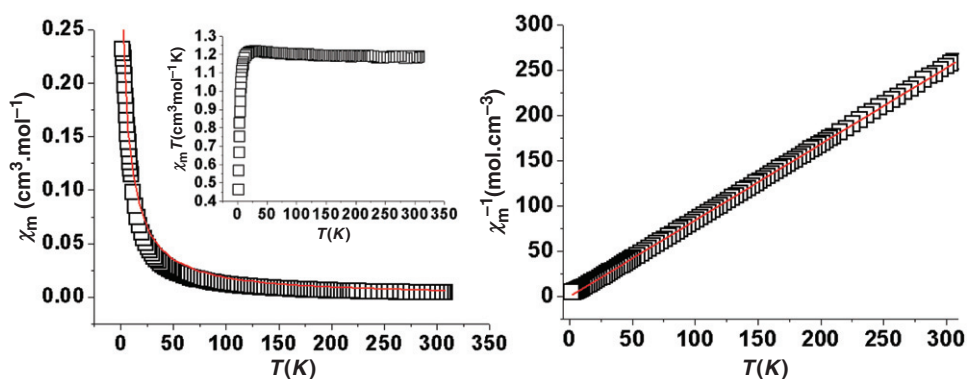


Figure 4. Magnetic susceptibility for SBU measured in an applied field of 5 kOe on a polycrystalline sample: (a) $\chi_M(T)$ vs. T , the inset is the plot of $\chi_M T$ vs. T and (b) Plot of $1/\chi_M(T)$ vs. T .

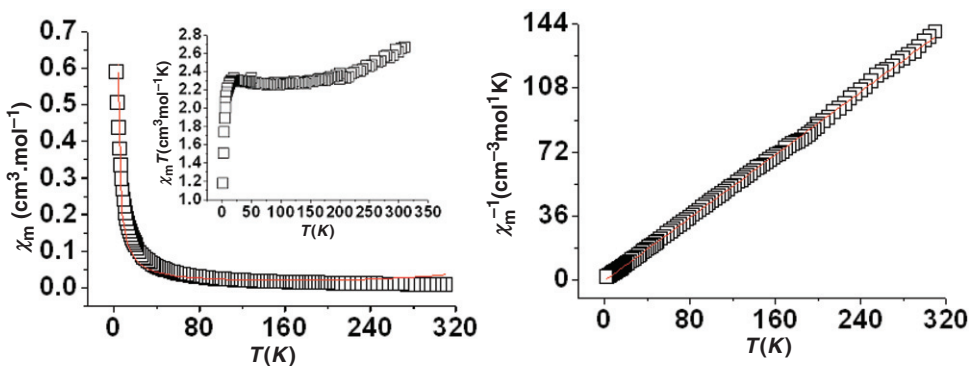


Figure 5. Magnetic susceptibility for LLC measured in an applied field of 5 kOe on a polycrystalline sample: (a) $\chi_M(T)$ vs. T , the inset is the plot of $\chi_M T$ vs. T and (b) Plot of $1/\chi_M(T)$ vs. T .

Replacing coordinated water with 4,4'-bipy, the magnetic properties were different at higher temperature. In SBU, as the temperature cooled, $\chi_M T$ slightly increased then decreased, while in LLC, the value of $\chi_M T$ first decreased and then slightly increased. This may be attributed to the different donors such that replacement of H_2O by 4,4'-bipy was accompanied by an increase of the weak antiferromagnetic coupling [37].

The value of $\chi_M T$ at 300 K for SBU was $1.18 \text{ cm}^3 \text{ K M}^{-1}$, lower than the spin-only value (for $S = 1$ of $2.24 \text{ cm}^3 \text{ K M}^{-1}$ with $g = 2.2$). The effective magnetic moment was $3.08 \mu\text{B}$, close to the typical value of $3.03 \mu\text{B}$ for octahedral complexes of Ni, indicative of a quenched orbital contribution. However, the value of $\chi_M T$ at 300 K for LLC was $2.61 \text{ cm}^3 \text{ K M}^{-1}$ and the effective magnetic moment was $4.57 \mu\text{B}$, both higher than the spin-only values, indicative of an unquenched orbital contribution [38] typical of the $^4\text{T}_{1g}$ ground state. The different effective magnetic moments for SBUs and LLC may be attributed to the different donors [37].

4. Conclusion

A ladderlike coordination polymer, $\{[\text{Ni}(2,2'\text{-bipy})(5\text{-npa})(4,4'\text{-bipy})0.5]\cdot(\text{H}_2\text{O})\}_n$, was synthesized based on $[\text{Ni}(2,2'\text{-bipy})(5\text{-npa})(\text{H}_2\text{O})]_n$ by polystep reaction. When 4,4'-bipy replaced the coordinated water of SBU, the target LLC was obtained with different magnetic properties.

Supplementary material

CCDC-691708, 696825 contains the supplementary crystallographic data of SBUs and LLC for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgements

We acknowledge financial support by the National Natural Science Foundation of China (grant no. 20871095).

References

- [1] X.X. Xu, Y. Lu, E. Wang, Y. Ma, X.L. Bai. *Cryst. Growth Des.*, **6**, 2029 (2006).
- [2] K. Uemura, K. Saito, S. Kitagawa, H. Kita. *J. Am. Chem. Soc.*, **128**, 16122 (2006).
- [3] K.E. Christensen, L. Shi, T. Conradsson, T.Z. Ren, M.S. Dadachov, X.D. Zou. *J. Am. Chem. Soc.*, **128**, 14238 (2006).
- [4] C. Biswas, P. Mukherjee, M.G.B. Drew, C.J. Gómez-García, J.M. Clemente-Juan, A. Ghosh. *Inorg. Chem.*, **46**, 10771 (2007).
- [5] Z.L. Chu, H.B. Zhu, D.H. Hu, W. Huang, S.H. Gou. *Cryst. Growth Des.*, **8**, 1599 (2008).
- [6] X.H. Li, S.Z. Yang, P.H. Xiao. *Cryst. Growth Des.*, **6**, 2392 (2006).
- [7] W. Ouellette, J.R. Galán-Mascarós, K.R. Dunbar, J. Zubieta. *Inorg. Chem.*, **45**, 1909 (2006).
- [8] M.O. Awaleh, F. Baril-Robert, C. Reber, A. Badia, F. Brisse. *Inorg. Chem.*, **47**, 2964 (2008).
- [9] X.X. Xu, Y. Lu, E. Wang, Y. Ma, X.L. Bai. *Cryst. Growth Des.*, **6**, 2029 (2006).
- [10] X.J. Zhang, Y.P. Tian, F. Jin, J.Y. Wu, Y. Xie, X.T. Tao, M.H. Jiang. *Cryst. Growth Des.*, **5**, 565 (2005).
- [11] C.Y. Niu, B.L. Wu, X.F. Zheng, H.Y. Zhang, H.W. Hou, Y.Y. Niu, Z.J. Li. *Cryst. Growth Des.*, **8**, 1566 (2008).
- [12] Q. Xu, R.Q. Zou, R.Q. Zhong. *Cryst. Growth Des.*, **8**, 2458 (2008).
- [13] L. Han, Y. Zhou, W.N. Zhao. *Cryst. Growth Des.*, **8**, 2052 (2008).
- [14] X.F. Huang, D.W. Fu, R.G. Xiong. *Cryst. Growth Des.*, **8**, 1795 (2008).
- [15] E.V. Anokhina, Y.B. Go, Y.J. Lee, T. Vogt, A.J. Jacobson. *J. Am. Chem. Soc.*, **128**, 9957 (2006).
- [16] B.Q. Chen, H. Lei, B.L. Wu, M.Y. Wu, Y.G. Huang, M.C. Hong. *Chinese J. Struct. Chem.*, **25**, 527 (2006).
- [17] Y.B. Go, X.Q. Wang, E.V. Anokhina, A.J. Jacobson. *Inorg. Chem.*, **44**, 8265 (2005).
- [18] H.B. Abourahma, B. Moulton, V. Kravtsov, M.J. Zaworotko. *J. Am. Chem. Soc.*, **124**, 9990 (2002).
- [19] C.D. Wu, L. Zhang, W.B. Lin. *Inorg. Chem.*, **45**, 7278 (2006).
- [20] H. Chun. *J. Am. Chem. Soc.*, **130**, 800 (2008).
- [21] G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Determination*, University of Göttingen, Germany (1997).

- [22] G.M. Sheldrick. *SHELXL-97-2, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
- [23] J. Yang, W.W. Bao, X.M. Ren, Y. Xu, X. Shen, D.R. Zhu. *J. Coord. Chem.*, **62**, 1809 (2009).
- [24] S. Salehzadeh, R. Golbedaghi, H.R. Khavasi. *J. Coord. Chem.*, **62**, 2532 (2009).
- [25] J. Li, J.Z. Li, H.Q. Zhang, Y. Zhang, J.Q. Li. *J. Coord. Chem.*, **62**, 2465 (2009).
- [26] L.F. Ma, L.Y. Wang, J.G. Wang, Y.F. Wang, X. Feng. *J. Coord. Chem.*, **60**, 1989 (2007).
- [27] X.T. Liu, Y.S. Xie, Q.L. Liu. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **37**, 301 (2007).
- [28] E.Q. Gao, Q.H. Zhao, J.K. Tang, D.Z. Liao, Z.H. Jiang, S.P. Yan. *J. Coord. Chem.*, **55**, 205 (2002).
- [29] H.T. Xu, Y.D. Li. *J. Mol. Struct.*, **693**, 11 (2004).
- [30] X.L. Hong, Y.Z. Li, H.M. Hu, Y. Pan, J.F. Bai, X.Z. You. *Cryst. Growth Des.*, **6**, 1221 (2006).
- [31] S.L. Ma, S. Ren. *J. Inorg. Organomet. Polym. Mater.*, **19**, 382 (2009).
- [32] K.S. Min, M.P. Suh. *J. Solid State Chem.*, **152**, 183 (2000).
- [33] X.P. Yang, J.H. Rivers, W.J. McCarty, M. Wiester, R.A. Jones. *New J. Chem.*, **32**, 790 (2008).
- [34] Y.B. Go, X.Q. Wang, V. Ekaterina, A. Anokhina, J. Jacobson. *Inorg. Chem.*, **43**, 5360 (2004).
- [35] J.H. Luo, M.C. Hong, R.H. Wang, R. Cao, L. Han, D.Q. Yuan, Z.Z. Lin, Y.F. Zhou. *Inorg. Chem.*, **42**, 4486 (2003).
- [36] A.K. Ghosh, D. Ghoshal, E. Zangrando, J. Ribas, N.R. Chaudhuri. *Inorg. Chem.*, **46**, 3057 (2007).
- [37] P. Román, C. Guzmán-Miralles, A. Luque, J.I. Beitia, J. Cano, F. Lloret, M. Julve, S. Alvarez. *Inorg. Chem.*, **35**, 3741 (1996).
- [38] O. Castillo, A. Luque, P. Román, F. Lloret, M. Julve. *Inorg. Chem.*, **40**, 5526 (2001).