

三核镍簇合物的合成、表征及晶体结构

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摘要: 合成了一种含有螯合双肟配体 2,2'-[(1,3-亚丙基)二氧双(氮次甲基)]二萘酚(H_2L)的三核镍(II)簇合物 $\{[NiL(THF)]_2(OAc)_2Ni\} \cdot THF$, 并通过红外光谱、差热-热重进行了结构表征, 同时测定了它的晶体结构。该簇合物晶体属三斜晶系, 空间群为 $P\bar{1}$ 。在镍(II)簇合物中, 含有 2 个配体单元(提供 N_2O_2 给予体)、2 个乙酸根离子和 2 个配位的四氢呋喃分子, 共同围绕镍(II)离子形成了 3 个稍微扭曲的八面体配位几何体。

关键词: 2,2'-[(1,3-亚丙基)二氧双(氮次甲基)]二萘酚; 镍(II)簇合物; 合成; 表征; 晶体结构
中图分类号: O614.81+3 **文献标识码:** A **文章编号:** 1001-4861(2009)03-0522-06

Synthesis, Characterization and Crystal Structure of a Trinuclear Ni(II) Cluster

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Abstract: A novel trinuclear nickel(II) cluster $\{[NiL(THF)]_2(OAc)_2Ni\} \cdot THF$ with chelating bisoxime ligand 2,2'-[(1,3-propylene)dioxybis(nitrilomethylidyne)]dinaphthol (H_2L) was synthesized and structurally characterized by IR spectra, TG-DTA and X-ray single crystal structure analysis. The cluster crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell parameters $a=0.969\ 78(17)$ nm, $b=1.367\ 7(2)$ nm, $c=2.422\ 4(3)$ nm, $\alpha=76.185(2)^\circ$, $\beta=86.921(3)^\circ$, $\gamma=77.865(2)^\circ$ and $V=3.050\ 2(8)$ nm³, $Z=2$, $R_1=0.058\ 0$, $wR_2=0.125\ 2$. In the Ni(II) cluster, there are two ligand moieties (which provide N_2O_2 donors), two acetate ions and two coordinated THF molecules, which result in the formation of three slightly distorted octahedral geometries around the Ni(II) ions. CCDC: 636045.

Key words: 2,2'-[(1,3-propylene)dioxybis(nitrilomethylidyne)]dinaphthol; nickel(II) cluster; synthesis; characterization; crystal structure

0 Introduction

The Schiff base compounds constitute an important class of ligands which have been extensively investigated in coordination chemistry mainly due to their facile synthesis and easily tunable steric, electronic, and catalytic properties. They are also useful in constructing supramolecular structures^[1,2]. The cobalt(II) and manganese(II) complexes with tetradentate Schiff base ligands which coordinate through N_2O_2 donor

atoms have been studied as oxygen-carriers and also as catalysts for water splitting system^[3]. Schiff base complexes are also known for their significant biological activities such as photosynthesis and transport of oxygen in mammalian and other respiratory systems^[4]. Furthermore, complexes of nickel(II) with a wide variety of Schiff bases having donor atoms such as N_2O_2 , N_4 and N_2S_2 around the metal ion have been used as catalysts for carbonylation, hydrogenation, hydroformylation and epoxidation reactions^[5,6]. Here we have synthesized a

收稿日期:2008-04-14。收修改稿日期:2008-12-27。

甘肃省教委科研基金项目(No.0604-01)和兰州交通大学“青蓝”人才工程基金项目(No.QL-03-01A)资助。

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Salen-type bisoxime ligand, 2,2'-[(1,3-propylene)dioxybis(nitrilomethylidyne)]dinaphthol (H_2L) and its corresponding Ni(II) cluster, $\{[NiL(THF)]_2(OAc)_2Ni\} \cdot THF$, which has three octahedral geometries in single molecule. The unit of cell contains two crystallographically independent but chemically identical trinuclear clusters.

1 Experimental

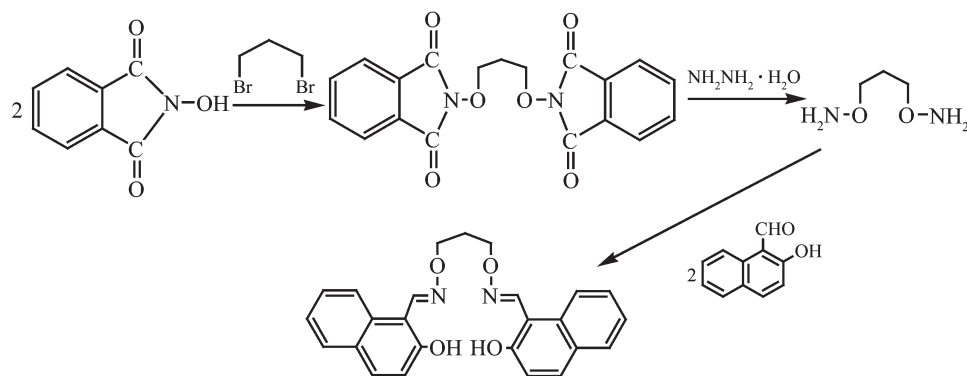
1.1 Reagents and physical measurements

2-Hydroxy-1-naphthaldehyde from Aldrich was used without further purification. 1,3-dibromopropane was dried and redistilled before using. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. Elemental

analysis for Ni was detected by an IRIS ER/S · WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a VERTEX70 FTIR spectrophotometer, with samples prepared as KBr ($500 \sim 4\,000\text{ cm}^{-1}$) and CsI ($100 \sim 500\text{ cm}^{-1}$) pellets. 1H NMR spectra were recorded on a Mercury-400BB spectrometer. The single crystal structure was determined on a Bruker Smart APEX CCD diffractometer. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

1.2 Synthesis of H_2L

The synthetic route of H_2L is show in Scheme 1.



Scheme 1 Synthetic route to H_2L

2,2'-[(1,3-Propylene)dioxybis (nitrilomethylidyne)] dinaphthol (H_2L) was synthesized according to an analogous method reported earlier^[7-11]. Yield, 49%, m.p. $160 \sim 161\text{ }^\circ\text{C}$, Anal. calcd. for $C_{25}H_{22}N_2O_4$ (%): C, 72.45; H, 5.35; N, 6.76; Found(%): C, 72.37; H, 5.39; N, 6.82; 1H NMR (400 MHz, $CDCl_3$) δ : 1.57 (s, 2H), 2.27 (t, $J=6.2\text{ Hz}$, 2H), 4.43 (t, $J=6.2\text{ Hz}$, 4H), 7.20 (d, $J=8.0\text{ Hz}$, 2H), 7.37 (t, $J=7.4\text{ Hz}$, 2H), 7.51 (t, $J=8.4\text{ Hz}$, 2H), 7.78 (d, $J=8.8\text{ Hz}$, 2H), 7.96 (d, $J=8.8\text{ Hz}$, 2H), 9.14 (s, 2H), 10.97 (s, 2H).

1.3 Synthesis of the Ni(II) cluster

A solution of Ni(II) acetate tetrahydrate (49.78 mg, 0.20 mmol) in ethanol (15 mL) was added dropwise to a solution of H_2L (82.06 mg, 0.20 mmol) in THF/acetonitrile (3:1) (24 mL) at room temperature, the color of the mixing solution turned to pale-green immediately. After continuing stirring for 6 h at room temperature, the

mixture solution was allowed to stand at room temperature for about three weeks, the solvent was partially evaporated and green rhombohedral crystals of the Ni(II) cluster were formed in 22.5% yield. Chemical analyses confirmed the composition. Anal. Calcd. for $C_{66}H_{70}N_4Ni_3O_{15}$ (%): C, 59.15; H, 5.32; N, 4.14; Ni, 13.11. Found (%): C, 59.36; H, 5.28; N, 4.20; Ni, 13.19.

1.4 Structure determination of the Ni(II) cluster

A single crystal with approximate dimensions of $0.46\text{ mm} \times 0.43\text{ mm} \times 0.41\text{ mm}$ was used for data collection. The diffraction data was collected on a Bruker Smart Apex CCD diffractometer equipped with a graphite monochromator in the range of $1.57^\circ < \theta < 25.01^\circ$ with ω scan mode at 298(2) K, using Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$). The structure was solved with direct methods and refined with full-matrix least-

squares techniques using the SHELXS-97 and SHELXL-97 programs, respectively. All hydrogen atoms were added theoretically.

Crystallographic data and structure refinement parameters are summarized in Table 1.

CCDC: 636045.

Table 1 Crystallographic data and structure refinement parameters for the cluster

Empirical formula	C ₆₆ H ₇₀ N ₄ Ni ₃ O ₁₅	<i>F</i> (000)	1 396
Formula weight	1 335.39	Crystal size / mm	0.46×0.43×0.41
<i>T</i> / K	298(2)	θ range / (°)	1.57~25.01
Wavelength / nm	0.071 073	Limiting indices	$-11 \leq h \leq 11, -15 \leq k \leq 16, -28 \leq l \leq 21$
Crystal system	Triclinic	Reflections collected	15 856
Space group	$P\bar{1}$	Independent reflections (R_{int})	10 581 (0.027 1)
<i>a</i> / nm	0.969 78(17)	Observed reflections [$I > 2\sigma(I)$]	7 053
<i>b</i> / nm	1.367 7(2)	Completeness to $\theta=5.01^\circ$ / %	98.2
<i>c</i> / nm	2.422 4(3)	Absorption correction	Semi-empirical from equivalents
α / (°)	76.185(2)	Max. and min. transmission	0.687 3 and 0.659 1
β / (°)	86.921(3)	Refinement method	Full-matrix least-squares on F^2
γ / (°)	77.865(2)	Data / restraints / parameters	10 581 / 0 / 898
<i>V</i> / nm ³	3.050 2(8)	Goodness-of-fit on F^2	1.025
<i>Z</i>	2	Final <i>R</i> indices [$I > 2\sigma(I)$]	0.058 0, 0.12 52
<i>D_c</i> / (Mg·m ⁻³)	1.454	<i>R</i> indices (all data)	0.097 9, 0.150 5
μ / mm ⁻¹	0.989	($\Delta\rho$) _{max} ($\Delta\rho$) _{min} / (e·nm ⁻³)	952, -566

2 Results and discussion

2.1 Crystal structure of the Ni(II) cluster

The crystal structure of the Ni(II) cluster reveals formation of symmetric trinuclear structure (Fig.1).

The Ni (II) cluster crystallizes in the triclinic system, space group $P\bar{1}$, and the unit cell contains two crystallographically independent but chemically identical trinuclear clusters (molecule **1** and **2**, Fig.1). The cluster consists of three nickel(II) atoms, two ligand

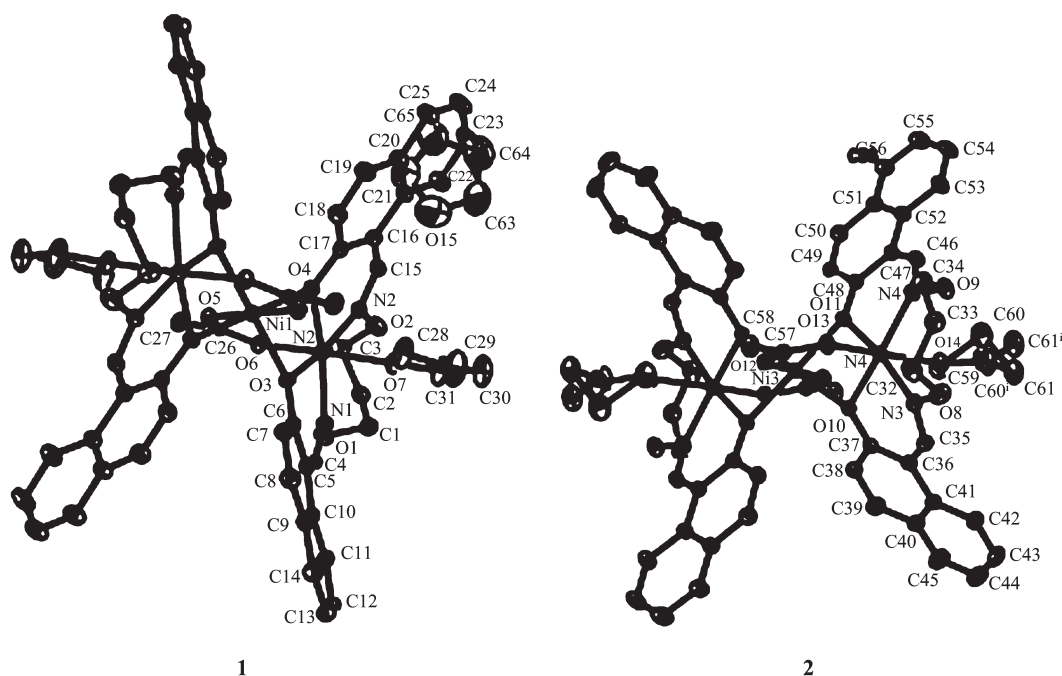
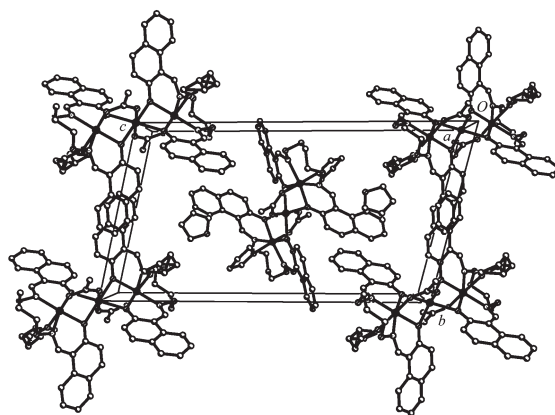


Fig.1 Structure of the Ni(II) cluster with the atom numbering, Displacement ellipsoids for non-H atoms are drawn at the 30% probability level, Each of the nickel atoms sit in an octahedral geometry

units, two acetate ions, and two coordinated THF molecules as expected from the analytical data. Each of the inner nickel atoms is hexa-coordinated. The nickel atom (Ni2) is located in the N_2O_2 moieties of the ligand. One oxygen atom (O7) from the THF molecule and one oxygen atom (O6) from the bridging acetate ion are also coordinated to Ni2. Consequently, around Ni2 is a slightly distorted octahedral geometry. In addition, the central nickel's (Ni1) coordination sphere is completed by quadruple μ -phenoxo oxygen atoms (O3, O4, O3ⁱ, O4ⁱ) from two [NiL] chelates, and both of oxygen atoms (O5, O5ⁱ) from the ligating acetate ions which adopts a familiar μ_{O-C-O} fashion, and constitutes another octahedral geometry. Furthermore, the trinuclear structure is probably stabilized by the two μ -acetate ligands, which neutralize the whole charge of the cluster (Fig.2).

The two independent molecules (molecule **1** and **2**, Fig.1) in the asymmetric unit have an almost-similar structure. The interatomic distances of Ni1-Ni2 (0.309 9(6) nm) and Ni3-Ni4 (0.305 6(6) nm) are different from each other, significantly longer than all the Ni-O and



H atoms are omitted for clarity

Fig.2 Packing diagram of the Ni(II) cluster along *c*-axis

Ni-N bonds in the cluster (Table 2). These similar to those of previously reported salen-type analogues of $\{[Ni(H_4Salpr)(H_2O)]_2(OAc)_2Ni\}^{[12]}$, $\{[Ni(Salpr)(NC_5H_5)]_2(OAc)_2Ni\}^{[12]}$, $\{[Ni(Salpr)(NC_5H_5)]_2(OAc)_2Ni\}^{[13]}$, $\{[Ni(Salpr)(DMF)]_2(NO_3)_2Ni\}^{[14]}$, $\{[Ni(Salpr)(DMSO)]_2(OAc)_2Ni\}^{[15]}$, $\{[Ni(Salpr)(DMF)]_2(OAc)_2Ni\}^{[16]}$, $[Zn_8L_4(H_2O)_3] \cdot 4.5H_2O^{[10]}$ and $[Co_8L_4(H_2O)_2X] \cdot 2H_2O \cdot 1.5CHCl_3 \cdot 0.5hexane(X=H_2O \text{ or } EtOH)^{[10]}$.

Table 2 Selected bond distances (nm) and bond angles ($^\circ$) for the cluster

Ni(1)-O(5) ⁱ	0.204 0(3)	Ni(2)-O(4)	0.203 2(3)	Ni(3)-O(11)	0.211 2(3)
Ni(1)-O(5)	0.204 0(3)	Ni(2)-N(2)	0.207 1(4)	Ni(3)-O(11) ⁱⁱ	0.211 2(3)
Ni(1)-O(3) ⁱ	0.209 1(3)	Ni(2)-N(1)	0.209 5(4)	Ni(4)-N(4)	0.201 2(5)
Ni(1)-O(3)	0.209 1(3)	Ni(2)-O(7)	0.216 1(4)	Ni(4)-O(11)	0.201 6(3)
Ni(1)-O(4) ⁱ	0.210 5(3)	Ni(3)-O(12) ⁱⁱ	0.202 6(4)	Ni(4)-O(10)	0.201 6(4)
Ni(1)-O(4)	0.210 5(3)	Ni(3)-O(12)	0.202 6(4)	Ni(4)-O(13)	0.201 7(4)
Ni(2)-O(6)	0.201 7(3)	Ni(3)-O(10) ⁱⁱ	0.209 1(3)	Ni(4)-N(3)	0.205 9(5)
Ni(2)-O(3)	0.202 4(3)	Ni(3)-O(10)	0.209 1(3)	Ni(4)-O(14)	0.222 5(4)
O(5) ⁱ -Ni(1)-O(5)	180.000(1)	O(4)-Ni(2)-N(2)	85.70(15)	O(12) ⁱⁱ -Ni(3)-O(11) ⁱⁱ	91.93(14)
O(5) ⁱ -Ni(1)-O(3) ⁱ	88.92(14)	O(6)-Ni(2)-N(1)	87.88(16)	O(12)-Ni(3)-O(11) ⁱⁱ	88.07(14)
O(5)-Ni(1)-O(3) ⁱ	91.08(14)	O(3)-Ni(2)-N(1)	85.81(15)	O(10) ⁱⁱ -Ni(3)-O(11) ⁱⁱ	78.61(13)
O(5) ⁱ -Ni(1)-O(3)	91.08(14)	O(4)-Ni(2)-N(1)	166.28(15)	O(10)-Ni(3)-O(11) ⁱⁱ	101.39(13)
O(5)-Ni(1)-O(3)	88.92(14)	N(2)-Ni(2)-N(1)	107.97(17)	O(11)-Ni(3)-O(11) ⁱⁱ	180.000(1)
O(3) ⁱ -Ni(1)-O(3)	180.00(19)	O(6)-Ni(2)-O(7)	176.78(14)	N(4)-Ni(4)-O(11)	86.63(15)
O(5) ⁱ -Ni(1)-O(4) ⁱ	88.41(14)	O(3)-Ni(2)-O(7)	88.11(14)	N(4)-Ni(4)-O(10)	166.78(18)
O(5)-Ni(1)-O(4) ⁱ	91.59(14)	O(4)-Ni(2)-O(7)	90.02(14)	O(11)-Ni(4)-O(10)	82.67(14)
O(3) ⁱ -Ni(1)-O(4) ⁱ	77.25(13)	N(2)-Ni(2)-O(7)	87.73(16)	N(4)-Ni(4)-O(13)	94.21(18)
O(3)-Ni(1)-O(4) ⁱ	102.75(13)	N(1)-Ni(2)-O(7)	89.36(16)	O(11)-Ni(4)-O(13)	90.73(16)
O(5) ⁱ -Ni(1)-O(4)	91.59(14)	O(12) ⁱⁱ -Ni(3)-O(12)	180.000(1)	O(10)-Ni(4)-O(13)	93.69(15)
O(5)-Ni(1)-O(4)	88.41(14)	O(12) ⁱⁱ -Ni(3)-O(10) ⁱⁱ	88.46(15)	N(4)-Ni(4)-N(3)	104.64(18)
O(3) ⁱ -Ni(1)-O(4)	102.73(13)	O(12)-Ni(3)-O(10) ⁱⁱ	91.54(15)	O(11)-Ni(4)-N(3)	167.89(16)

Continued Table 2

O(3)-Ni(1)-O(4)	77.25(13)	O(12) ⁱⁱ -Ni(3)-O(10)	91.54(15)	O(10)-Ni(4)-N(3)	85.53(16)
O(4)-Ni(1)-O(4)	180.000(1)	O(12)-Ni(3)-O(10)	88.46(15)	O(13)-Ni(4)-N(3)	92.77(18)
O(6)-Ni(2)-O(3)	93.33(14)	O(10) ⁱⁱ -Ni(3)-O(10)	180.00(17)	N(4)-Ni(4)-O(14)	83.13(17)
O(6)-Ni(2)-O(4)	93.05(14)	O(12) ⁱⁱ -Ni(3)-O(11)	88.07(14)	O(11)-Ni(4)-O(14)	93.16(15)
O(3)-Ni(2)-O(4)	80.47(13)	O(12)-Ni(3)-O(11)	91.93(14)	O(10)-Ni(4)-O(14)	89.69(15)
O(6)-Ni(2)-N(2)	91.55(16)	O(10) ⁱⁱ -Ni(3)-O(11)	101.39(13)	O(13)-Ni(4)-O(14)	175.15(15)
O(3)-Ni(2)-N(2)	165.55(15)	O(10)-Ni(3)-O(11)	78.61(13)	N(3)-Ni(4)-O(14)	84.01(17)

Symmetry transformations used to generate equivalent atoms: ⁱ $-x+2, -y+1, -z+1$; ⁱⁱ $-x, -y+2, -z+2$.

2.2 IR spectra analysis of H₂L and the Ni(II) cluster

IR spectra details of H₂L and the Ni(II) cluster are shown in Fig.3. The bands due to $\nu_{C=N}$ and ν_{Ar-O} of the cluster are lowered by 6 and 48 cm⁻¹, respectively, as compared to H₂L values ($\nu_{C=N}$ and ν_{Ar-O} appear at 1 604 and 1 238 cm⁻¹, respectively). These provide evidence for the coordination of H₂L with Ni(II) ions. Meanwhile, a bending vibration of naphtholic alcohol in H₂L at 1 278 cm⁻¹, which disappears in the cluster, indicating the oxygen in the naphtholic alcohol of the cluster has been deprotonated and coordinated to the Ni(II) ions. In addition, infrared spectrum of the Ni(II) cluster shows the expected absorption band due to the stretching mode of THF at 1 039 cm⁻¹, indicating the presence of THF molecules.

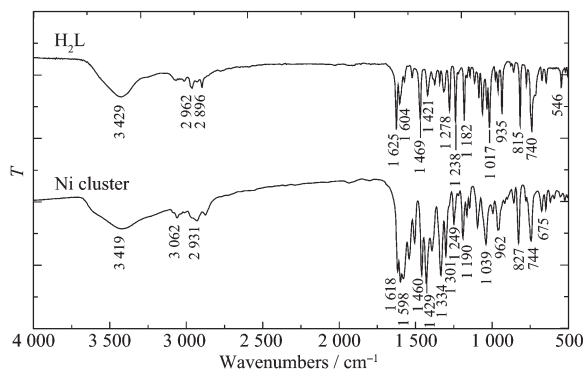


Fig.3 Infrared absorption spectra of H₂L and the Ni(II) cluster

The far-infrared spectrum of the Ni(II) cluster was also obtained in the region 500~100 cm⁻¹ in order to identify frequencies due to the Ni-O and Ni-N bonds. The IR spectrum of the cluster shows vibrational absorption frequencies at 472 cm⁻¹ and 410 cm⁻¹, which are assigned to $\nu(Ni-O)$ and $\nu(Ni-N)$, respectively. These assignments are consistent with the literature frequency

values^[17].

2.3 TG-DTA analysis of the Ni(II) cluster

The thermal decomposition process of the cluster can be divided into four stages. The initial weight loss occurs in the range of 61 to 108 °C. The TG curve shows that the weight loss corresponding to this temperature range is 5.29% that roughly coincides with the value of 5.40%, calculated for the loss of one crystallizing tetrahydrofuran molecule. The second stage degradation temperature is in the range of 125 to 242 °C with the mass loss of 10.5%, in which two coordinated tetrahydrofuran molecules are removed with theoretical loss of 10.8%. Then, two acetate ions indicate the 8.2% weight loss from 245 to 270 °C (theoretical residual value was 8.8%). The fourth weight loss starts from 272 to 380 °C with decomposition of the compound. The TG curve shows around 82.8% weight loss at 600 °C indicating the complete removal of organic part of the compound. The main product was NiO with a residual value of 17.2% (theoretical residual value was 16.6%).

References:

- [1] Sun S S, Stern C L, Nguyen S T, et al. *J. Am. Chem. Soc.*, **2004**,**126**:6314~6326
- [2] Ziessel R. *Coord. Chem. Rev.*, **2001**,**216**:195~223
- [3] Watkinson M, Fondo M, Bermejo M R, et al. *J. Chem. Soc.*, **1999**:31~36
- [4] Ramesh M, Chandrasekar K B, Reddy K H. *Indian J. Chem.*, **2000**,**39A**:1337~1342
- [5] Venkataramanan N S, Kuppuraj G, Rajagopal S. *Coord. Chem. Rev.*, **2005**,**249**:1249~1268
- [6] Che C M, Huang J S. *Coord. Chem. Rev.*, **2003**,**242**:97~113
- [7] Dong W K, Ding Y J. *Cryst. Res. Technol.*, **2008**,**43**:321~326

- [8] Dong W K, Shi J Y, Xu L, et al. *Appl. Organometal. Chem.*, **2008**,**22**:89~96
- [9] Dong W K, Feng J H. *Acta Crystallogr.*, **2006**,**E62**:o3577 ~ o3578
- [10] Akine S, Dong W K, Nabeshima T. *Inorg. Chem.*, **2006**,**45**: 4677~4684
- [11] Dong W K, Duan J G. *J. Coord. Chem.*, **2008**,**61**:781~788
- [12] Reglinski J, Taylor M K, Kennedy A R. *Inorg. Chem. Commu.*, **2006**,**9**:736~739
- [13] Reglinski J, Morris S, Stevenson D E. *Polyhedron*, **2002**,**21**: 2167~2174
- [14] Atakol O, Arici C, Tahir M N, et al. *Anal. Sci.*, **1999**,**15**:933~934
- [15] Ulku D, Ercan F, Atakol O, et al. *Acta Crystallgr.*, **1997**,**C53**: 1056~1057
- [16] Elmali A, Elerman V, Svoboda I, et al. *Z. Naturforsch.*, **1995**, **B51**:665~668
- [17] DONG Wen-Kui(董文魁), SHI Jun-Yan(史军妍), ZHONG Jin-Kui(钟金魁), et al. *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, **2008**,**24**:10~14