

研究简报

## 一种新的三维超分子化合物 $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})]\cdot 2(\text{hmt})\cdot 4\text{H}_2\text{O}$ 的合成和晶体结构(fum=反丁烯二酸根; hmt=六次甲基四胺)

刘琦<sup>\*,1</sup> 徐正<sup>2</sup> 郁开北<sup>3</sup>

(<sup>1</sup> 江苏工业学院化学工程系, 常州 213016)

(<sup>2</sup> 南京大学配位化学国家重点实验室, 配位化学研究所, 南京 210093)

(<sup>3</sup> 中国科学院成都有机化学研究所, 成都 610041)

关键词: 镍; 晶体结构; 反丁烯二酸根; 六次甲基四胺

中图分类号: O614.81\*3

文献标识码: A

文章编号: 1001-4861(2006)06-1095-04

## Synthesis and Crystal Structure of One Novel Three-dimensional Supramolecular Compound $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})]\cdot 2(\text{hmt})\cdot 4\text{H}_2\text{O}$ (fum=fumarate; hmt=hexamethylenetetramine)

LIU Qi<sup>\*,1</sup> XU Zheng<sup>2</sup> YU Kai-Bei<sup>3</sup>

(<sup>1</sup>Department of Chemical Engineering, Jiangsu Polytechnic University, Changzhou, Jiangsu 213016)

(<sup>2</sup>Coordination Chemistry Institute and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)

(<sup>3</sup>Chengdu Institute of organic Chemistry, Chinese Academy of Sciences, Chengdu 610041)

**Abstract:** The synthesis of nickel supramolecular compound with hexamethylenetetramine and fumarate ligands is reported. The compound  $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})]\cdot 2(\text{hmt})\cdot 4\text{H}_2\text{O}$  (**1**) (fum=fumarate; hmt=hexamethylenetetramine) were characterized by elemental analysis, crystal structure, IR. Compound **1** crystallizes in the triclinic system, space group  $P\bar{1}$ , and with  $Z=1$ . Cell parameters:  $a=0.9346(1)$ ,  $b=0.9338(1)$ ,  $c=0.9388(2)$  nm,  $\alpha=79.46(1)^\circ$ ,  $\beta=77.84(1)^\circ$ ,  $\gamma=61.296(7)^\circ$ . Every metal ion has a octahedral coordination geometry formed by six oxygen atoms from six water molecules, and the relative independent components  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , fumarate anions, hmt and  $\text{H}_2\text{O}$  molecules are linked together by two kinds of hydrogen bonds ( $\text{O}-\text{H}\cdots\text{O}$ , and  $\text{O}-\text{H}\cdots\text{N}$ ) to form a three-dimensional structure. CCDC: 256355.

**Key words:** Nickel; crystal structure; fumarate; hexamethylenetetramine

## 0 Introduction

Pronounced interest has recently been focused on the crystal engineering of supramolecular architectures organized by coordinated bonds or hydrogen bonds, due to their potential applications in developing new

materials with gas storage<sup>[1-4]</sup>, selection separation<sup>[5]</sup>, catalysis<sup>[6]</sup> and optoelectronics<sup>[3,7]</sup>. One of the synthesis methods used to construct the functional compounds is that octahedral coordination metal ions connects to polydentate ligand such as 4,4'-bipyridine, fumarate and so on to form multi-dimensional supramolecular

收稿日期: 2005-10-31。收修改稿日期: 2006-03-23。

江苏省教育厅自然科学基金(No.05KJB15002)和江苏工业学院自然科学基金资助项目。

\*通讯联系人。E-mail: liuqi62@163.com; Tel: 0519-3290185

第一作者: 刘琦, 男, 43岁, 副教授, 博士; 研究方向: 功能配合物和纳米化学。

polmer<sup>[8~15]</sup>. Recent years, hmt (hexamethylenetetramine), a potential tetradentate ligand or hydrogen bond acceptor, has been used by us and other research groups to react with metal ions to prepare supramolecular polymer<sup>[16~23]</sup>. As the continuing of our work, we now report the synthesis and crystal structure of the compound  $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})] \cdot 2(\text{hmt}) \cdot 4\text{H}_2\text{O}$  (**1**).

## 1 Experimental section

### 1.1 Materials and Physical Measurements

Fumaric acid,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and hexamethylenetetramine (hmt) were used as purchased. Element analyses(C, H, N) were determined on a Perkin-Elmer 2400 microanalysis instrument. IR absorption spectrum (KBr pellet) was recorded on a Nicolet FTIR 170X spectrophotometer.

### 1.2 Preparation of $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})] \cdot 2(\text{hmt}) \cdot 4\text{H}_2\text{O}$

Synthetic process of  $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})] \cdot 2(\text{hmt}) \cdot 4\text{H}_2\text{O}$  (**1**) is as follows: 1 mmol of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 4 mmol of hmt were dissolved in 5 mL of water. To this solution, an aqueous solution (5 mL) containing fumaric acid (1 mmol) and hmt (2 mmol) was added. The resulting green solution was allowed to stand at ambient temperature for one week, yielding green crystals in yield (60%). Anal. calcd. for  $\text{C}_{16}\text{H}_{46}\text{N}_8\text{NiO}_{14}$ (%): C, 30.34; H,

7.32. N, 17.70. Found(%): C, 30.30; H 7.28. N, 17.65. IR spectrum (KBr,  $\text{cm}^{-1}$ ): 3 255 (s, br), 2 438 (w), 1 690(m), 1 578(s), 1 459(s), 1 380(s), 1 238(s), 1 211(w), 1 051(w), 1 006(s), 810(s), 753(m), 692(s), 591(w), 508(s).

### 1.3 X-ray crystallography

Single-crystal X-ray diffraction measurement of **1** was carried out with a Siemens P4 diffractometer at 296(2) K. Intensities of reflections were measured using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.071\,073\text{ nm}$ ) with the  $\omega$  scans mode in the range of  $2.23^\circ < \theta < 25.98^\circ$ . The structure was solved by direct methods (SHELXS-97)<sup>[24]</sup> and refined by full-matrix least-squares methods on  $F^2$  with the SHELXL-97 program package. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. The hydrogen atoms of water molecules were found by difference Fourier syntheses, and the other hydrogen atoms were located in calculated position and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1, the selected bond lengths (nm) and bond angles ( $^\circ$ ) are given in Table 2, and the hydrogen bonds parameters are presented in Table 3, respectively.

CCDC: 256355.

**Table 1** Summary of crystal data, data collection and structure refinement for the  $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})] \cdot 2(\text{hmt}) \cdot 4\text{H}_2\text{O}$  (**1**)

Formula	$\text{C}_{16}\text{H}_{46}\text{N}_8\text{NiO}_{14}$	Volume / $\text{nm}^3$	0.669 25(19)
Formula weight	633.32	Z	1
Color	Green	Density (calculated) / ( $\text{Mg} \cdot \text{m}^{-3}$ )	1.504
Crystal size / mm	$0.56 \times 0.54 \times 0.20$	Absorption coefficient / $\text{mm}^{-1}$	0.771
Temperature / K	296(2)	$F(000)$	338
Wavelength / nm	0.071 073	$\theta$ range / ( $^\circ$ )	2.23~25.98
Crystal system	Triclinic	Index ranges ( $h, k, l$ )	-11/10, -11/0, -11/11
Space group	$P\bar{1}$	Reflections collected	3 033
Unit cell dimensions		Independent reflections	2 749 ( $R_{\text{int}}$ )
$a$ / nm	0.934 6(1)	Refinement method	Full-matrix least squares on $F^2$
$b$ / nm	0.933 8(1)	Data / restraints / parameters	2749/10/219
$c$ / nm	0.938 8(2)	Goodness-of-fit on $F^2$	1.077
$\alpha$ / ( $^\circ$ )	79.46(1)	Final $R, wR$ indices [ $I < 2\sigma(I)$ ]	0.026 7, 0.066 7
$\beta$ / ( $^\circ$ )	77.84(1)	$R, wR$ indices (all data)	0.029 8, 0.067 6
$\gamma$ / ( $^\circ$ )	61.296(7)	Largest diff. peak and hole/( $\text{e} \cdot \text{nm}^{-3}$ )	243 and 231

**Table 2 Selected bond lengths (nm) and angles ( $^\circ$ ) for compound 1**

Ni-O(1)	0.204 13(12)	Ni-O(2) <sup>a</sup>	0.203 06(13)	Ni-O(2)	0.203 06(13)
Ni-O(3)	0.207 93(13)	N(1)-C(1)	0.147 4(2)	C(7)-C(7) <sup>b</sup>	0.130 8(4)
C(7)-C(8)	0.150 7(2)	O(4)-C(8)	0.124 1(2)		
O(2)-Ni-O(1)	90.65(6)	O(2)-Ni-O(1) <sup>a</sup>	89.35(6)	O(1)-Ni-O(1) <sup>a</sup>	180.00(8)
O(2)-Ni-O(3) <sup>a</sup>	93.24(6)	O(1)-Ni-O(3)	84.64(5)	O(2) <sup>a</sup> -Ni-O(3) <sup>a</sup>	86.76(6)
Ni-O(1)-H(10A)	120.1(16)	Ni-O(2)-H(20A)	130.0(18)	Ni-O(3)-H(30B)	120.1(17)
C(3)-N(1)-C(1)	108.24(14)	N(1)-C(1)-N(2)	111.89(13)	N(1)-C(1)-H(1A)	109.2
C(7)b-C(7)-C(8)	123.6(2)	O(4)-C(8)-O(5)	126.60(17)	O(4)-C(8)-C(7)	115.41(15)
O(5)-C(8)-C(7)	117.99(16)				

Symmetry codes: <sup>a</sup>  $-x+1, -y, -z$ ; <sup>b</sup>  $-x+1, -y, -z+1$ **Table 3 Hydrogen bonding geometry for compound 1**

D-H...A	D-H / nm	H...A / nm	D...A / nm	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
O(1)-H10A...O(4)	0.082 4(10)	0.193 8(10)	0.275 78(19)	173(2)
O(1)-H10B...N(1) <sup>c</sup>	0.081 9(10)	0.203 0(10)	0.284 65(19)	175(2)
O(2)-H20A...O(6) <sup>d</sup>	0.081 6(10)	0.186 3(10)	0.267 7(2)	175(3)
O(2)-H20B...N(3) <sup>e</sup>	0.080 4(10)	0.206 6(11)	0.286 2(2)	170(2)
O(3)-H30A...O(5) <sup>f</sup>	0.081 6(10)	0.196 3(11)	0.276 18(19)	166(2)
O(3)-H30B...N(2) <sup>f</sup>	0.081 8(10)	0.208 2(11)	0.289 38(19)	171(2)
O(6)-H60A...N(4)	0.081 2(10)	0.204 4(11)	0.284 9(2)	171(3)
O(6)-H60B...O(7) <sup>e</sup>	0.082 4(10)	0.191 4(11)	0.273 3(2)	173(3)
O(7)-H70B...O(4) <sup>e</sup>	0.081 6(10)	0.194 4(11)	0.274 7(2)	168(2)
O(7)-H70A...O(5)	0.081 3(10)	0.191 2(12)	0.271 0(2)	167(3)

Symmetry codes: <sup>c</sup>  $1-x, 1-y, 1-z$ ; <sup>d</sup>  $x, y-1, z$ ; <sup>e</sup>  $x, 1-y, 1-z$ ; <sup>f</sup>  $x, y, z-1$ .

## 2 Results and discussion

Fig.1 shows the structure of **1**. The geometries around each metal center are all octahedral; the six oxygen atoms from six water molecules occupy the equatorial positions and the axial ones. Selected bond lengths and angles are given in Table 2. The metal-oxygen bonds are in the range 0.203 06 (13) to 0.207 93(13) nm for **1**, the difference of the Ni-O distances are likely due to the different environment of water molecules. The bond angles around each metal center range from  $84.64(5)^\circ$  to  $180.00(8)^\circ$  for **1**. The metal ions containing species are all located on the inversion centers. Each  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cation is connected with neighboring two fumarate anions via hydrogen bonds existing between coordinated water molecules and fumarate anions ( $\text{O}-\text{H}\cdots\text{O}(\text{fumarate})$ ), forming a one-dimensional chain along  $c$  axis (shown in Fig.1 and 2). As can be seen in Fig.1 and 2, hmt, as a hy-

drogen acceptor, is linked with coordinated water molecule via hydrogen bond ( $\text{O}-\text{H}\cdots\text{N}(\text{hmt})$ ), resulting each  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cation is surrounded by six hmt molecules and each hmt molecule surrounded by three  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cations. Besides, another hydrogen bond

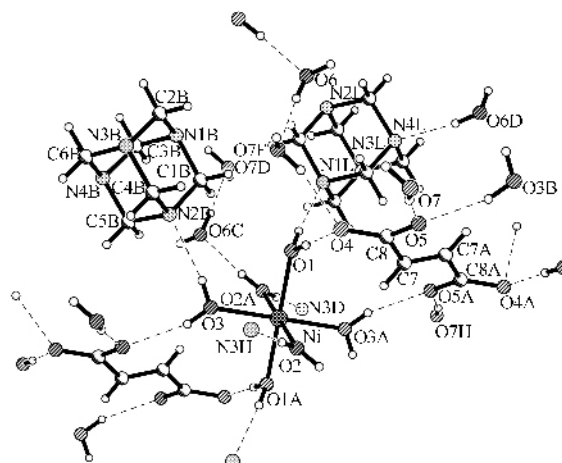


Fig.1 Molecular structure of  $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})]\cdot 2(\text{hmt})\cdot 4\text{H}_2\text{O}$  with some neighboring atoms and molecules linked by hydrogen bonds

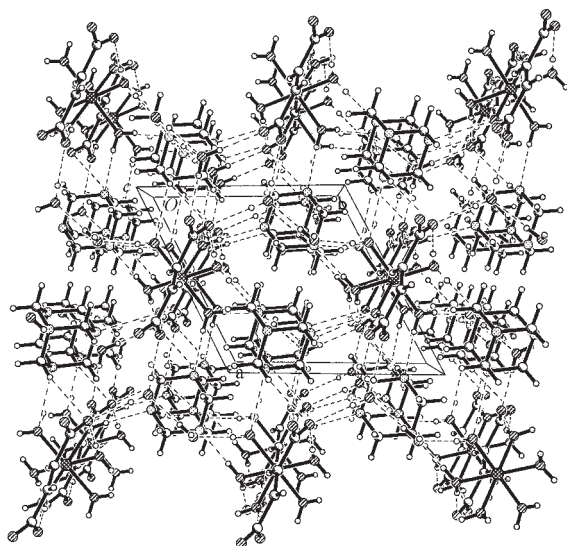


Fig.2 Molecular packing diagram of  $[\text{Ni}(\text{H}_2\text{O})_6(\text{fum})] \cdot 2(\text{hmt}) \cdot 4\text{H}_2\text{O}$  along  $c$  axis

exists between the fourth N atom of hmt molecule and a lattice water molecule (such as  $\text{N4L} \cdots \text{H}-\text{O6D}$ ). Thus, the relative independent components  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , fumarate anions, hmt and  $\text{H}_2\text{O}$  molecules are linked together by two kinds of hydrogen bonds ( $\text{O}-\text{H} \cdots \text{O}$ , and  $\text{O}-\text{H} \cdots \text{N}$ ) to form a three-dimensional structure. It is worth mention that the one-dimensional chains consisted of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and fumarate anions are actually located in the hexagonal channels comprised of hmt molecules, as shown in Fig.2. Similar structure have been found in reported compound  $[\text{Co}(\text{H}_2\text{O})_6\text{Cl}_2] \cdot 2(\text{hmt}) \cdot 4\text{H}_2\text{O}$ <sup>[25]</sup>.

## References:

- [1] Rosi N L, Eckert J, Eddaoudi M, et al. *Science*, **2003**, **300**: 1127~1129
- [2] Pan L, Sander M B, Huang X, et al. *J. Am. Chem. Soc.*, **2004**, **126**:1308~1309
- [3] Kitagawa S, Kitaura R, Noro S I. *Angew. Chem. Int. Ed. Engl.*, **2004**, **43**:2334~2375
- [4] Kondo M, Yoshitomi T, Seki K, et al. *Angew. Chem. Int. Ed. Engl.*, **1997**, **36**:1725~1727
- [5] Xiong R, You X, Abranham B F, et al. *Angew. Chem. Int. Ed. Engl.*, **2001**, **40**:4422~4425
- [6] Fujita M, Kwon Y J, Washizu S, et al. *J. Am. Chem. Soc.*, **1994**, **116**:1151~1152
- [7] (a) Russell V A, Evans C C, Li W, et al. *Science*, **1997**, **276**: 575~579
- (b) Lehn J M. *Angew. Chem. Int. Ed. Engl.*, **1990**, **29**:1304~1319
- [8] Batten S R, Robson R. *Angew. Chem. Int. Ed. Engl.*, **1998**, **37**:1460~1494
- [9] Moulton B, Zaworotko M J. *Chem. Rev.*, **2001**, **101**:1629~1658
- [10] Papaefstathiou G S, MacGillivray L R. *Coord. Chem. Rev.*, **2003**, **246**:169~184
- [11] Forster P M, Cheetham A K. *Angew. Chem. Int. Ed.*, **2002**, **41**:457~459
- [12] Konar S, Mukherjee P S, Zangrando E, et al. *Angew. Chem. Int. Ed. Engl.*, **2002**, **41**:1561~1563
- [13] Lee E, Kim Y J, Jung D Y. *Inorg. Chem.*, **2002**, **41**:501~506
- [14] Mori W, Takamizawa S. *J. Solid. State. Chem.*, **2000**, **152**: 120~129
- [15] Liao Y C, Liao F L, Chang W K, et al. *J. Am. Chem. Soc.*, **2004**, **126**:1320~1321
- [16] (a) Liu Q, Li Y Z, Song Y, et al. *J. Solid. State. Chem.*, **2004**, **177**:4701~4705
- (b) Liu Q, Li Y Z, Liu H, et al. *J. Mol. Struct.*, **2005**, **733**:25~28
- [17] (a) Liu Q, Sun X Q, Zou J Z, et al. *J. Coord. Chem.*, **2002**, **55**:1021~1027
- (b) Liu Q, Li B L, Xu Z, et al. *Transition. Met. Chem.*, **2002**, **27**:786~789
- [18] (a) Liu Q, Li B L, Xu Z, et al. *J. Coord. Chem.*, **2003**, **56**: 771~777
- (b) Liu Q, Sun X Q, Zhu Y Q, et al. *Transition. Met. Chem.*, **2001**, **26**:369~371
- [19] LIU Qi(刘琦), XI Hai-Tao(席海涛), SUN Xiao-Qiang(孙小强), et al. *Jiegou Huaxue (Chinese J. Struct. Chem.)*, **2002**, **21**:55~358
- [20] (a) Carlucci L, Ciani G, Proserpio D M, et al. *Inorg. Chem.*, **1997**, **36**:1736~1737
- (b) Carlucci L, Ciani G, Proserpio D M, et al. *J. Solid State Chem.*, **2000**, **152**:211~220
- [21] (a) Tong M L, Zheng S L, Chen X M. *Chem. Commun.*, **1999**:561~562
- (b) Zheng S L, Tong M L, Yu X L, et al. *J. Chem. Soc. Dalton. Trans.*, **2001**:586~592
- (c) Zheng S L, Tong M L, Fu R W, et al. *Inorg. Chem.*, **2001**, **40**:3562~3569
- (d) Zheng S L, Tong M L, Chen X M. *Coord. Chem. Rev.*, **2003**, **246**:185~202
- [22] Moulton B, Lu J, Zaworotko M J. *J. Am. Chem. Soc.*, **2001**, **123**:9224~9225
- [23] Batten S R, Hoskins B F, Robson R. *Inorg. Chem.*, **1998**, **37**: 3432~3434
- [24] Sheldrick G M, *SHELXS-97, Program for X-ray Crystal Structure Determination*, Göttingen University, Germany, **1997**.
- [25] LI Bao-Long(李宝龙), SONG Le-Xin(宋乐新), DING Jian-Gang(丁建刚), et al. *Jiegou Huaxue (Chinese J. Struct. Chem.)*, **1998**, **17**:209~212