第 28 卷第 12 期 无 机 化 学 学 报 Vol.28 No.12
2012 年 12 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 2650-2654

以 *N*-乙酰基水杨酰肼及咪唑为配体的三核镍(Ⅱ)配合物的合成和晶体结构

吴琼洁*,[1] 陈小华[2] 蔡碧琼[1] 吴 丹[1]
([1]福建农林大学生命科学学院,福州 350002)
([2]福建师范大学化学与材料学院,福州 350007)

摘要:合成了 1 个含 *N*-乙酰基水杨酰肼(H_3ashz)和咪唑(imdz)的三核镍(Ⅱ)配合物[Ni_3(ashz)$_2$(imdz)$_2$]·2DMF,并通过元素分析、红外光谱、紫外光谱、热分析以及 X-射线单晶衍射等手段进行表征。结构分析结果表明标题化合物属于单斜晶系,$P2_1/c$ 空间群,晶胞参数为 a=1.028 0(2) nm,b=1.499 2(3) nm,c=1.523 1(5) nm,β=114.16(2)°,V=2.140 1(9) nm^3,Z=2,D_c=1.516 g·cm^{-3},μ=1.372 mm^{-1},F(000)=1 012。配合物中,2 个反式排列的五啮配体 ashz^{3-}的 2 个 N-N 肼基桥联 3 个 Ni(Ⅱ)原子,形成了 1 个含 Ni-N-N-Ni-N-N-Ni 核心的直线型三核镍配合物,其中相邻 Ni 原子间距为 0.462(1) nm。

关键词:镍(Ⅱ)配合物;合成;晶体结构;热稳定性分析
中图分类号:O614.81+3 **文献标识码**:A **文章编号**:1001-4861(2012)12-2650-05

Synthesis and Crystal Structure of Trinuclear Nickel(Ⅱ) Complex with *N*-Acetylsalicylhydrazide and Imidazole Ligands

WU Qiong-Jie*,[1] CHEN Xiao-Hua[2] CAI Bi-Qiong[1] WU Dan[1]
([1]*College of Life Science, Fujian Agriculture and Forestry University, Fuzhou* 350002, *China*)
([2]*College of Chemistry and Materials Science, Fujian Normal University, Fuzhou* 350007, *China*)

Abstract: Employing *N*-acetylsalicylhydrazide (H_3ashz), imidazole (imdz) as mixed ligands, a new trinuclear nickel(Ⅱ) compound [Ni_3(ashz)$_2$(imdz)$_2$]·2DMF has been synthesized and characterized by elemental analysis, IR and X-ray diffraction structural analysis. Crystal data: monoclinic, space group $P2_1/n$ with a=1.028 0(2) nm, b=1.499 2(3) nm, c=1.523 1(5) nm, β=114.16(2)°, V=2.140 1(9) nm^3, Z=2, D_c=1.516 g·cm^{-3}, μ=1.372 mm^{-1}, F(000)=1 012. In the title complex, two μ_2-bridged ashz^{3-} ligands bound to three nickel centers in a linear array. The three nickel atoms are directly linked together by two trans diazine (N-N) bridges, with the neighboring nickel atomic separations of 0.462(1) nm. CCDC: 902486.

Key words: nickel(Ⅱ) complex; synthesis; crystal structure; thermal stability analysis

Recently, research on multidentate ligands and their complexes has been grown and has been subject of numerous reports[1-3]. Due to their inherent coordination functionalities, there has recently been a resurgence of interest in structural chemistry of polynuclear metal compounds with the trianionic pentadentate *N*-acylsalicylhydrazide ligands having flexible N-N single bonds. They have been used in the system of self-assembly in metallacrowns with different nuclearities and ring-sizes based on trivalent metal ions such as

收稿日期:2012-03-28。收修改稿日期:2012-09-17。
福建农林大学校青年教师基金(No.08B10);福建省教育厅科技项目(No.JB10007)资助项目。
*通讯联系人。E-mail:wqiongj_jane@163.com

Mn(Ⅲ), Fe(Ⅲ), Co(Ⅲ) and Ga(Ⅲ) [4-9], and a few trinuclear complexes based on bivalent metal ions such as Ni(Ⅱ) and Zn(Ⅱ) [10-17]. However, among those trinuclear compounds reported, the supramolecular coordination chemistry of *N*-acyl-salicylhydrazide ligands with hydrogen-bonding donor/acceptor functionalities has rarely been reported[15-17].

Herein, we report the synthesis and structure of one new trinuclear nickel complex $[Ni_3(ashz)_2(imdz)_2]\cdot 2DMF$, in which $ashz^{3-}$ ligand, imdz and DMF are *N*-acetylsalicylhydrazidate, imidazole and dimethylformamide, respectively. The title complex presents a hydrogen-bond 1D chain constructed from trinuclear structural units with a linear Ni_3 arrangement.

1 Experimental

1.1 Reagents and physical measurements

The Schiff base ligand H_3ashz was synthesized according to the reported method[10]. All starting chemicals were of analytical grade and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried with an Elementar Vario EL Ⅲ microanalyser. IR spectra were recorded on a Perkin-Elmer spectrum 2000 spectrophotometer with KBr pellets in the range of 4 000~400 cm^{-1}. Electronic spectra were recorded on a UV-1 900 UV/VIS spectrophotometer using ethanol as the solvent. Thermal analyses were performed on a TAS200 thermogravimetric analyzer, with a heating rate of 9 ℃·min^{-1} under a nitrogen atmosphere.

1.2 Synthesis of the compound $[Ni_3(ashz)_2(imdz)_2]\cdot 2DMF$

To a mixture solution of MetOH (15 mL) and DMF (3 mL) of H_3ashz (0.1 mmol) and imdz (0.1 mmol), a methanol solution (10 mL) of $NiCl_2\cdot 2H_2O$ (0.1 mmol) was added gradually with stirring. The resulting red solution was further stirred for 1 h and filtered. The red crystals separated were collected after several days. Analysis Calcd. for $C_{36}H_{44}N_{14}O_8Ni_3$ (%): C 44.25, H 4.55, N 20.08; found(%): C 44.37, H 4.46, N 20.19.

1.3 Crystal structure determination

A red single crystal with dimensions of 0.18 mm×0.25 mm×0.47 mm was selected and mounted on a glass fiber. Crystallographic data were collected at a Rigaku RAPID Weissengberg IP diffractometer with graphitemonochromatized Mo $K\alpha$ radiation (λ= 0.071 073 nm) and the ω scan mode. The structure was solved by direct method with SHELXS-97[18] and refined by fullmatrix least squares calculations with SHELXL-97[19]. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located from the geometrical calculation and refined isotropically. Crystallographic data and structure refinement data of the title complex are listed in Table 1.

CCDC: 902486.

Table 1　Crystallographic data for the title complex

Formula	$C_{36}H_{44}N_{14}O_8Ni_3$	$F(000)$	1 012
Molecular weight	976.98	θ_{min}, θ_{max} / (°)	3.09, 27.48
Crystal system	Monoclinic	Index range (h, k, l)	−13~12, −19~19, −19~19
Space group	$P2_1/c$	No. of independent reflections	4 739 (R_{int}=0.092 1)
a / nm	1.028 0(2)	No. of observed reflections	2 798
b / nm	1.499 2(3)	Parameters	280
c / nm	1.523 1(5)	Goodness of fit on F^2	1.05
β / (°)	114.26(2)	R	0.064 8
V / nm^3	2.140 1(9)	wR	0.116 8
Z	2	$(\Delta/\sigma)_{max}$	0
D_c / (g·cm^{-3})	1.516	$\Delta\rho_{max}$, $\Delta\rho_{min}$ / (e·nm^{-3})	1 065, −612
μ / mm^{-1}	1.372		

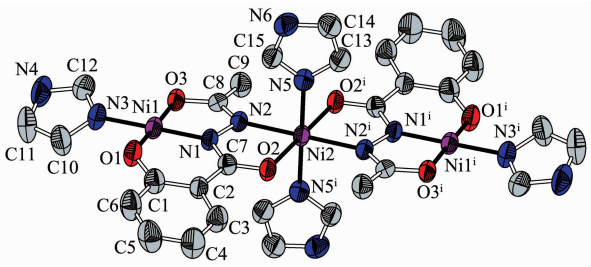
$R=\sum||F_o|-|F_c||/|F_o|$; $wR=\{\sum[w(F_o^2-F_c^2)^2]/[\sum w(F_o)^2]\}^{1/2}$.

2 Results and discussion

2.1 Crystal structure

As shown in Fig.1, the main fragment in the title complex is a trinuclear nickel compound including two μ_2-bridged ashz^{3-} ligands bound to three nickel centers in a linear array. The three nickel atoms are directly linked together by two trans diazine (N-N) bridges, with the Ni1…Ni2 separation of 0.462(1) nm, Ni1…Ni2…Ni1^{i} (symmetry code: ^{i} $-x$, $-y+1$, $-z$) angle of 180.0° and the Ni1-N1-N2-Ni2 torsion angle of 179.4(2)°.

The central Ni2 atom is located on the crystallographic inversion center with either of the other two terminal nickel atoms located 0.462(1) nm away. The Ni2 atom is six-coordinated by two coordinated imidazole nitrogen atoms (N5, N5^{i}) in axial positions, and the two carbonyl oxygen atoms (O2, O2^{i}) and the two hydrazine nitrogen atoms (N2, N2^{i}) from the two ashz^{3-} groups in the equatorial plane, conferring an elongated octahedral geometry.



All hydrogen atoms are omitted for clarity; Symmetry code: ^{i} $-x$, $-y+1$, $-z$

Fig.1 Molecular structure of the title complex with 30% thermal ellipsoids

The basal plane is ideally planar and the Ni2 atom completely lies in the equatorial plane. The terminal Ni1 atom is coordinated in a square-planar geometry composed of the other hydrazine nitrogen N1, carbonyl oxygen O3 and phenolic oxygen O1 of one ashz^{3-} ligand, as well as one coordinated imdz nitrogen N3. There is no deviation of the Ni1 center from the N_2O_2 square-plane, with the maximum and minimum deviations from the mean plane constituted by O1, O3, N1, N3 and Ni1 being 0.005 9(2) and 0.000 3(2) nm, respectively. As a result, each ashz^{3-} ligand is κ^2 (O,N)-chelated to Ni2 and κ^3(O, N, O)-chelated to Ni1.

The selected bond lengths and angles of the title complex are given in Table 2. On the equatorial plane, the Ni2-O (carbonyl) and Ni2-N (hydrazide) bond lengths are 0.206 0(3) nm and 0.206 5(3) nm, respectively and the axial bond lengths of Ni2-N5 is 0.212 1(4) nm, which are in tht range of the Ni-N, Ni-O bond lengths in octahedral coordination[10-13]. In the square-plane on the two sides, the bond lengths of Ni1-O (phenolic), Ni1-O (acyloxy) and Ni1-N (hydrazide) are of 0.184 1(4) nm, 0.184 4(3) nm and 0.182 2(3) nm, respectively, which are comparable to those observed in nickel(Ⅱ) compounds having the same coordinating atoms [17,21]. The distance Ni1-N (imdz) in the square-planar coordination configuration is 0.190 5(4) nm, consistent with the value (0.190 3(4) nm) observed in the trinuclear nickel(Ⅱ) complex [17]. The bond lengths in the ligand moieties are comparable with the related Ni(Ⅱ) compounds[10,13,17].

As illustrated in Fig.2 and Table 3, in the title

Table 2 Selected bond lengths (nm) and angles (°) for the title complex

Ni1-N1	0.182 2(3)	Ni1-O1	0.184 1(4)	Ni1-O3	0.184 4(3)
Ni1-N3	0.190 5(4)	Ni2-O2	0.206 0(3)	Ni2-N2	0.206 5(3)
Ni2-N5	0.212 1(4)	O1-C1	0.134 1(6)	O2-C7	0.127 2(5)
O3-C8	0.130 9(5)	N1-C7	0.133 0(6)	N1-N2	0.140 7(5)
N2-C8	0.130 2(6)				
N1-Ni1-O1	94.60(16)	N1-Ni1-O3	84.20(15)	O1-Ni1-O3	176.51(17)
N1-Ni1-N3	173.88(19)	O1-Ni1-N3	90.39(18)	O3-Ni1-N3	91.02(17)
O2-Ni2-N2	78.09(14)	O2-Ni2-N2^{i}	101.91(14)	O2-Ni2-N5^{i}	91.93(15)
N2-Ni2-N5^{i}	90.13(15)	O2-Ni2-N5	88.07(15)	N2-Ni2-N5	89.87(15)

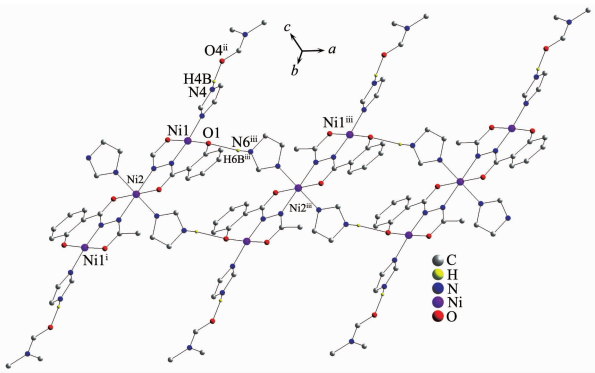
Symmetry code: ^{i} $-x$, $-y+1$, $-z$.

Table 3　Hydrogen-bond geometry for the title complex

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A)/ nm	∠(DHA) / (°)
N4–H4B···O4^{ii}	0.086	0.189	0.274 1(9)	168.0
N6–H6B···O1^{iii}	0.086	0.198	0.282 5(6)	169.0

Symmetry codes: ^{ii} x+1, y, z; ^{iii} x−1, y, z.

complex there exist two different hydrogen bonds, playing an important role in the supramolecular assembly process. Firstly, there are two intermolecular N4–H4B(imdz)···O4^{ii}(DMF) (symmetry code: ^{ii} x+1, y, z) hydrogen bonds with the N4 ··· O4^{ii} distance and N4–H4B···O4^{ii} angle of 0.274 1(9) nm and 168.0° in each [Ni_3(ashz)$_2$(imdz)$_2$] molecule. At the same time, the neighboring trinuclear nickel complex molecules are joined into an extended one-dimensional chain along the *a* axis by the N6–H6B(imdz)···O1^{iii}(carbonyl) (symmetry code: ^{iii} x−1, y, z) hydrogen bonds with the N6···O1^{iii} distance and N6–H6B···O1^{iii} angle of 0.282 5(6) nm and 169.0°. In this uniform chain-like arrangement, Ni1 atom and Ni2^{iii} are bridged by a imidazole molecular, with the Ni1 ··· Ni2^{iii} distance being 0.763 3(2) nm.



H atoms not involved in hydrogen bonding have been omitted; Symmetry codes: ^{i} −x, −y+1, −z; ^{ii} x+1, y, z; ^{iii} x−1, y, z

Fig.2　1D chain structure of the title complex along *a* axis by intermolecular hydrogen bonding interactions

2.2 IR spectra

The IR spectra of the title complex do not display the C=O stretch of the amide functionality observed for the free ligand at *ca.* 1 650~1 678 cm^{-1}, suggesting the deprotonation and enolization of the CONH group and coordination to the Ni(Ⅱ) ions[20-21]. A new band appearing in *ca.* 1 245 cm^{-1} in the compound was assigned to the ν(C-O) (enolate) mode[22]. The strong band at 1 611 cm^{-1} associated with ν(C=N) of the free ligand shifts to a lower wave number (observed at 1 597 cm^{-1}) indicating the deprotonation of the CONH groups and coordination to the Ni(Ⅱ) ion. Furthermore, the deprotonation and coordination can also be confirmed by the bands at 658 cm^{-1} and 563 cm^{-1} attributed to Ni-O bond and Ni-N bond, respectively[11].

2.3 Electronic spectra

The electronic spectra were recorded in solid state for the free ligand and the title complex (Fig.3). They both have absorptions locating in the range of 200~285 and 300~350 nm corresponding to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions[20]. In the complex an intense band at *ca.* 379 nm is assignable to the ligand-to-metal charge transfer (LMCT) transition[21].

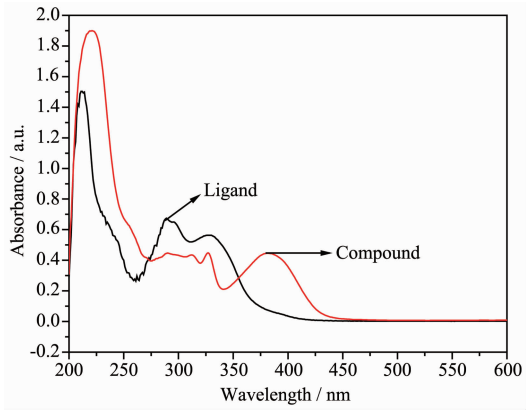


Fig.3　UV spectra of ligand and the title complex

2.4 Thermal analysis

The DSA-TGA curves of the title complex exhibit two weight loss stages (Fig.4). The first weight loss of 14.10% occurred over the temperature range 128~164 ℃ with the DSA endothermic peak at 159 ℃, corresponding to the removal of two unligated DMF molecules (calcd. 14.76%). The second weight loss of 29.70% between 164 and 300 ℃ with the DSA endothermic peak at 274 ℃ and exothermic peak at 288 ℃ may be attributed to the loss of four coordinated imidazole ligands (calcd. 27.87%). The results show that the temperature is not high enough

for the compound to lose the other part.

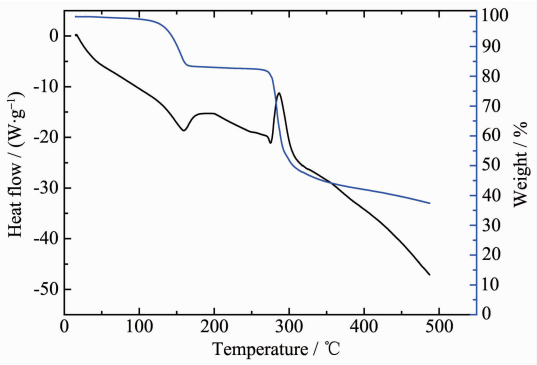


Fig.4 DSA-TGA curves of the title complex

References:

[1] Kwak B, Rhee H, Park S, et al. *Inorg. Chem.*, **1998**,**37**:3599-3602

[2] John R P, Lee K, Lah M S. *Chem. Commun.*, **2004**:2660-2661

[3] Luo W, Sun X Z, Hu K, et al. *Transition Met. Chem.*, **2008**, **33**:295-299

[4] Lin S, Liu S X, Huang J Q, et al. *J. Chem. Soc., Dalton Trans.*, **2002**:1595-1601

[5] John R P, Lee K, Kim B J, et al. *Inorg. Chem.*, **2005**,**47**:7109-7121

[6] Kwak B, Rhee H, Park S, et al. *Polyhedron*, **2000**,**19**:1985-1994

[7] Kim I, Kwak B, Lah M S. *Inorg. Chim. Acta*, **2001**,**317**:12-20

[8] Liu S X, Lin S, Lin B Z, et al. *Angew. Chem. Int. Ed.*, **2001**, **40**:1084-1087

[9] Lin S, Liu S X, Lin B Z. *Inorg. Chim. Acta*, **2002**,**328**:69-73

[10]YANG Ming-Xing(杨明星), LIN Shen(林深), YU Ping(余萍), et al. *Chin. J. Chem*(*Zhongguo Huaxue*), **2005**,**23**:1407-1411

[11]Xiao F P, Jin L F. *Z. Anorg. Allg. Chem.*, **2008**,**634**:397-400

[12]QIU Xiao-Yang(仇晓阳), XU Mao-Tian(徐茂田), ZHU Hai-Liang(朱海亮), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2010**,**26**:355-359

[13]YANG Ming-Xing(杨明星), LIN Shen(林深), CHEN Li-Juan(陈丽娟), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2003**,**19**:433-436

[14]Luo W, Meng X G, Sun X Z, et al. *Inorg. Chem. Commun.*, **2007**,**10**:1351-1354

[15]Lin S, Yang M X, Liu S X. *Polyhedron*, **2007**,**26**:4793-4798

[16]Luo W, Meng X G, Xiang J F, et al. *Inorg. Chim. Acta*, **2008**,**361**:2667-2676

[17]Chen X H, Wu Q J, Lu W, et al. *Inorg. Chem. Commun.*, **2011**,**14**:694-696

[18]Sheldrick G M. *SHELXS*-97, *Program for X-ray Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

[19]Sheldrick G M. *SHELXL*-97, *Program for X-ray Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

[20]WU Qiong-Jie(吴琼洁), CHEN Xiao-Hua(陈小华), CAI Bi-Qiong(蔡碧琼), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2012**,**28**:201-206

[21]CHEN Xiao-Hua(陈小华), WU Qiong-Jie(吴琼洁), LIANG Zhi-Yu(梁志瑜), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2009**,**25**:910-914

[22]Seena E B, Mathew N, Kuriakose M, et al. *Polyhedron*, **2008**,**27**:1455-1462