



含硫镍金属镍配合物 $[\text{Ni}(\text{C}_{13}\text{H}_7\text{Br}_2\text{NOS})_2(\text{DMF})] \cdot (\text{C}_3\text{H}_7\text{O})$ 的合成与晶体结构

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关键词: 席夫碱; 镍(II)配合物; 晶体结构; 电化学性质; 热重分析

中图分类号: O614.81+3

文献标识码: A

文章编号: 1001-4861(2008)05-0823-04

Synthesis and Crystal Structure of Sulfur-containing Nickel Coordination $[\text{Ni}(\text{C}_{13}\text{H}_7\text{Br}_2\text{NOS})_2(N,N'\text{-dimethylformamide})] \cdot (\text{C}_3\text{H}_7\text{O})$

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Abstract: The complex, $[\text{Ni}(\text{C}_{13}\text{H}_7\text{Br}_2\text{NOS})_2(\text{DMF})] \cdot (\text{C}_3\text{H}_7\text{O})$ (DMF=*N,N'*-dimethylformamide), was synthesized and characterized by the element analysis, IR and X-ray diffraction single crystal structure determination. The title complex crystallizes in monoclinic system, space group $P2_1/n$, with $a=8.297\ 6(15)$ nm, $b=12.866(2)$ nm, $c=31.889(3)$ nm, $\beta=95.024(2)^\circ$, and $V=3\ 391.3(9)$ nm³, $Z=4$, $R=0.075\ 2$, $wR=0.176\ 8$. The nickel iron is six-coordinated by three O atoms, two N atoms, one S from the Schiff base and one O atom from DMF ligand, forming a octahedron coordination geometry. Schiff bases are bridged by the two S atoms. The molecules in the crystal are linked through intermolecular $\text{Br} \cdots \text{Br}$, $\text{C}-\text{H} \cdots \text{O}$, $\text{S} \cdots \text{Br}$ interactions. Its electrochemical property is reported. CCDC: 675768.

Key words: Schiff base; nickel(II) complex; crystal structure; electrochemical measurements; thermal analysis

The sulfur-containing Schiff base derived metal ion complexes have been extensively studied in recent years owing to their great variety of biological activity ranging from antimalarial, antibacterial, antitumoral, antiviral activities etc^[1,2]. Moreover, most of them are applied in modifying electrochemical sensor^[3~6]. The sulfur-containing Schiff base compound is of great interest in various aspects of chemistry. We report herein the synthesis and crystal structure of the

complex resulting from the condensation of 2-amino-benzenethiol-3,5-Bibromo-2-hydroxy-benzaldehyde, of $\text{Ni}(\text{CH}_3\text{COO})_2$. The structure is discussed and electrochemical property and TG analysis is studied.

1 Experimental

1.1 Synthesis of $[\text{Ni}(\text{C}_{13}\text{H}_7\text{Br}_2\text{NOS})_2(N,N'\text{-dimethylformamide})] \cdot (\text{C}_3\text{H}_7\text{O})$

A solution of 3,5-dibromosalicylaldehyde (1.0

收稿日期: 2007-08-27。收修改稿日期: 2008-01-23。

广西教育厅学科软环境建设基金资助项目(No.D200352)。

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mmol, 0.278 g) in ethanol (10 mL) was put in a flask. To this solution, 2-aminobenzenethiol (1.0 mmol, 0.128 g) in ethanol (10 mL) was added slowly. The mixture was refluxed at 50 °C for 1.0 h. Then a DMF solution (5 mL) of $\text{Ni}(\text{CH}_3\text{COO})_2$ (1.0 mmol, 0.248 g) and NaOH (0.5 mmol, 0.02 g) was added slowly and reaction 3 h. After cooling to room temperature, the solution was filtered twice. Single crystals of the title compound were obtained after 2 months. Anal. Calcd for $\text{Ni}[(\text{C}_{13}\text{H}_7\text{Br}_2\text{NOS})_2(\text{DMF})]\cdot(\text{C}_3\text{H}_7\text{O})$ (%): C 38.38; H 2.41; N 4.70; O 5.92. Found (%): C 38.18; H 2.59; N 4.54; O 6.05.

1.2 Crystal structure determination

A single crystal of the title complex with dimensions of 0.19 mm \times 0.18 mm \times 0.17 mm was selected for the structure determination. X-ray single-crystal diffraction carried out on a Bruker Smart 1000 CCD diffractometer at 298(2) K. A total of 5 922 unique reflections were collected, of which 3 066 with $I > 2\sigma(I)$ were observed. The unit cell parameters and data collection were performed with a Mo $K\alpha$ radiation ($\lambda = 0.071\,073$ nm). The unit cell dimensions were obtained with the least-squares refinements and the structure was solved by direct methods, and refined by full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located on the calculated positions and refined isotropically. The title complex crystallizes in monoclinic system with space group $P2_1/n$, $a = 8.297\,6(15)$

nm, $b = 12.866(2)$ nm, $c = 31.889(3)$ nm, $\beta = 95.024(2)^\circ$, and $V = 3\,391.3(9)$ nm³, $Z = 4$. The final cycle of refinement converged to, $R = 0.075\,2$, $wR = 0.176\,8$. $R = 0.066\,4$, $wR = 0.147\,4$ ($w = 1/[s^2(F_o^2) + (0.092\,6P)^2 + 9.937\,7P]$, where $P = (F_o^2 + 2F_c^2)/3$, $S = 1.032$, $(\Delta\rho)_{\text{max}} = 1\,174\text{ e}\cdot\text{nm}^{-3}$ and $(\Delta\rho)_{\text{min}} = -1\,238\text{ e}\cdot\text{nm}^{-3}$. All calculations were performed by using SHELXTL package.

CCDC: 675768.

2 Discussion

2.1 Crystal structure

Selected bond lengths and bond angles are listed in Table 1. The molecular structure is shown in Fig.1 and a crystal packing diagram in Fig.2. The Ni iron is six-coordinated by Schiff bases and one DMF molecule. The linkage of one Schiff base to the metal atom is accomplished through the phenol oxygen (O2), Mercapto sulfur (S2) and amino nitrogen atom (N2). Thus one set of five-membered chelate ring and a six-membered chelate ring are formed. The other Schiff base is coordinated through the phenol oxygen (O1) and the amino nitrogen atom (N1), and form a six-membered chelate ring with metal atom Ni (Ni1). The solvent DMF is coordinated by Carboxyl oxygen (O3), so the center metal atom is six coordinated. The Ni-O distances are Ni1-O1 0.199 3(7) nm; Ni1-O2 0.196 6(8) nm; Ni1-O3 0.208 2(7) nm. It is normal that the coordination capacity of phenol oxygen is stronger than carboxyl oxygen^[7,8].

Table 1 Selected bond lengths (nm) and bond angles ($^\circ$) of the complex

Ni1-O2	1.966(8)	Br3-C17	1.874(13)	N3-C28	1.464(14)
Ni1-O1	1.993(7)	Br4-C19	1.889(12)	O1-C3	1.271(12)
Ni1-N2	2.065(9)	N1-C1	1.285(13)	O2-C16	1.291(13)
Ni1-N1	2.080(9)	N1-C8	1.416(13)	O3-C27	1.227(13)
Ni1-O3	2.082(7)	N2-C14	1.279(13)	S1-C9	1.732(12)
Ni1-S2	2.438(3)	N2-C21	1.416(13)	S1-S2	2.069(4)
Br1-C4	1.872(12)	N3-C27	1.348(13)	S2-C22	1.760(11)
Br2-C6	1.865(12)	N3-C29	1.440(15)		
O2-Ni1-O1	87.5(3)	N2-Ni1-N1	94.6(3)	O2-Ni1-S2	170.9(2)
O2-Ni1-N2	89.2(3)	O2-Ni1-O3	95.2(3)	O1-Ni1-S2	101.1(2)
O1-Ni1-N2	175.7(3)	O1-Ni1-O3	90.2(3)	N2-Ni1-S2	82.1(2)
O2-Ni1-N1	93.5(3)	N2-Ni1-O3	87.5(3)	N1-Ni1-S2	89.5(2)
O1-Ni1-N1	88.3(3)	N1-Ni1-O3	171.2(3)	O3-Ni1-S2	82.2(2)

We know that the coordination case of two Schiff bases which is linked by S1-S2 is different from above. The length of bond S1-S2 0.206 94 nm is quite similar to that reported for S-S 0.207 4 nm. The Schiff base (including S1) is not like the schiff base (including S2) which was in one face forming a π bond. Two benzol cycle was distorted because of bond S-S. The S2 links three atoms through a novel μ_3 square bridging coordination. There are intermolecular hydrogen bonds in the title compound: C-H \cdots O 0.255 93 nm, 149.2(1) $^\circ$,

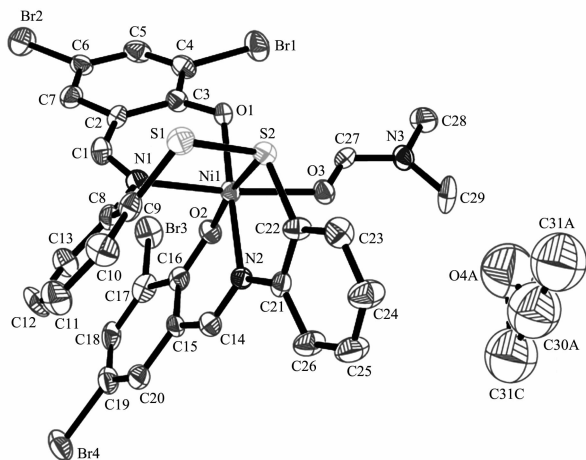


Fig.1 Molecular structure of the title complex

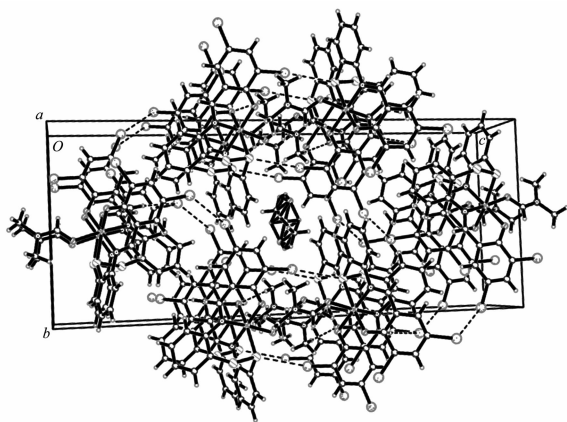
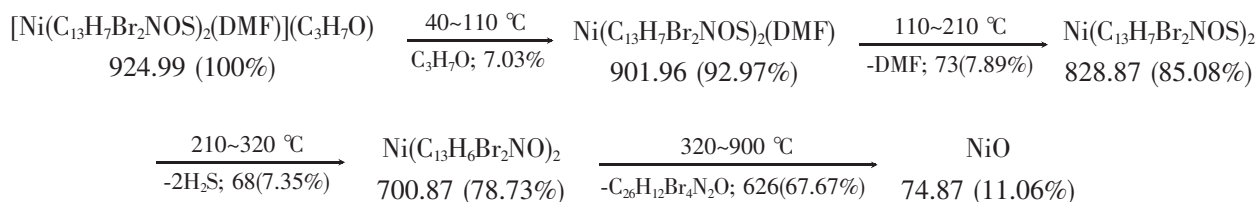


Fig.2 Packing diagram of the title complex



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which make the structure more stable. It is proved that Halogen role exists in the compound^[9]. The length Br \cdots Br is 0.376 54 nm, S \cdots Br is 0.340 2 nm.

2.2 Electrochemical measurements

Fig.3 indicates the cyclic voltammograms of the complex on platinum working electrode in DMF. It displays two reduction processes. The first reduction is a reversible two electron process with a peak separation of 0.680 1 V, and may be assigned to -N=CH/-NH-CH₂- process. The other reduction with a peak of -0.689 5 V probably belongs to Ni(II)/Ni(III) process.

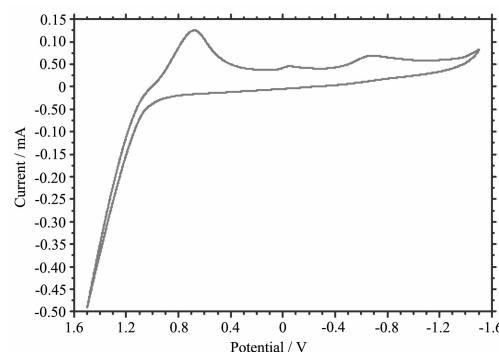


Fig.3 Cyclic voltammograms of the title complex

2.3 Thermal analysis

The complex decomposed in four main steps. The first step observed in the range 40~110 $^\circ\text{C}$ with mass loss of 7.03%, was assigned to the solution moleculars. The second step found in the range 110~210 $^\circ\text{C}$, was assigned to the DMF molecular. The third step found in the range 210~320 $^\circ\text{C}$, was found to be split and the sum of its mass loss was approximate to 7.35% which may due to the decomposition of the remaining part of the H₂S. The forth step found in the range 320~900 $^\circ\text{C}$ was assigned to the complete removal of the schiff base moiety leaving NiO.

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