芳酰腙配体与 Ni(II)和 Co(II)配合物的水热合成与晶体结构

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摘要: 由苯亚甲基苯乙酮和苯甲酰肼合成一种新型双齿(O、N)酰腙配体(苯亚甲基苯乙酮苯甲酰腙)。由水热法合成了两种配合物[M(babh)$_2$(py)$_2$](M=Ni,**1**;Co,**2**;Hbabh=苯亚甲基苯乙酮苯甲酰腙,py=吡啶),并用元素分析、红外、热重及 X-射线单晶衍射对其进行了表征。晶体结构分析结果表明:两个化合物均属单斜晶系,空间群均是 $P2_1/n$。化合物 **1** 和 **2** 通过分子间弱的 C−H$\cdots\pi$ 堆积形成二维片状超分子层。

关键词: 席夫碱;酰腙配体;水热合成;配合物;晶体结构

Hydrothermal Synthesis and Crystal Structure of Ni(II) and Co(II) Complexes with Hydrazone Ligand

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Abstract: A new bidentate ON hydrazone ligand, has been designed and synthesized by benzylidene acetophenone with benzoyl hydrazine (Hbabh). Two coordination compounds, namely [M(babh)$_2$(py)$_2$] (M=Ni, **1**; Co, **2**; Hbabh=benzylidene acetophenone benzoyl hydrazone, py=pyridine), have been hydrothermally synthesized and characterized by analytical, IR, TG analysis and single-crystal X-ray diffraction measurements. The two compounds crystallize in the Monoclinic space group $P2_1/n$. A view of 2D sheet structure in **1** and **2** are packed alongside with each other through weak C−H$\cdots\pi$ interactions. CCDC: 819582, **1**; 819583, **2**.

Key words: Schiff base; hydrazone ligand; hydrothermal synthesis; complexes; crystal structure

Schiff bases have been of great importance in many of the areas of chemistry. In recent years, transition metal complexes of asymmetrical Schiff base ligands have attracted enormous attentions due to their diversity of molecular structures[1-4] and important properties, such as catalytic, magnetic, fluorescent and electrochemical properties[5-8]. The chemical properties of complexes can be tuned to force metal ions to adopt unusual coordination geometry. The size and preferred coordination geometry of the metal ion control the
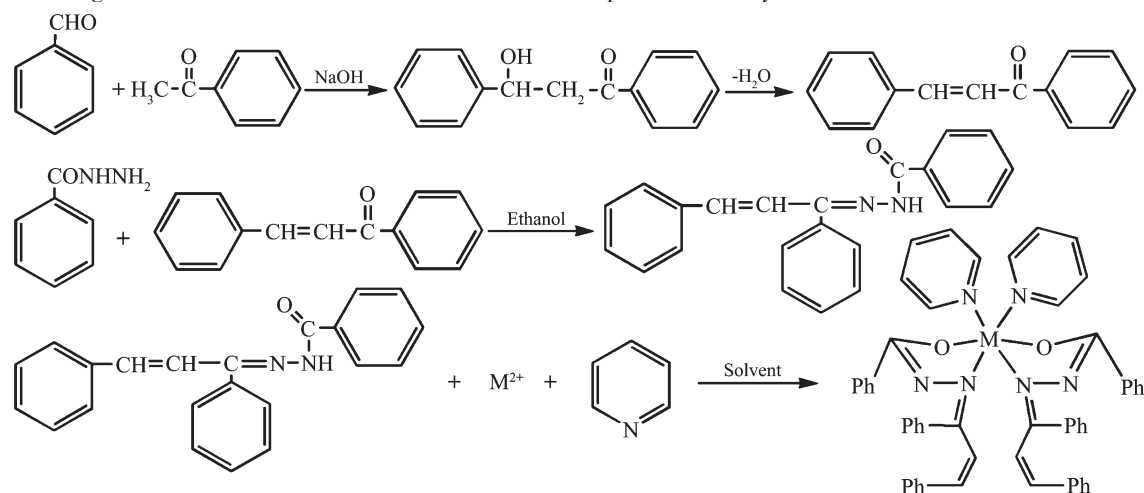
structure of the condensation products[9]. The environment around the metal centre "as coordination geometry, number of coordinated ligands and their donor group" is the key factor for metalloproteins to carry out specific functions[10]. Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility and diverse range of applications[11]. Hydrazone is an important compound of Schiff bases. In terms of chemical field hydrazones have been attracting much attention because of their

biological activities, chemical and industrial versatility, and strong tendency to chelate to transition metals[12-13], lanthanide metals[14] and main group metals[15-16]. In the hydrazone complexes, the hydrazone ligand can be acted as a neutral or mononegative bidentate ligand, or even as a dianionic ligand depending on the donor atoms of the ligands and the reaction conditions.

To the best of our knowledge, the Schiff bases are normally with O, N, O donors set[17]. The present work is a part of our study on the metal complexes of benzylidene acetophenone benzoyl hydrazone. Herein we report the synthesis, structure of two mononuclear compounds [Ni(babh)$_2$(py)$_2$] and [Co(babh)$_2$(py)$_2$]. The procedure of synthesis is shown in Scheme 1.

Scheme 1   Synthetic route of the compound

1   Experimental

1.1   Materials and measurements

All starting materials and solvents used in this work were of analytical grade and used as purchased from Sinopharm Chemical Reagent Co. Ltd without further purification. Elemental analyses (C, H, N) were performed using a Vario EL elemental analyzer. FTIR spectrum was measured as KBr pellets on a Nicolet Nexus FTIR spectrometer in the 4 000~400 cm^{-1} region. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer Pyris-1, Thermogravimetric analyzer operating at a heating rate of 10 K·min^{-1} in a flow of dry oxygen-free nitrogen at 20 mL· min^{-1}. The crystal structures were determined by single-crystal X-ray diffraction. SHELXS97, SHELXL97 software were then used for structure solution and refinement correspondingly.

1.2   Preparation of the ligand (Hbabh)

Acetophenone (6.01 g, 0.05 mol), benzaldehyde (5.31 g, 0.05 mol) and sodium hydroxide (25 mL, concentration: 10%) were mixed in 15 mL ethanol at room temperature and the mixture was refluxed for 8 h stirringly. Then the crystals were precipitated and collected by filtration. Finally the product was recrystallized from ethanol and dried under reduced pressure to give compound of benzylidene acetophenone. Yield: 71%. The schematic diagram showing the synthesis of it is shown in Scheme 1. Anal. Calcd.(%) for C$_{15}$H$_{12}$O: C, 86.50; H, 5.81; N, 0. Found (%): C, 86.41; H, 5.72; N, 0. Selected IR (KBr pellet, cm^{-1}): ν(C=C)ar 1 598, 1 503; ν(C=O) 1 741; ν(C=C) 1 650.

Benzoyl hydrazine (3.13 g, 0.023 mol) was dissolved in anhydrous ethnol (30 mL) at room temperature and heated at 373 K. Benzylidene acetophenone (4.79 g, 0.023 mol) was added into the mixture. Subsequently, the mixture was refluxed for 7~8 h, and then cooled to room temperature. The crystals were precipitated and collected by filtration. The product was recrystallized from ethanol and dried under reduced pressure to give compound benzylidene acetophenone benzoyl hydrazone (Hbabh). Yield: 68%. (synthetic route is described as Scheme 1). Anal. Calcd.(%) for C$_{22}$H$_{18}$N$_2$O: C, 80.98; H, 5.56; N, 8.59. Found(%): C, 80.82; H, 5.51; N, 8.49. Selected IR (KBr pellet, cm^{-1}): ν(C=C) 1 602; ν(C=O) 1 682; ν(C=N) 1 628; ν(C-N) 1 215.

1.3　Preparation of the complex 1 and 2

A mixture of Hbabh (0.032 6 g, 0.10 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.029 1 g, 0.10 mmol), pyridine (0.007 9 g, 0.10 mmol), and H_2O (5.00 mL), several drops of DMF were placed in a Parr Teflon-lined stainless steel vessel (25 mL), and then the vessel was sealed and heated at 413 K for 3 d. After the mixture was slowly cooled to room temperature, several red crystals were obtained. Anal. Calcd. (%) for $C_{54}H_{44}NiN_6O_2$: C, 74.75; H, 5.11; N, 9.69. Found(%): C, 74.69; H, 5.18; N, 9.61. Selected IR (KBr pellet, cm^{-1}): ν(C=C) 1 545; ν(C-N) 1 209; ν(N-H) 3 244; ν(C-O) 1 276.

A mixture of Hbabh (0.032 6 g, 0.10 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.029 1 g, 0.10 mmol), pyridine (0.007 9 g, 0.10 mmol), and H_2O (5.00 mL), several drops of methanol solution were placed in a Parr Teflon-lined stainless steel vessel (25 mL), and then the vessel was sealed and heated at 413 K for 3 d. After the mixture was slowly cooled to room temperature, several red crystals were obtained. Anal. Calcd. (%) for $C_{54}H_{44}Co N_6O_2$: C, 74.73; H, 5.11; N, 9.69. Found (%): C, 74.78; H, 5.16; N, 9.65. Selected IR (KBr pellet, cm^{-1}): ν(C=C) 1 548; ν(C-N) 1 206; ν(N-H) 3 248; ν(C-O) 1 275.

1.4　X-ray crystal structure determinations

Diffraction intensities for the two complexes were collected on a Bruker SMART 1000 CCD area-detector with Mo $K\alpha$ radiation (λ =0.071 073 nm) using an ω scan mode at 298±2 K (compound **1** and **2**). Diffraction intensity data were collected in the θ range of 1.68°~25.05° for compound **1** and **2**. The collected data were reduced using the SAINT program[18], and empirical absorption corrections were performed using the SADABS program[19]. Two structures were solved by direct methods and refined using full-matrix least square techniques on F^2 with the program SHELX-97[20]. Crystallographic data are given in Table 1. Selected bond distances and angles are given in Table 2.

CCDC: 819582, **1**; 819583, **2**.

Table 1　Crystal data and structure refinement for complexes 1~2

Complexes	**1**	**2**
Empirical formula	$C_{54}H_{44}NiN_6O_2$	$C_{54}H_{44}CoN_6O_2$
Formula weight	867.66	867.88
Temperature / K	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / nm	1.352 5(6)	1.356 11(18)
b / nm	2.415 3(9)	2.389 3(3)
c / nm	1.409 7(6)	1.409 01(19)
β / (°)	96.121(7)	95.818(3)
V / nm^3	4.579(3)	4.542(10)
Z	4	4
D_c / (g·cm^{-3})	1.259	1.269
$F(000)$	1 816	1 812
θ rang for data collection / (°)	1.68~25.05	1.68~25.05
Absorption coefficient / mm^{-1}	0.472	0.426
Reflections collected / unique (R_{int})	18 939 / 8 083 (0.091 8)	23 454 / 8 035 (0.049 4)
Final R indices ($I>2\sigma(I)$)	0.073 8, 0.176 4	0.055 2, 0.133 9
R indices (all data)	0.154 6, 0.241 6	0.091 1, 0.157 1
Largest diff. peak and hole / nm^{-3}	620, −807	833, −463

Table 2　Selected bond distances (nm) and bond angles (°) for complexes

|			**1**		
Ni(1)-O(2)	0.202 9(3)	Ni(1)-O(1)	0.205 6(4)	Ni(1)-N(4)	0.210 0(5)
Ni(1)-N(5)	0.210 5(5)	Ni(1)-N(2)	0.212 1(5)	Ni(1)-N(6)	0.213 2(5)

Continued Table 2

O(2)-Ni(1)-O(1)	174.68(15)	O(2)-Ni(1)-N(5)	88.67(17)	O(2)-Ni(1)-N(2)	105.72(16)
O(2)-Ni(1)-N(4)	77.36(16)	O(1)-Ni(1)-N(5)	86.45(17)	O(1)-Ni(1)-N(2)	76.35(16)
O(1)-Ni(1)-N(4)	107.53(16)	N(4)-Ni(1)-N(5)	166.02(18)	N(4)-Ni(1)-N(2)	93.93(17)
N(5)-Ni(1)-N(2)	89.27(18)	O(2)-Ni(1)-N(6)	86.91(17)	O(1)-Ni(1)-N(6)	91.26(17)
N(4)-Ni(1)-N(6)	86.64(18)	N(5)-Ni(1)-N(6)	93.25(19)	N(2)-Ni(1)-N(6)	167.19(18)
2					
Co(1)-O(2)	0.204 0(2)	Co(1)-O(1)	0.204 9(2)	Co(1)-N(5)	0.214 9(3)
Co(1)-N(3)	0.215 3(3)	Co(1)-N(1)	0.217 8(3)	Co(1)-N(6)	0.219 3(3)
O(2)-Co(1)-O(1)	175.09(10)	N(5)-Co(1)-N(3)	163.11(12)	O(2)-Co(1)-N(6)	87.05(11)
O(2)-Co(1)-N(5)	87.50(11)	O(2)-Co(1)-N(1)	106.44(10)	O(1)-Co(1)-N(6)	91.92(11)
O(1)-Co(1)-N(5)	87.83(11)	O(1)-Co(1)-N(1)	74.96(10)	N(5)-Co(1)-N(6)	95.73(12)
O(2)-Co(1)-N(3)	75.77(10)	N(5)-Co(1)-N(1)	88.81(11)	N(3)-Co(1)-N(6)	85.83(11)
O(1)-Co(1)-N(3)	108.95(10)	N(3)-Co(1)-N(1)	93.68(11)	N(1)-Co(1)-N(6)	165.98(12)

2　Results and discussion

2.1　Structure descriptions of the compound 1

As shown in Fig.1, there is one independent molecule in the asymmetric unit. Compound **1** is mononuclear six-coordinated nickel. The coordination environment of Ni is comprised of two pyridine ligands and two hydrazone ligands (two O atoms, four N atoms). The nickel(Ⅱ) center in **1** adopts a similar to distorted octahedron configuration. N2, N4, N6 and N5 constitute a pyramid´s bottom. O1 and O2 occupy the top position, which complete the coordination environment of Ni center. The bond lengths of Ni(1)-N(4), Ni(1)-N(5), Ni(1)-N(2) and Ni(1)-N(6) are 0.210 0(5), 0.210 5(5), 0.212 1(5) and 0.213 2(5) nm, respectively, these data indicate the bonds are very close to the complex with identical coordination[21]. The Ni(1)-O(1), Ni(1)-O(2) bond distances are 0.205 6(4) nm, and 0.202 9(3) nm, respectively, which are shorter than reported[22]. C(7)-N(1) (0.134 5(7) nm) and C(14)-N(2) (0.133 1(7) nm) are longer than the C=N double bond (0.130 nm), but shorter than the C-N single bond (0.144 3 nm). Different angles around the nickel atom and their sum of 360.01° indicate a nearly coplanar geometry of the metal environment. The O(1)-Ni(1)-O(2) angle is 174.68°, which indicates that O(2) and O(2) are closely located at the vertical line of the plane. The bonds of C(7)-O(1) (0.126 9(6) nm), C(29)-O(2) (0.128 5(6) nm), C(7)-N(1) (0.134 5(7) nm), C(29)-N(3) (0.132 3(6) nm) are com-

pared with C-O (0.143 nm), C=O (0.120 nm), C-N (0.147 nm), C=N (0.127 nm) suggesting an keto coordination model for ligands. Bond lengths of C(6)-C(7) (0.151 1(8) nm) and C(14)-C(15) (0.144 6(7) nm) confirm the sp^2 hybridization of carbon atom[23]. The mononuclear units in **1** are packed alongside with each other through weak C−H⋯π interactions. Along with this shortest interaction (the distance H48...centroid of ring C30-C35 is 0.270 4 nm, angle between C(48)−H(48)⋯Cg9 is 115.170° and the distance C(48)⋯Cg9 is 0.558 3 nm) propagating crystallographic a axis with the formation of a 2D sheet structure (Fig.2). The distance of C−H⋯π contact is typical for this type of interac-

H atoms are omitted for clarity
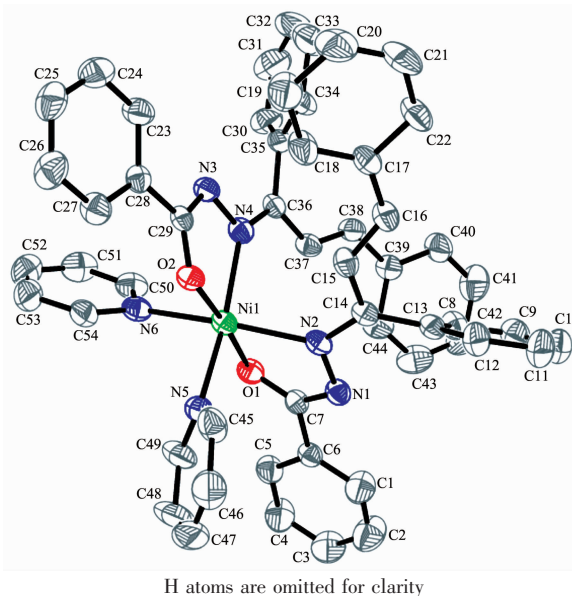
Fig.1　Molecular structure of the title compound **1**

tions. For **1**, Cg9 phenyl ring C30-C35 at $-0.5+x$, $0.5-y$, $-0.5+z$.
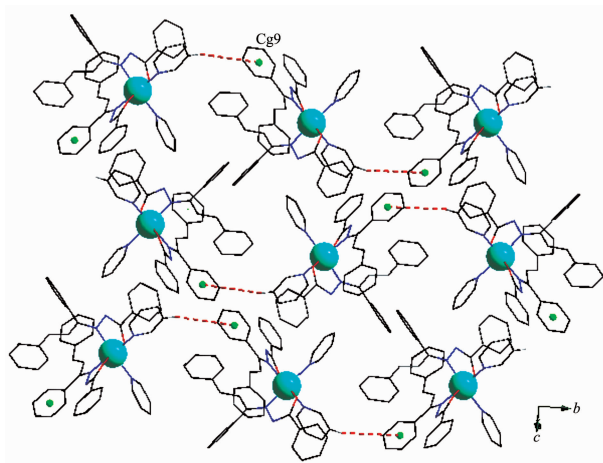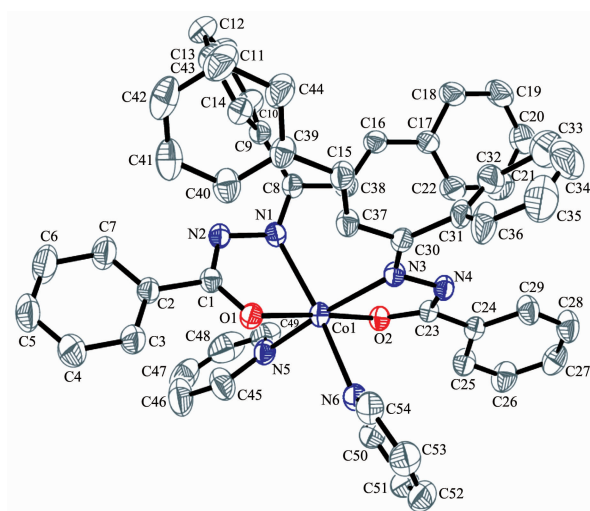

Symmetry code: Cg9: $-0.5+x$, $0.5-y$, $-0.5+z$

Fig.2   A view of 2D sheet structure in **1** formed through
C−H⋯π interactions

### 2.2   Structure descriptions of the compound 2

As shown in Fig.3, there is one independent molecule in the asymmetric unit. Compound **2** is mononuclear six-coordinated cobalt. The coordination environment of Co is comprised of two pyridine ligands and two hydrazone ligands (two O atoms, four N atoms). The cobalt(Ⅱ) center in **2** adopts a structure which is similar to octahedral. O1, N3, O2 and N5 constitute the pyramid′s bottom. N1 and N6 occupy the top position, which complete the coordination environment of Co center. The bond lengths of Co(1)-N(1), Co(1)-N(3), Co(1)-N(5) and Co(1)-N(6) are 0.217 8(3), 0.215 3(3),

0.214 9(3) and 0.219 3(3) nm. These are very close to the complex with identical coordination that has been reported in previous work[24]. The Co(1)-O(1) and Co(1)-O(2) bond distances are 0.204 9(2) and 0.204 0(2) nm, respectively. However, these bonds are longer than reported[24]. C(8)-N(1) (0.130 8(4) nm), C(1)-N(2) (0.131 4(4) nm) and C(45)-N(5) (0.132 0(5) nm) are longer than the C=N double bond (0.130 nm) but shorter than the C-N single bond (0.144 3 nm). Different angles around the nickel atom and their sum of 360.05° indicate a nearly coplanar geometry of the metal environment. The N(2)-Co(1)-N(6) angle is 165.98°, which indicates that N(1) and N(6) are closely located at the vertical line of the plane. The bonds of C(1)-O(1) (0.128 6(4) nm), C(23)-O(2) (0.128 0(4) nm), C(1)-N(2) (0.131 4(47) nm), C(23)-N(4) (0.131 5(4) nm) are compared with C-O (0.143 nm), C=O (0.120 nm), C-N (0.147 nm), C=N (0.127 nm) suggesting an keto coordination model for ligands. Bond lengths of C(1)-C(2) (0.148 9(5) nm) and C(8)-C(15) (0.145 2(5) nm) confirm the sp^2 hybridization of carbon atom[23]. The mononuclear units in **2** are packed alongside with each other through weak C−H⋯π interactions. Along with this shortest interaction (the distance H18...centroid of ring C50-N6 is 0.285 4 nm, angle between C(18)−H(18)...Cg4 is 138.628° and the distance C(18)⋯Cg4 is 0.373 3 nm) propagating crystallographic a-axis, another relatively weak C−H⋯π interaction (the distance

H atoms are omitted for clarity

Fig.3   Molecular structure of the title compound **2**
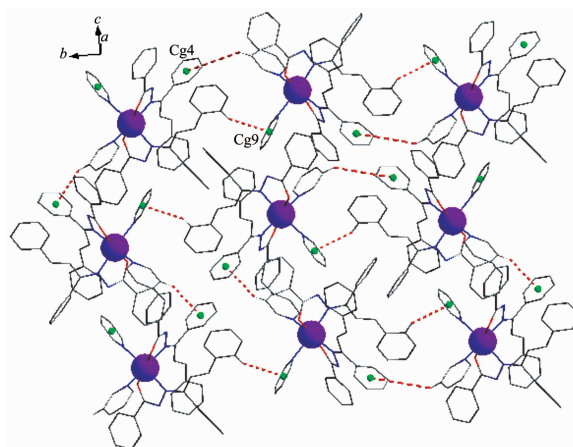
Symmetry code: Cg4: $1.5-x$, $-0.5+y$, $0.5-z$; Cg9: $1.5-x$, $0.5+y$, $0.5-z$

Fig.4   A view of 2D sheet structure in **2** formed through
C−H⋯π interactions

H46⋯centroid of ring C31-C36 is 0.264 6 nm, angle between C(46)−H(46)⋯Cg9 is 113.902° and the distance C(46)⋯Cg9 is 0.541 7 nm) runs in the direction of *a*-axis with the formation of a two-dimensional network (Fig.4). The distance of C−H⋯π contact is typical for this type of interactions. For **2**, Cg4 pyridine ring C50-N6 at 1.5−*x*, −0.5+*y*, 0.5−*z*; Cg9 phenyl ring C31-C36 at 1.5−*x*, 0.5+*y*, 0.5−*z*.

2.3　Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out to examine the thermal stability of the two compounds. The crushed single-crystal sample was heated up to 1 000 ℃ in N$_2$ at a heating rate of 10 ℃·min^{-1}.

The TG curves for **1** show that it is stable up to 232.3 ℃ without any weight loss, which means the compound could retain structural integrity to 232.3 ℃. From 232.3 to 477.8 ℃, the total loss of 72.7% is consistent with the pyrolysis of coordinated benzoyl hydrazine fragments and benzene-methyl phenylethyl fragments. From 476.9 to 827.2 ℃, the total loss of 17.0% is consistent with the pyrolysis of pyridyl fragments and the final residue was probably NiO (remaining weight: found: 8.7%, calcd. 10.3%).

The TG curves for **2** show that it is stable up to 221.3 ℃ without any weight loss, which means the compound could retain structural integrity to 221.3 ℃. From 221.3 to 843.7 ℃, the total loss of 89.5% is consistent with the pyrolysis of benzyl fragments, benzene-methyl phenylethyl fragments and pyridyl fragments. The final residue was probably CoO (remaining weight: found: 9.8%, calcd. 10.5%).

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