

基于水杨酰基缩对硝基水杨酰肼及吗啡啉的三核镍(II) 配合物的合成、晶体结构与磁性质

陈小华^{*,1} 陈奎治¹ 谢春玲²

(¹ 福建师范大学材料科学与工程学院, 福州 350007)

(² 福建师范大学化学与化工学院, 福州 350007)

摘要: 合成了 1 个含水杨酰基缩对硝基水杨酰肼($H_3-o-nbzshz$)和单齿 *N*-杂环分子吗啡啉(Mf)的镍(II)配合物 $[Ni_3(o-nbzshz)_2(DMF)_2(Mf)_2] \cdot 2H_2O$, 并通过元素分析、红外、热分析以及单晶衍射等手段进行表征。标题配合物是由肼基 N-N 单键桥联 3 个金属中心形成的具有晶体学中心对称性的三核镍配合物结构, $Ni1 \cdots Ni2$ 原子间距为 0.458 6(1) nm。在配合物中, 对称的 $Ni1$ 原子与中间的 $Ni2$ 原子分别形成平面正方形和轴向伸长的八面体的配位构型。配合物通过分子间氢键作用构筑成二维超分子网络结构。并通过变温磁化率研究了化合物的磁性质。

关键词: 三核镍(II)配合物; Schiff 碱; 晶体结构; 磁性质

中图分类号: O614.81*3 文献标识码: A 文章编号: 1001-4861(2014)06-1464-05

DOI: 10.11862/CJIC.2014.193

Synthesis, Crystal Structure and Magnetic Property of Trinuclear Nickel(II) Complex Based on *N*-*o*-Nitrobenzoylsalicylhydrazide and Morpholine Ligands

CHEN Xiao-Hua^{*,1} CHEN Kui-Zhi¹ XIE Chun-Ling²

(¹ College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China)

(² College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, China)

Abstract: A nickel(II) complex $[Ni_3(o-nbzshz)_2(DMF)_2(Mf)_2] \cdot 2H_2O$ with *N*-*o*-nitrobenzoylsalicylhydrazide ($H_3-o-nbzshz$) and monodentate N-donor heterocycle, morpholine (Mf) has been synthesized and characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. The complex reveals a centrosymmetric trinuclear structure, in which the three nickel(II) centers are bridged by two N-N single bridges. The $Ni1 \cdots Ni2$ separation is 0.458 6(1) nm. The central nickel atom adopts an axially elongated octahedral geometry whereas the nickel atoms on the two sides have square-planar coordination geometry. The complex forms an infinite 2D network structure by intermolecular hydrogen bonds. The magnetic property has been investigated by variable temperature magnetic susceptibility measurement. CCDC: 954042.

Keywords: trinuclear nickel(II) complex; Schiff base; crystal structure; magnetic property

In recent years, self-assemblies of coordination compounds to form one-, two- and three-dimensional supramolecules have been of much interest. The

general strategies used for self-assemblies into such extended supramolecular network structures are based on the metal ion's preference for different coordination

收稿日期: 2013-10-16。收修改稿日期: 2014-02-01。

福建省教育厅(No.JB2010007)资助项目。

*通讯联系人。E-mail: xiaohuachen03@163.com

geometry, and use of weak intermolecular interactions such as hydrogen bonding and π - π interactions^[1-3]. By now due to their inherent coordination functionalities, *N*-acyl-salicylhydrazide ligands have been utilized in the systems of self-assembly in metallocrowns with different ring-sizes and nuclearities based on trivalent 3d metal ions such as Fe³⁺, Ga³⁺, Co³⁺ and Mn³⁺^[4-6], and a few trinuclear complexes based on bivalent 3d metal ions such as Ni²⁺ and Cu²⁺^[2-3,7-16]. However, among these trinuclear complexes reported, the supramolecular coordination chemistry of *N*-acyl-salicylhydrazide ligands with hydrogen-bonding donor/acceptor functionalities has been less well explored. As a contribution to this field, we have previously reported the structures of a one-dimensional and two three-dimensional chain Ni(II) complexes containing these kinds of ligands, within which the strategies used for the extended assemblies are intermolecular hydrogen bonding interactions^[2-3,16].

In the following account, we have described the synthesis, characterization and structure of [Ni₃(*o*-nbzshz)₂(DMF)₂(Mf)₂]·2H₂O with *N*-*o*-nitrobenzoylsalicylhydrazide as the common ligand and neutral *N*-donor morpholine as the ancillary ligand. As far as we know, the title complex is the first example of a trinuclear nickel(II) complex with morpholine as the ancillary ligand; exhibits an infinite 2D network structure.

1 Experimental

1.1 Reagents and physical measurements

The ligand (H₃-*o*-nbzshz) was synthesized according to the reported method^[8]. All other chemicals were analytical reagent grade and used without further purification. Elemental analyses for C, H, and N 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. Thermogravimetric curves were measured on a Perkin-Elmer Diamond TG/DTA at a heating rate of 5 °C·min⁻¹ from room temperature to 800 °C under air. Temperature-dependent magnetic susceptibility measurement was carried out on

powdered sample using a Quantum Design MPMS-7XL SQUID magnetometer.

1.2 Synthesis of the title complex

A methanol solution (5 mL) of Ni(CH₃COO)₂·4H₂O (1 mmol) was added to a stirred DMF solution (5 mL) of H₃-*o*-nbzshz (1 mmol). After stirring for 30 min, 0.5 mL morpholine was added to the mixed solution, which was then stirred for another 1 h at the room temperature and filtered. Red crystals of the title complex suitable for X-ray diffraction were obtained after several days. Yield: 37%. Anal. Calcd. for C₄₂H₅₂N₁₀Ni₃O₁₆(%): C, 44.68; H, 4.64; N, 12.41. Found (%): C, 44.75; H, 4.48; N, 12.56. IR (KBr pellet, cm⁻¹): 3 380 (w); 3 210 (vs); 1 660 (s); 1 607 (vs); 1 421(s), 1 340 (s); 1 247 (s); 662 (w); 518 (w), 450(w).

1.3 Crystal structure determination

A red single crystal with dimensions of 0.16 mm×0.25 mm×0.42 mm was selected and mounted on a glass fiber. Diffraction data were collected at a Rigaku RAPID Weissengberg IP diffractometer with graphite-monochromated Mo *K*α radiation (λ=0.071 073 nm) and the ω scan mode. A total of 23 952 reflections and 5 769 unique ones were collected in the range of 3.14°≤θ≤27.48° with *R*_{int}=0.063 7, of which 4 452 reflections with *I*>2σ(*I*) were used for structure solution. The structure was solved by direct method with SHELXS-97^[17] and refined by full-matrix least squares calculations with SHELXL-97^[18]. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were positioned geometrically and refined using a riding mode. The crystallographic data is listed in Table 1.

CCDC: 954042.

2 Results and discussion

2.1 Crystal structure

As shown in Fig.1, the title complex is of centrosymmetrical trinuclear structure type with a Ni-N-Ni-N-N core. The three nickel(II) ions linked by two deprotonated ligands *o*-nbzshz³⁻ exhibit alternating square-planar and octahedral coordination geometries, which are similar to the related trinuclear nickel(II) complexes reported^[2-3,7-16]. The central Ni2 is located at

Table 1 Crystal data and structure refinement for the title complex

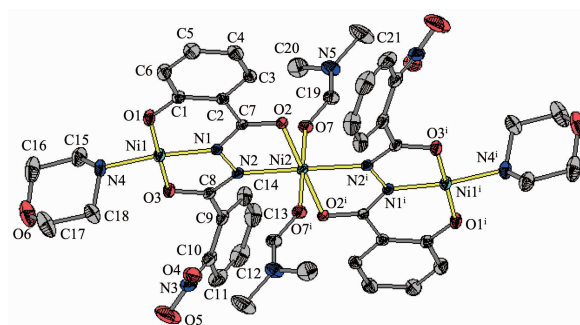
Formula	C ₄₂ H ₅₂ N ₁₀ Ni ₃ O ₁₆	<i>T</i> / K	293
Formula Weight	1 129.07	μ / mm ⁻¹	1.186
Crystal size / mm	0.16×0.25×0.42	<i>F</i> (000)	1 172
Crystal system	<i>P</i> 2 ₁ / <i>c</i>	θ range / (°)	3.14 to 27.48
Space group	Monoclinic	Index ranges	-16 ≤ <i>h</i> ≤ 16, -12 ≤ <i>k</i> ≤ 12, -25 ≤ <i>l</i> ≤ 25
<i>a</i> / nm	1.304 3(5)	Reflections collected / unique	23 952 / 5 769 (<i>R</i> _{int} =0.063 7)
<i>b</i> / nm	0.973 8(3)	Observed reflections	4 452
<i>c</i> / nm	1.992 3(9)	Number of parameters	245
β / (°)	95.10(2)	<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.041 0, 0.102 0
<i>V</i> / nm ³	2.521(2)	Goodness-of-fit on <i>F</i> ²	1.041
<i>Z</i>	2	($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / (e·nm ⁻³)	340, -441
<i>D</i> _c / (g·cm ⁻³)	1.488	(Δ/σ) _{max}	0.000

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}$$

a crystallographic inversion center and bound to two carbonyl oxygen atoms (O2, O2ⁱ), two hydrazine nitrogen atoms (N2, N2ⁱ), of two ligand molecules and two oxygen atoms (O7, O7ⁱ) of coordinated DMF molecules. This N₂O₄ donor set forms an elongated octahedral coordination geometry around the Ni2 ion. The equatorial plane of the octahedron defined by O2, N2, O2ⁱ and N2ⁱ around Ni2 is perfectly planar and the Ni2 lies in this plane. Ni1 and Ni1ⁱ (symmetry code: ⁱ -*x*+1, -*y*+1, -*z*), which occupy the terminal positions, are centrosymmetrically related to each other, hence atoms Ni1, Ni2 and Ni1ⁱ lie in a line with the angle of 180°. The Ni1...Ni2 separation is 0.458 6(1) nm and the Ni1-N1-N2-Ni2 torsion angle is 173.56 (9)°. The atoms O1, O3, N1 and N4 forming a square-plane around Ni1 atom on the side are almost coplanar with the average deviation from the mean plane of 0.006 9 (1) nm, and the Ni1 is 0.000 1(1) nm

out of this plane.

The selected bond lengths and bond angles are listed in Table 2. On the equatorial plane, the Ni2-O2 bond length is 0.203 1(2) nm and the Ni2-N2 bond length is 0.205 9(2) nm. The axial bond distance of Ni2-O7 is 0.212 1(2) nm. These values are consistent



Water molecules and all hydrogen atoms are omitted; for clarity; Symmetry code: ⁱ -*x*+1, -*y*+1, -*z*

Fig.1 Molecular structure of the title complex with 20% thermal ellipsoids

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

Ni(1)-O(1)	0.181 8(2)	Ni(1)-N(1)	0.181 6(2)	Ni(1)-O(3)	0.185 3(2)
Ni(1)-N(4)	0.192 8(2)	Ni(2)-O(2)	0.203 1(2)	Ni(2)-N(2)	0.205 9(2)
Ni(2)-O(7)	0.212 1(2)	O(1)-C(1)	0.132 2(3)	O(2)-C(7)	0.127 5(3)
O(3)-C(8)	0.129 2(3)	N(1)-C(7)	0.132 6(3)	N(1)-N(2)	0.141 3(3)
N(2)-C(8)	0.130 4(3)				
O(1)-Ni(1)-N(1)	95.80(9)	O(1)-Ni(1)-O(3)	175.75(9)	N(1)-Ni(1)-O(3)	84.43(8)
O(3)-Ni(1)-N(4)	90.67(9)	N(1)-Ni(1)-N(4)	173.4(1)	O(1)-Ni(1)-N(4)	89.4(1)
O(2)-Ni(2)-N(2)	78.79(7)	O(2) ⁱ -Ni(2)-N(2)	101.21(7)	O(2)-Ni(2)-O(7) ⁱ	87.74(7)
N(2)-Ni(2)-O(7) ⁱ	90.82(8)	O(2)-Ni(2)-O(7)	92.26(7)	N(2)-Ni(2)-O(7)	89.18(8)

Symmetry code: ⁱ -*x*+1, -*y*+1, -*z*.

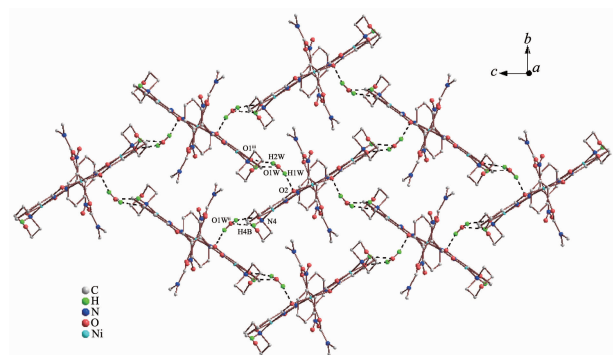
Table 3 Hydrogen bond lengths and bond angles for the title complex

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠DHA / (°)
O(1W)-H(1W)···O(2)	0.084(2)	0.205(3)	0.282 9(3)	155(3)
N(4)-H(4B)···O(1W) ⁱⁱ	0.091	0.213	0.292 4(4)	145.3
O(1W)-H(2W)···O(1) ⁱⁱⁱ	0.084(2)	0.212(2)	0.284 0(3)	144(2)

Symmetry codes: ⁱⁱ $-x+1, y-1/2, -z+1/2$; ⁱⁱⁱ $-x+1, y+1/2, -z+1/2$.

with the Ni-N, Ni-O bond distances in octahedral geometries^[2-3,7-16]. The Ni-N and Ni-O bond distances for Ni1, Ni1ⁱ atoms (on average, 0.187 2(2) nm and 0.183 5(2) nm, respectively) are comparable with the related trinuclear complexes^[2-3,7-16].

In the crystal structure, the two solvent water molecules are hydrogen bonded to their parent $[\text{Ni}_3(o\text{-nbzshz})_2(\text{DMF})_2(\text{Mf})_2]$ unit through one pair of water-carbonyl O1W-H1W···O2 hydrogen bonds (O1W···O2 0.282 9(3) nm). Then each $[\text{Ni}_3(o\text{-nbzshz})_2(\text{DMF})_2(\text{Mf})_2] \cdot 2\text{H}_2\text{O}$ moiety is connected to four adjacent $[\text{Ni}_3(o\text{-nbzshz})_2(\text{DMF})_2(\text{Mf})_2] \cdot 2\text{H}_2\text{O}$ units by two pairs of intermolecular N4-H4B···O1Wⁱⁱ (symmetry code: ⁱⁱ $-x+1, y-1/2, -z+1/2$; N4···O1Wⁱⁱ 0.292 4 (4) nm) and O1W-H2W···O1ⁱⁱⁱ (symmetry code: ⁱⁱⁱ $-x+1, y+1/2, -z+1/2$; O1W···O1ⁱⁱⁱ 0.284 0 (3) nm) hydrogen bonds, giving rise to a 2D network structure parallel to bc plane (Fig.2).



Symmetry code: ⁱⁱ $-x+1, y-1/2, -z+1/2$; ⁱⁱⁱ $-x+1, y+1/2, -z+1/2$; H atoms not involved in hydrogen bonding have been omitted

Fig.2 2D network structure of the title complex

2.2 Thermogravimetric analysis

To study the stability of the title complex, thermogravimetric analysis (TGA) was performed. The TG curve (Fig.3) of the title complex exhibits three weight loss stages. The weight losses of 32.4% in the range of 120 to 440 °C in the first and second step are attributed to the removal of two water molecules, two

coordinated DMF and two coordinated morpholine molecules (Calcd. 31.6%). A further decomposition occurred over 440 °C, with a mass remnant of 20.4 % at about 600 °C consistent with the deposition of NiO (Calcd. 19.9%).

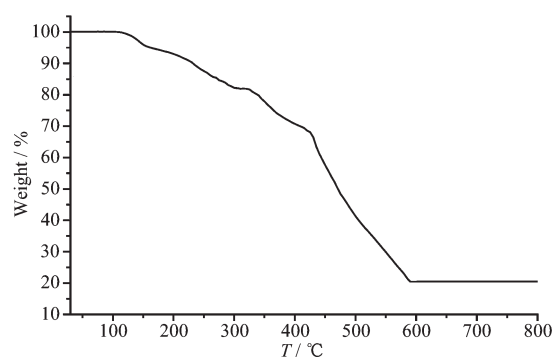
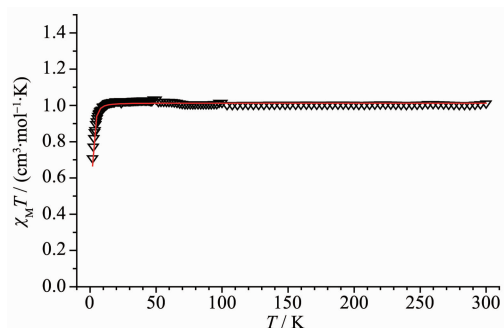


Fig.3 TG curve of the title complex

2.3 Magnetic property

The magnetic property of the title complex has been investigated by variable temperature magnetic susceptibility measurement in the solid state. The complex has two four-coordinated, square-planar Ni(II) ions that are treated as low spin and diamagnetic. Additionally, there is one six-coordinated Ni(II) ion that is paramagnetic^[2,19]. The magnetic properties of the complex in the form of $\chi_M T$ vs T plots are shown in Fig.4. At room temperature, the $\chi_M T$ value is $1.0 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ which is a typical value for an isolated Ni(II) ion with $g > 2.00$. $\chi_M T$ is practically constant to about 30 K and then decreases to $0.4 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. This feature indicates typical paramagnetic behavior for a Ni(II) ion in which the D parameter and/or intermolecular interactions (usually antiferromagnetic) are active at low temperature^[20]. In an attempt to calculate the D value, we have fitted the experimental $\chi_M T$ value to the formula given by Kahn for a mononuclear Ni(II) ion considering the zero field split (ZFS) of the $S=1$ ground state^[20]. The best fit value are $|D|=3.8 \text{ cm}^{-1}$ and $g(\text{average})=2.01$. The D value is

consistent with that typical for Ni(II) ions (close to 5~8 cm⁻¹).



Solid line is fit to the experimental data (see text)

Fig.4 $\chi_M T$ vs T plot of the complex

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