

镍、钴超分子配合物的合成、晶体结构及理论计算

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摘要: 通过水热法合成了 2 个新的金属-有机超分子配合物 $[\text{Ni}(\text{eoba})(\text{phen})(\text{H}_2\text{O})_2] \cdot 0.58\text{H}_2\text{O}$ (**1**) 和 $[\text{Co}(\text{eoba})(\text{phen})_2] \cdot \text{H}_2\text{O}$ (**2**) ($\text{H}_2\text{eoba} = 4,4'$ -(乙烷-1,2-二氧基)-二苯甲酸, phen=菲咯啉), 并对其进行了元素分析、红外光谱、热重和 X 射线单晶衍射测定。配合物 **1** 和 **2** 是同构的, 每个配合物都是六配位的, 菲咯啉分子上的 2 个氮原子、4,4'-(乙烷-1,2-二氧基)-二苯甲酸配体上的 2 个氧原子和 2 个配位水分子与金属配位。此外, 还用高斯 09 程序 PBE0/LANL2DZ 方法对配合物 **1** 进行了自然键轨道(NBO)分析, 计算结果表明配位原子与 Ni 原子之间存在着共价作用。

关键词: 水热合成; 晶体结构; 镍配合物; 钴配合物; 自然键轨道

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Syntheses, Crystal Structures and Theoretical Calculations of Nickel/Cobalt Supramolecular Coordination Compounds

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Abstract: Two new metal-organic supramolecular coordination compounds $[\text{Ni}(\text{eoba})(\text{phen})(\text{H}_2\text{O})_2] \cdot 0.58\text{H}_2\text{O}$ (**1**) and $[\text{Co}(\text{eoba})(\text{phen})_2] \cdot \text{H}_2\text{O}$ (**2**) ($\text{H}_2\text{eoba} = 4,4'$ -(ethane-1,2-diylidioxy)dibenzoic acid, phen=phenanthroline) have been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG and single-crystal X-ray diffraction. Complexes **1** and **2** are isomorphous. Each is six-coordinated by two nitrogen atoms from phen molecule, two carboxylate oxygen atoms from eoba ligand and two coordinated water molecules. In addition, natural bond orbital (NBO) analysis of **1** was performed by the PBE0/LANL2DZ method in Gaussian 03 Program. The calculation results show obvious covalent interaction between the coordinated atoms and Ni(II) atom. CCDC: 1417662, **1**; 1417663, **2**.

Keywords: hydrothermal synthesis; crystal structure; nickel complex; cobalt complex; natural bond orbital

0 Introduction

Recently, there has been much interest in the construction of coordination compounds due to their

versatile structures and interesting topologies^[1-4] as well as their potential applications as functional materials in the fields of molecular magnetism, catalysis, gas sorption and optoelectronic devices^[5-9].

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The most useful building blocks for constructing organic-inorganic hybrid coordination compounds are carboxylate and N-donor ligands. Aromatic carboxylate ligands have been extensively employed in the construction of various dimensional coordination compounds because of their abundant coordination modes and high structural stability for functional materials applications^[10-16].

In this aspect, the chelating ligand phenanthroline (phen) have been widely used in the construction of metal-organic coordination polymers^[17]. In addition, as a versatile ligand, 4,4'-(ethane-1,2-diylidioxy)dibenzoic acid (H_2eoba) has been hardly used to construct coordination compounds containing transition metals^[18].

To explore the combination effects of this neutral ligand phen and anionic ligand, we synthesize coordination compounds of Co(II) and Ni(II) containing these ligands. Herein, we report the synthesis and characterizations of two new coordination compounds, namely, $[Ni(eoba)(phen)(H_2O)_2] \cdot 0.58H_2O$ (**1**) and $[Co(eoba)(phen)(H_2O)_2] \cdot H_2O$ (**2**), which exhibit two-dimensional (2D) supramolecular network structures.

1 Experimental

1.1 General procedures

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectrum was recorded in the range of 4 000~400 cm^{-1} on a Nicolet 6700 spectrometer using a KBr pellet. TG studies were performed on a Perkin-Elmer TGA7 analyzer. Powder X-ray diffraction (PXRD) patterns were obtained on Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\ 056\ nm$) at room temperature.

1.2 Synthesis

$[Ni(eoba)(phen)(H_2O)_2] \cdot 0.58H_2O$ (**1**): A mixture of $Ni(OAc)_2 \cdot 4H_2O$ (0.050 g, 0.2 mmol), H_2eoba (0.045 g, 0.15 mmol), phen (0.027 g, 0.15 mmol), H_2O (10 mL) and C_2H_5OH (1 mL) was put in a 30 mL Teflon-lined stainless steel vessel, and then the vessel was sealed and heated at 150 $^{\circ}C$ for 5 days. After the reaction mixture was slowly cooled down to room temperature

at the rate of 5 $^{\circ}C \cdot h^{-1}$, green block crystals were collected by filtration and washed with distilled water in 43% yield (based on Ni). Anal. Calcd. for $C_{28}H_{25.16}N_2NiO_{8.58}$ (%): C, 57.42; H, 4.33; N, 4.78. Found (%): C, 56.92; H, 4.09; N, 4.07. IR (cm^{-1}): 3 071w, 1 606 m, 1 588m, 1 509m, 1 425s, 1 383m, 1 244s, 1 167w, 1 069w, 937w, 849m, 789w, 670w.

$[Co(eoba)(phen)(H_2O)_2] \cdot H_2O$ (**2**): A mixture of $Co(OAc)_2 \cdot 4H_2O$ (0.053 g, 0.2 mmol), H_2eoba (0.045 g, 0.15 mmol), phen (0.027 g, 0.15 mmol) and H_2O (10 mL) was put in a 30 mL Teflon-lined stainless steel vessel, and then the vessel was sealed and heated at 150 $^{\circ}C$ for 5 days. After the reaction mixture was slowly cooled down to room temperature at the rate of 5 $^{\circ}C \cdot h^{-1}$, pink block crystals were collected by filtration and washed with distilled water in 42% yield (based on Co). Anal. Calcd. for $C_{28}H_{26}CoN_2O_9$ (%): C, 56.67; H, 4.42; N, 4.72. Found (%): C, 56.18; H, 4.11; N, 4.16. IR (cm^{-1}): 3 401w, 1 606m, 1 589m, 1 513m, 1 426s, 1 387m, 1 244s, 1 167w, 1 141w, 1 068w, 941 w, 850m, 788w.

1.3 Structure determination

Single-crystal diffraction data of **1** and **2** were respectively collected on a Bruker SMART APEX-CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ ($\lambda=0.071\ 073\ nm$) radiation at room temperature. The structure was solved by direct methods with SHELXS-97 program^[19] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97^[20]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. The details of the crystal parameters, data collection and refinement for **1** and **2** are summarized in Table 1, and selected bond parameters are given in Table 2.

CCDC: 1417662, **1**; 1417663, **2**.

2 Results and discussion

2.1 IR spectrum

For complex **1**, the carboxylates are coordinated with its asymmetric and symmetric stretching appearing at 1 606 ($\nu(OCO)_{\text{asym}}$) and 1 425 cm^{-1} ($\nu(OCO)_{\text{sym}}$)^[21], respectively. The $\Delta\nu$ ($\nu(OCO)_{\text{asym}} - \nu(OCO)_{\text{sym}}$) is 181

Table 1 Crystal data and structure refinement for **1** and **2**

Complex	1	2
Formula	C ₂₈ H _{25.16} N ₂ NiO _{8.58}	C ₂₈ H ₂₆ CoN ₂ O ₉
Formula weight	585.65	593.44
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / nm	1.361 94(12)	1.370 8(5)
<i>b</i> / nm	2.014 88(18)	2.023 7(5)
<i>c</i> / nm	1.010 63(9)	1.015 8(5)
β / (°)	105.125 0(10)	105.071(5)
<i>V</i> / nm ³	2.677 2(4)	2.721 0(18)
<i>Z</i>	4	4
<i>D_c</i> / (g·cm ³)	1.453	1.449
θ range / (°)	1.85~26.11	1.84~25.89
<i>F</i> (000)	1 215	1 228
Reflections collected / unique	14 542 / 5 312	14 559 / 5 274
Goodness-of-fit on <i>F</i> ²	1.060	1.129
<i>R_{int}</i>	0.016 3	0.025 8
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.032 8, 0.099 5	0.040 9, 0.093 3

Table 2 Selected bond lengths (nm) and bond angles (°) for **1** and **2**

1					
Ni(1)-O(1)	0.208 67(14)	Ni(1)-O(2)	0.212 17(14)	Ni(1)-O(7)	0.205 60(15)
Ni(1)-O(8)	0.201 47(16)	Ni(1)-N(1)	0.207 94(16)	Ni(1)-N(2)	0.207 44(17)
O(8)-Ni(1)-O(7)	85.70(7)	N(2)-Ni(1)-N(1)	80.06(7)	O(8)-Ni(1)-O(2)	101.52(7)
O(8)-Ni(1)-N(2)	99.89(7)	O(8)-Ni(1)-O(1)	163.99(7)	O(7)-Ni(1)-O(2)	92.08(6)
O(7)-Ni(1)-N(2)	94.48(7)	O(7)-Ni(1)-O(1)	93.02(6)	N(2)-Ni(1)-O(2)	157.95(6)
O(8)-Ni(1)-N(1)	90.49(7)	N(2)-Ni(1)-O(1)	96.05(6)	N(1)-Ni(1)-O(2)	94.75(6)
O(7)-Ni(1)-N(1)	172.73(6)	N(1)-Ni(1)-O(1)	92.34(6)	O(1)-Ni(1)-O(2)	62.55(5)
2					
Co(1)-O(1)	0.216 0(2)	Co(1)-O(2)	0.212 99(19)	Co(1)-O(1W)	0.202 9(2)
Co(1)-O(2W)	0.208 13(19)	Co(1)-N(1)	0.215 2(2)	Co(1)-N(2)	0.212 9(2)
O(1W)-Co(1)-O(2W)	85.49(8)	O(2W)-Co(1)-O(2)	95.55(8)	N(2)-Co(1)-N(1)	77.59(9)
O(1W)-Co(1)-N(2)	103.18(10)	N(2)-Co(1)-O(2)	153.52(9)	O(2)-Co(1)-N(1)	93.85(8)
O(2W)-Co(1)-N(2)	94.47(9)	O(1W)-Co(1)-N(1)	91.20(9)	O(1W)-Co(1)-O(1)	162.64(8)
O(1W)-Co(1)-O(2)	101.99(9)	O(2W)-Co(1)-N(1)	170.50(8)	O(2W)-Co(1)-O(1)	92.26(8)
N(2)-Co(1)-O(1)	94.15(9)	O(2)-Co(1)-O(1)	61.03(7)	N(1)-Co(1)-O(1)	93.51(8)

cm⁻¹, showing the presence of bidentate linkage of carboxylates in the dianions. Thus the carboxylates coordinate to the metal as bidentate ligands via the carboxylate groups^[22].

The IR spectrum of complex **2** is similar to complex **1** with the $\Delta\nu$ ($\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}$) of 180 cm⁻¹ showing the presence of bidentate linkages of

carboxylates in the dianions.

2.2 Description of the structure

A single-crystal X-ray diffraction study reveals that complexes **1** and **2** are isostructural. They all crystallize in monoclinic space group *P*2₁/*c* and feature a 2D network structure. Here, we only describe the complex **1**. The coordination environment of Ni(II)

in complex **1** is shown in Fig.1. There are one Ni(II) ion, one eoba ligand, one phen ligand, two coordinated water molecules and 0.58 lattice water molecules in the asymmetric unit. Each Ni(II) ion is six-coordinated by two nitrogen atoms (N(1), N(2)) from one phen molecule, two carboxylate oxygen atoms (O(1), O(2)) from one eoba ligand and two coordinated water molecules, showing a distorted octahedral geometry. The bond distances of Ni-O in complex **1** fall in the range of 0.201 47(16)~0.212 17(14) nm, and those of Ni-N in 0.207 94(16)~0.207 44(17) nm. The coordination angles around the Ni atom vary from 62.55(5)° to 172.73(6)°. In the coordination environment, the two carboxylate oxygen atoms (O(1), O(2)), one nitrogen atom (N(2)) and one coordinated water molecules (O(8)) are located in the basal plane, whereas the other coordinated water molecules (O(7)) and nitrogen atom (N(1)) occupy the axial positions from the opposite directions.

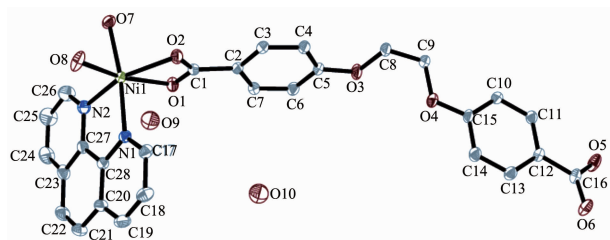
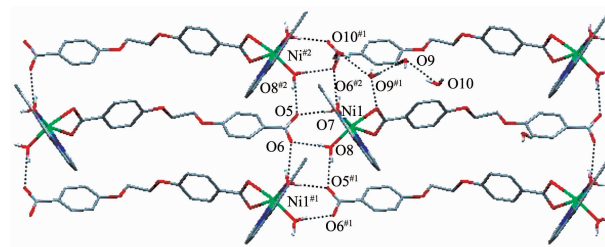


Fig.1 View of the asymmetric unit of **1** with the ellipsoids at the 30% probability level

In **1**, the phen ligand adopts typical chelating-conformation, while each eoba ligand adopts μ_2 coordination mode. Further investigation of the crystal packing of complex **1** suggests that there are persistent O-H...O hydrogen bonding interactions

(Fig.2) between carboxylate oxygen atoms and water molecules of eoba ligands (Table 3) and are usually important in the synthesis of supramolecular architecture^[23]. Moreover, there are π - π interactions in complex **1** between pyridine rings of phen ligands and between benzene rings of eoba ligands (Table 4). Therefore, through hydrogen bonds and π - π interactions, complex **1** is further extended into a two-dimensional supramolecular network framework.



Symmetry codes: #1 $x, -y-1/2, z-1/2$; #2 $x, y+1, z$

Fig.2 View of the hydrogen bonds interactions of complex **1**

To investigate whether the analyzed crystal structure is truly representative of the bulk materials, X-ray powder diffraction (PXRD) technology has been performed for the complex at room temperature (Fig.3).

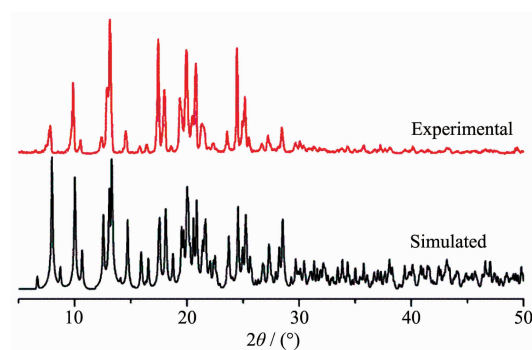


Fig.3 PXRD analysis of complex **1**

Table 3 Hydrogen bonds for complex **1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O(7)-H(7A)...O(6) ^{#1}	0.086 7	0.192 9	0.276 7	162.08
O(7)-H(7B)...O(5) ^{#2}	0.084 0	0.187 3	0.271 2	178.07
O(8)-H(8A)...O(5) ^{#3}	0.092 5	0.180 2	0.271 0	166.58
O(8)-H(8B)...O(6) ^{#2}	0.084 1	0.180 0	0.262 8	167.75
O(9)-H(9C)...O(10) ^{#4}	0.085 0	0.253 0	0.293 2	110.02
O(9)-H(9D)...O(9) ^{#4}	0.085 0	0.194 6	0.259 9	132.83
O(10)-H(10A)...O(6) ^{#5}	0.085 0	0.216 8	0.298 1	159.96
O(10)-H(10B)...O(9) ^{#4}	0.085 0	0.212 3	0.293 2	159.02

Symmetry codes: #1 $x, -y-1/2, z-1/2$; #2 $x, y+1, z$; #3 $x, -y-1/2, z+1/2$; #4 $-x+1, -y, -z$; #5 $-x+1, y+1/2, -z+1/2$

Table 4 Parameters between the planes

Plane	Distance between centroids / nm	Dihedral angle / (°)	Perpendicular distance of plane (<i>I</i>) on ring <i>J</i> / nm	Perpendicular distance of plane (<i>J</i>) on ring <i>I</i> / nm
N(1)C(17)C(18)C(19)C(20)C(28)(I)→ N(1')C(17')C(18')C(19')C(20')C(28')(J) ^{#1}	0.346 72(12)	0	0.327 95(8)	0.327 95(8)
C(10)C(11)C(12)C(13)C(14)C(15)(I)→ C(10')C(11')C(12')C(13')C(14')C(15')(J) ^{#2}	0.387 74(13)	0	0.359 39(9)	0.359 39(9)

Symmetry codes: ^{#1} $-x+1, -y, -z+1$; ^{#2} $-x+2, -y-1, -z+1$

The main peak positions observed are in good agreement with the simulated ones. Although minor differences can be found in the positions, widths, and intensities of some peaks, the bulk synthesized materials and analyzed crystal can still be considered as homogeneous. The differences may be due to the preferred orientation of the powder samples^[24-25].

2.3 Thermal analysis

To study the thermal stability of **1** and **2**, thermogravimetric (TG) analyses were performed on polycrystalline samples under a nitrogen atmosphere from 20 to 1 000 °C at a heating rate of 10 °C·min⁻¹. For compound **1**, the TG curve (Fig.4) reveals that the first weight loss of 10.3% from 21 to 120 °C corresponds to the removal of water molecules (Calcd. 7.9%). Upon further heating, an obvious weight loss (79.6%) occurs in the temperature range of 355~795 °C, corresponding to the release of eoba and phen ligands (Calcd. 82.0%). After 795 °C, no weight loss is observed, which means the complete decomposition of **1**. For compound **2**, the TG curve is similar to **1**. The first weight loss of 11.2% from 21 to 90 °C corresponds to the removal of water molecules (Calcd. 12.2%), and an obvious weight loss (67.6%) occurs in

the temperature range of 350~796 °C corresponds to the release of eoba and phen ligands (Calcd. 69.0%).

3 Theoretical calculation

All calculations in this work were carried out with the Gaussian09 program^[26]. The parameters of the molecular structure for calculation were all from the experimental data of the complex. Natural bond orbital (NBO) analysis was performed by density functional theory (DFT)^[27] with the PBE0^[28] hybrid functional and the LANL2DZ basis set^[29].

The selected natural atomic charges, natural electron configuration, wiberg bond indices and NBO bond orders for the complex are shown in Table 5. It is indicated that the electronic configurations of Ni(II) ion, N and O atoms are $4s^{0.29}3d^{8.32}4p^{0.44}$, $2s^{1.31}2p^{4.20}$ and $2s^{1.60-1.71}2p^{4.99-5.20}$, respectively. Based on the above results, one can conclude that the Ni(II) ion coordination with N and O atoms is mainly on $4s$, $3d$, and $4p$ orbitals. N atoms form coordination bonds with Ni(II) ion using $2s$ and $2p$ orbitals. 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 N atoms of phen ligand, two O atoms of eoba ligand and two coordinated water molecules^[28-29]. Thus, according to valence-bond theory, the atomic net charge distribution and the NBO bond orders of the complex **1** (Table 5) shows the obvious covalent interaction between the coordinated atoms and Ni(II) ion. The differences of the NBO bond orders for Ni-O and Ni-N bonds make their bond lengths be different^[30], which is in good agreement with the X-ray crystal structural data of complex **1**.

As can be seen from the Fig.5, lowest unoccupied molecular orbital (LUMO) is mainly

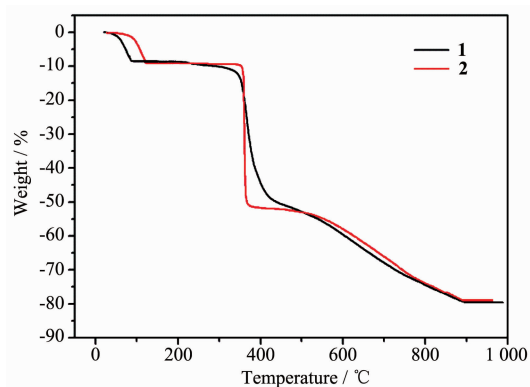
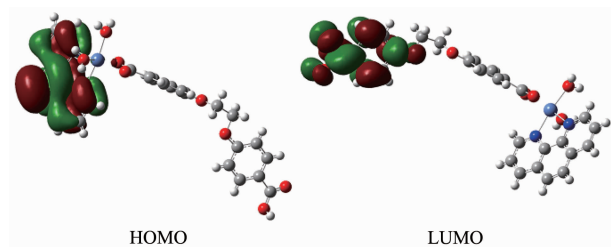


Fig.4 TG curves of complexes **1** and **2**

Table 5 Natural atomic charges, natural valence electron configurations, wiberg bond indexes and NBO bond orders for the complex **1**

Atom	Net charge	Electron configuration	Bond	Wiberg bond index	NBO bond order
Ni(1)	0.937 03	[core]4s ^{0.203} d ^{8.324} p ^{0.44}			
O(1)	-0.708 36	[core]2s ^{1.692} p ^{5.01}	Ni-O(1)	0.250 5	0.271 8
O(2)	-0.700 11	[core]2s ^{1.702} p ^{4.99}	Ni-O(2)	0.267 6	0.287 0
O(7)	-0.889 49	[core]2s ^{1.682} p ^{5.20}	Ni(1)-O(7)	0.216 2	0.279 1
O(8)	-0.816 65	[core]2s ^{1.602} p ^{5.20}	Ni(1)-O(8)	0.232 1	0.289 8
N(1)	-0.525 81	[core]2s ^{1.312} p ^{4.20}	Ni(1)-N(1)	0.281 2	0.357 3
N(2)	-0.521 86	[core]2s ^{1.312} p ^{4.20}	Ni(1)-N(2)	0.277 0	0.357 6

composed of eoba ligand, whereas highest occupied molecular orbital (HOMO) mainly consists of phen ligand. So, the charge transfer from ligand to ligand may be inferred from some contours of molecular orbital of complex **1**.

Fig.5 Frontier molecular orbital of complex **1**

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