

配合物 $[\text{Ni}(\text{Pht})(\text{Medpq})(\text{H}_2\text{O})_3]_n$ 的水热合成、 表征及自然键轨道(NBO)分析

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摘要: 采用水热法合成了一种新型金属配合物 $[\text{Ni}(\text{Pht})(\text{Medpq})(\text{H}_2\text{O})_3]_n$ (**1**) (Pht=phthalic acid, Medpq=2-methyldipyrido[3, 2-f:2', 3'-h]quinoxaline), 并对其进行了元素分析、红外光谱、热重表征、X 射线单晶衍射测定和理论计算。在晶体中, Ni(II)与来自于 Medpq 分子上的 2 个氮原子, 邻苯二甲酸上的 1 个氧原子及来自于 3 个不同的配位水分子上的 3 个氧原子配位, 形成畸变的八面体构型。整个晶体由 Pht-Ni-Medpq 单元组成零维结构。应用 Gaussian03W 程序, 在 HF/LANL2DZ 水平上对标题化合物的自然键轨道(NBO)进行了分析, 结果表明 Ni(II)与配位原子间的价键类型都属于共价键范畴。

关键词: 邻苯二甲酸; 晶体结构; 水热合成; 镍(II)配合物; 自然键轨道

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Hydrothermal Synthesis, Characterization and Natural Bond Orbital(NBO) Analysis of $[\text{Ni}(\text{Pht})(\text{Medpq})(\text{H}_2\text{O})_3]_n$ Complex

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Abstract: A metal-organic complex $[\text{Ni}(\text{Pht})(\text{Medpq})(\text{H}_2\text{O})_3]_n$ (**1**) (Pht=phthalic acid, Medpq=2-methyldipyrido[3, 2-f:2', 3'-h]quinoxaline) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG, single-crystal X-ray diffraction and theoretical calculations. In the crystal structure, the nickel atom is hexa-coordinated with two nitrogen atoms from Medpq ligand, one oxygen atom from Pht ligand and three oxygen atoms from three different coordination water molecules, assuming a slightly distorted octahedral geometry. Furthermore, it exhibits a zero-dimensional structure with Pht-Ni-Medpq as building units. Natural bond orbital (NBO) analysis was performed by using the NBO method built in Gaussian03 Program. The calculation results show there is the obvious covalent interaction between the coordinated atoms and Ni(II) ion. CCDC: 794823.

Key words: phthalic acid; crystal structure; hydrothermal synthesis; nickel(II) complex; natural bond orbital

Organic molecules containing carboxylic acid have been used as building blocks in crystal engineering and many complexes^[1-2]. Phthalic acid is a well-known

versatile ligand, which has been extensively used in the design of complexes due to a variety of its bonding abilities^[4].

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At the same time, more and more attention has been paid to the study of synthesis and characterization of complexes with heterocyclic ligands like 1,10-phenanthroline (phen) and its derivatives^[3-9]. 1,10-phenanthroline (phen) and its derivatives are reported to show a broad spectrum uses, such as gas adsorption, ion exchange, magnetism, heterogeneous catalysis, luminescence and nonlinear optics^[10-17]. 2-methyldipyrido[3,2-f:2',3'-h]quinoxaline (Medpq) as a derivative of phen and possessing an extended aromatic system, is a planar rigid bidentate chelating reagent which can not only act as a terminal ligand but also potentially provide supramolecular interactions such as aromatic stacking to construct intriguing structures. By hydrothermal reaction of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with phthalic acid in the presence of Medpq, a new Ni(II) carboxylate complex $[\text{Ni}(\text{Pht})(\text{Medpq})(\text{H}_2\text{O})_3]_n$ was obtained and its synthesis, characterizations, theoretical calculations, and crystal structure will be reported in this paper.

1 Experimental

1.1 Materials

The Medpq ligand was synthesized according to the literature method^[3-4]. $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Pht and NaOH were purchased commercially and used without further purification.

1.2 Instrument and measurements

Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; thermal gravimetric measurements (TG) were performed on a NETZSCH STA 449C analyzer.

1.3 Synthesis of the title complex

The complex **1** was prepared from a mixture of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.248 g, 1 mmol), Pht (0.166 g, 1 mmol), Medpq (0.248 g, 1 mmol) and H_2O (8 mL) in an 18 mL Teflon-lined autoclave under autogenous pressure at 165 °C for five days. After cooling to room temperature, green block crystals of **1** were collected by filtration and washed with distilled water in 70% yield (based on Ni). Anal. Calcd. for $\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_7\text{Ni}$ (%): C, 53.17; H, 3.08; N, 10.79. Found(%): C, 53.16; H, 3.10; N, 10.78. IR (KBr, cm^{-1}): 3 252m (respectively ascribed to the stretching vibrations of H_2O , which indicates the existence of water molecules), 1 634s, 1 547s, 1 485m, 1 401s, 1 303w, 1 262w, 1 088m, 818m, 738m.

1.4 Structure determination

A single crystal with dimensions of 0.31 mm×0.27 mm×0.22 mm was mounted on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) by using an φ - ω scan mode ($4.36^\circ < 2\theta < 52.76^\circ$) at 293(2) K. The structure was solved by direct methods with SHELXS-97 program^[18] and refined by SHELXL 97^[19] using full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. All hydrogen atoms were placed in calculated positions and refined as riding mode, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. The detailed crystallographic data and structure refinement parameters for the title complex is summarized in Table 1.

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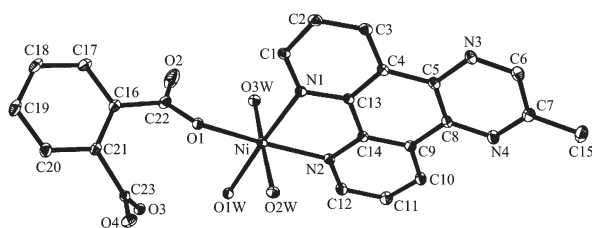
Table 1 Crystallographic data for the title complex

Empirical formula	$\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_7\text{Ni}$	$\alpha / (^\circ)$	75.22(3)
Formula mass	519.11	$\beta / (^\circ)$	81.13(3)
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.554	$\gamma / (^\circ)$	76.82(3)
$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	0.928	V / nm^3	1.109 4(4)
Crystal system	Triclinic	Z	2
Space group	$P\bar{1}$	$R_1, wR_2 (I>2\sigma(I))$	0.087 3, 0.145 9
Crystal size / mm	0.31×0.27×0.22	$F(000)$	532
a / nm	0.789 82(16)	Collected reflections	10 969
b / nm	1.134 5(2)	Goodness-of-fit (GOF) on F^2	1.12
c / nm	1.321 9(3)		

2 Result and discussion

2.1 Description of crystal structure

Single-crystal X-ray diffraction analysis reveals that the complex [Ni(Pht)(Medpq)(H₂O)₃]_n crystallizes in *P* $\bar{1}$ space group and consists of a zero-dimensional structure. The molecular structure of the the complex **1** is shown in Fig.1. There are one Ni(II) ion, one Pht ligand, one Medpq ligand and three coordination water molecules in the asymmetric unit. The Ni(II) ion is hexacoordinated with six atoms (N(1), N(2), O(1), O(1W), O(2W), O(3W)) from Medpq ligand, Pht ligand and three coordination water molecules, assuming a slightly distorted octahedral geometry. The Ni-O bond distance in the complex **1** are in the range of 0.203 3(3) ~0.212 0(3) nm, the Ni-N(1) bond distance is 0.207 5(3) nm and Ni-N(2) bond distance is 0.209 1(4) nm, the N(O)-Ni-O(N) angles range from 78.76(13)° to

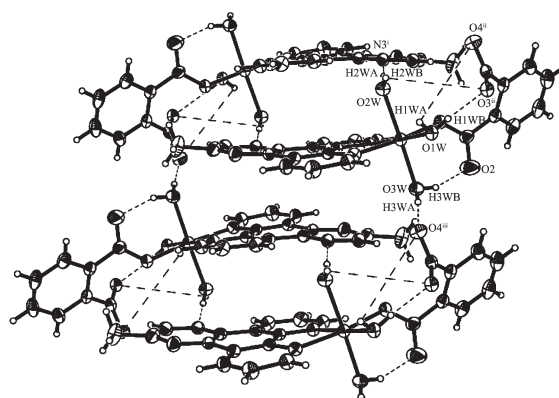


Hydrogen atoms are omitted for clarity

Fig.1 Local coordination environment of the complex **1**

177.54(13)°. The selected important bond parameters are given in Table 2.

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architectures^[20]. There are persistent strong O–H···O and O–H···N hydrogen bonding interactions between crystal molecules, coordinated water molecule and Pht ligands (Table 3), which play an important role in stabilizing the network structure and controlling the orientation of intra ligands. Furthermore, the complex **1** is extended into a two-dimensional layer structure (Fig.2). At the same time, There are π - π interactions in the complex **1**, aromatic ring of Medpq ligand and symmetry of the



Symmetry codes: ⁱ 2-*x*, 1-*y*, 1-*z*; ⁱⁱ 2-*x*, 1-*y*, 2-*z*; ⁱⁱⁱ *x*-1, *y*, *z*

Fig.2 View of two-dimensional layer structure of the complex **1** showing hydrogen interactions

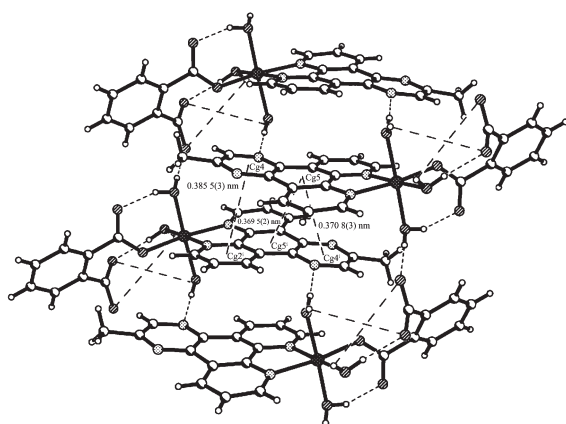
Table 2 Selected bond lengths (nm) and angles (°) for the title complex

Ni-N(1)	0.207 5(3)	Ni-N(2)	0.209 1(4)	Ni-O(1)	0.203 3(3)
Ni-O(1W)	0.204 5(3)	Ni-O(2W)	0.212 0(3)	Ni-O(3W)	0.204 8(3)
N(1)-Ni-N(2)	78.76(13)	N(1)-Ni-O(1)	94.47(13)	N(1)-Ni-O(1W)	176.71(13)
N(1)-Ni-O(2W)	88.63(13)	N(1)-Ni-O(3W)	91.96(14)	N(2)-Ni-O(1)	171.91(12)
N(2)-Ni-O(1W)	99.29(13)	N(2)-Ni-O(2W)	85.65(13)	N(2)-Ni-O(3W)	92.12(14)
O(1)-Ni-O(1W)	87.14(12)	O(1)-Ni-O(2W)	89.73(13)	O(1)-Ni-O(3W)	92.69(13)
O(1W)-Ni-O(2W)	88.52(13)	O(1W)-Ni-O(3W)	90.82(13)	O(2W)-Ni-O(3W)	177.54(13)

Table 3 Hydrogen bond lengths and angles for the title complex

D-H···A	<i>d</i> (D-H) / nm	<i>d</i> (H···A) / nm	<i>d</i> (D···A) / nm	∠D-H···A / (°)
O(2W)-HW(2A)···N3	0.082 0(4)	0.214 0(2)	0.292 7(5)	161(4)
O(2W)-HW(2B)···O3	0.083 0(18)	0.192 6(19)	0.275 0(4)	172(4)
O(3W)-HW(3A)···O4	0.085 0(4)	0.191 0(4)	0.275 7(5)	175(5)
O(1W)-HW(1A)···O4	0.084 3(19)	0.182 0(3)	0.263 0(4)	161(6)
O(1W)-HW(1B)···O3	0.085 0(4)	0.192 0(2)	0.276 8(4)	175(5)
O(3W)-HW(3B)···O2	0.083 0(4)	0.184 0(2)	0.262 2(5)	156(5)

two adjacent equivalent of aromatic ring have π - π interactions with distance between $\text{cg}(2)^i \rightarrow \text{cg}(4)$ ring centroids is 0.385 5(3) nm, $\text{cg}(4)^i \rightarrow \text{cg}(5)$ is 0.370 8(3) nm and $\text{cg}(5) \rightarrow \text{cg}(5)^i$ is 0.369 5(2) nm (defined rings Cg(2): N1-C1-C2-C3-C4-C13, Cg(4): N3-C5-C8-N4-C7-C6 and Cg(5): C4-C5-C8-C9-C14-C13, symmetry code: $^i 1-x, 1-y, 1-z$). These adjacent aromatic columns are piled up, and the complex **1** is extended into a three-dimensional supramolecular framework (Fig.3).



Symmetry code: $^i 1-x, 1-y, 1-z$

Fig.3 View of three-dimensional supramolecular framework of the complex **1** showing π - π stacking interactions between the adjacent aromatic ring of Medpq ligand

2.2 Thermal analysis

The TG curve of **1** shows that the first weight loss of 9.64% from 54.9 to 149.7 °C corresponds to the removal of coordination water molecules (calcd. 10.40%). Upon further heating, an obvious weight loss (26.85%) occurs in the temperature range of 149.7 ~ 436.6 °C, corresponding to the release of Pht ligand (calcd. 28.89%). Obvious weight loss (47.59%) occurs in the temperature range of 436.6~1 189.5 °C, corresponds to the release of Medpq ligand (calcd. 46.32%). No weight loss is observed after 1 189.5 °C, indicating the complete decomposition of **1**. The residual weight 15.92% (calcd. 14.39%) corresponds to NiO.

2.3 Theoretical calculations

The Gaussian03 program^[21] was used in the calculation. The parameters of the molecular structure for calculation were all from the experimental data of the complex **1**. Natural bond orbital (NBO) analysis was

performed by Hartree-Forck method in LANL2DZ basis set.

The selected natural atomic charges and natural electron configuration for the complex **1** is shown in Table 4. It is indicated from Table 4 that the electronic configurations of Ni(II) ion, N and O atoms are $4s^{0.20}3d^{8.16}5p^{0.02}$, $2s^{1.37-1.38}2p^{4.23-4.25}3p^{0.02}$ and $2s^{1.54-1.72}2p^{5.23-5.31}3p^{0.01-0.02}$, respectively. Based on the above results, one can conclude that the Ni(II) ion coordination with N and O atoms is mainly on 3d and 4s orbits (the electron number of 5p orbit is so small that can be omitted). N atoms form coordination bonds with Ni(II) ion by using 2s and 2p. In the same way, all O atoms supply electrons of 2s and 2p to Ni(II) ion and form the coordination bonds. Therefore, the Ni(II) ion obtained some electrons from two nitrogen atoms of Medpq ligand, one oxygen atom of Pht ligand and three oxygen atoms of three different coordination water molecules. Thus, according to valence-bond theory the atomic net charge distribution in the complex **1** (See Table 4) shows the obvious covalent interaction between the coordinated atoms and Ni(II) ion. As can be seen from the Fig.4, the LUMO orbital are composed of d nickel

Table 4 Selected natural atomic charges (e) and natural electron configuration for the title complex

Atom	Net charge	Electron configuration
Ni	1.616 46	[core]4s(0.20)3d(8.16)5p(0.02)
N(1)	-0.632 61	[core]2s(1.38)2p(4.23)3p(0.02)
N(2)	-0.641 39	[core]2s(1.37)2p(4.25)3p(0.02)
O(1)	-0.796 85	[core]2s(1.54)2p(5.23)3p(0.02)
O(1W)	-0.989 11	[core]2s(1.67)2p(5.31)3p(0.01)
O(2W)	-0.983 58	[core]2s(1.72)2p(5.26)3p(0.01)
O(3W)	-0.953 63	[core]2s(1.67)2p(5.27)3p(0.01)

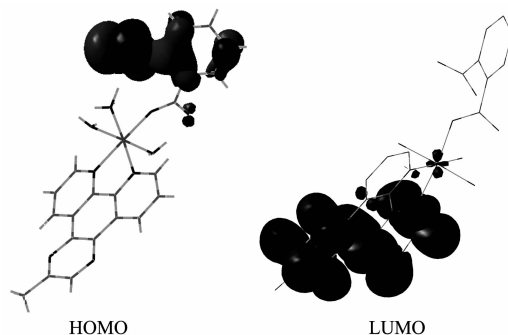


Fig.4 Molecular orbitals of the complex **1**

orbital and the π orbitals of Medpq ligand, whereas the HOMO orbital consists of the π orbitals mainly from Pht ligand.

3 Conclusions

In summary, we have prepared a novel metal-organic complex by the combination of phthalic and 2-methyldipyrido[3,2-f:2',3'-h]quinoxaline Ligands, it has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG, single-crystal X-ray diffraction and theoretical calculations. It is lucky to crystallize in heterocyclic ligands space group. Thus it opens a new avenue to explore functional molecule-based materials.

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