

基于 Schiff Base 配体及吡啶环的铜(II)、镍(II) 配合物构筑、表征与热稳定性

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摘要: 用缓慢挥发法和水热法分别合成了镍配合物 NiLPy(L=5-溴-2-羟基苯基苯基酮-4-甲氧基苯甲酰肼, Py=吡啶)(**1**)及铜配合物 Cu(babh)₂(Py)(Hbabh=查尔酮苯甲酰肼, Py=吡啶)(**2**), 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。晶体结构表明:**1** 属三斜晶系, $P\bar{1}$ 空间群;**2** 属单斜晶系, Pc 空间群。化合物 **1** 和 **2** 分别通过分子间弱的 C-H $\cdots\pi$ 与 C-H \cdots N 作用堆积形成二维片状超分子层。热重分析表明配合物 **1** 和 **2** 分别处于 225 和 170 °C 以下温度时很稳定。

关键词: 席夫碱; 镍配合物; 铜配合物; 晶体结构; 热失重分析

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Construction, Characterization and Thermostability of Copper(II), Nickel(II) Complexes Based on Schiff Base Ligands and Pyridine Ring

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Abstract: The title complexes, NiLPy (L=5-bromo-2-hydroxyphenyl benzophenone 4-methoxy benzoylhydrazone, Py=pyridine) (**1**) and Cu(babh)₂(Py)(Hbabh=benzylidene acetophenone benzoyl hydrazone, Py=pyridine) (**2**), were respectively synthesized by slow evaporation and hydrothermal synthesis, which were characterized by elemental analysis, IR, TG analysis and single-crystal X-ray diffraction measurements. **1** crystallizes in the triclinic space group $P\bar{1}$. **2** crystallize in the monoclinic space group Pc . A view of 2D sheet structure in **1** and **2** are respectively packed alongside with each other through weak C-H $\cdots\pi$ and C-H \cdots N interactions. The TG analysis shows that the complexes **1** and **2** are stable below 225 and 170 °C, respectively. CCDC: 841410, **1**; 819584, **2**.

Key words: Schiff base; nickel complex; copper complex; crystal structure; thermo-gravimetric analysis

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff^[1] in 1864. Schiff base is a compound with a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl

or alkyl group, not hydrogen. Schiff bases in a broad sense have the general formula R¹R²C=NR³, where R are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. Schiff bases have been of great importance in many of the areas of chemistry. Transition

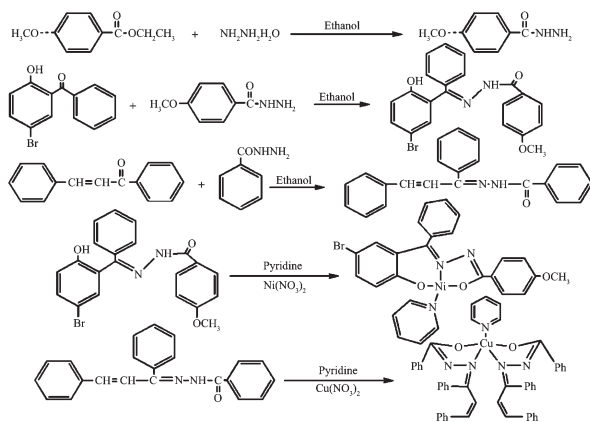
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metal complexes of asymmetrical Schiff base ligands have attracted enormous attentions due to their diversity of molecular structures^[2-4] and important properties, such as magnetic, fluorescent^[5-6], catalytic^[7] and biological activity^[8-10]. The preparation of a new ligand was perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Since the electron donor and electron acceptor properties of the ligands, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies^[11-12]. Acyl hydrazone is a kind of important schiff base. Hydrazones were important class of ligands, such ligands have interesting ligation properties due to presence of several coordination sites^[13]. Hydrazone ligands create an environment similar to biological systems by usually making coordination through oxygen and nitrogen atoms.

To the best of our knowledge, the chemical properties of complexes can be tuned to force metal ions to adopt unusual coordination geometry. The present work is a part of our study on the metal complexes of benzoyl hydrazone. Herein we report the synthesis, structure and thermostability of the compounds, NiLPy and Cu(babh)₂(Py). The procedure of synthesis is shown in Scheme 1.



Scheme 1 Synthetic route of the compounds

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. FT-IR spectrum was measured as KBr pellets on a Nicolet Nexus FT-IR 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 °C·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.

1.2 Preparation of the ligands

Ethyl benzoate (3.00 g, 0.02 mol) was dissolved in anhydrous ethanol (15 mL) at room temperature and heated at 363 K. Hydrazine hydrate (1.50 g, 0.024 mol) was added into the mixture. After being refluxing for 10 h, the mixture was cooled to room temperature. 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 benzoyl hydrazone. Yield: 80.06%. The schematic diagram showing the synthesis of it is shown in Scheme 1. Anal. Calcd.(%) for C₇H₈N₂O: C, 61.72; H, 5.88; N, 20.54. Found (%): C, 61.75; H, 5.92; N, 20.58. Selected IR (KBr pellet, cm⁻¹): ν(C=C) 1 596, 1 525; ν(C-N) 1 204; ν(C=O) 1 722; ν(N-H) 3 248.

Ethyl anisate (3.58 g, 0.02 mol) was dissolved in anhydrous ethanol (15 mL) at room temperature and heated at 363 K, followed by the addition of hydrazine hydrate (1.50 g, 0.024 mol). Subsequently, the mixture was refluxed for 10 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 of 4-methoxybenzhydrazide. Yield: 79.24%. (synthetic route is described as Scheme 1). Anal. Calcd. (%) for C₈H₁₀N₂O₂: C, 57.94; H, 6.12; N, 16.91. Found (%): C, 57.82; H, 6.07; N, 16.86. Selected IR (KBr pellet, cm⁻¹): ν(C=C) 1 589, 1 518; ν(C-N) 1 203; ν(C=O) 1 682; ν(N-H) 3 253.

4-Methoxybenzhydrazide (3.32 g, 0.02 mol) was dissolved in anhydrous ethanol (20 mL) at room temperature and heated at 363 K, followed by the addition of 5-bromo-2-hydroxyphenyl benzophenone (5.54 g, 0.02 mol). Subsequently, the mixture was refluxed for 6 h, and then cooled to room temperature.

The crystals were precipitated and collected by filtration. The product was recrystallized from ethanol-water and dried under reduced pressure to give compound 5-bromo-2-hydroxyphenyl benzophenone-4-methoxy benzoyl hydrazone. Yield: 71.08%. (synthetic route is described as Scheme 1). Anal. Calcd. (%) for $C_{21}H_{17}N_2O_3Br$: C, 60.86; H, 4.01; N, 6.54. Found (%): C, 59.31; H, 4.03; N, 6.59. Selected IR (KBr pellet, cm^{-1}): ν (C=C) 2 972; ν (C=O) 1 649; ν (C=N) 1 597; ν (C-N) 1 209.

Benzoyl hydrazine (2.72 g, 0.02 mol) was dissolved in anhydrous ethanol (20 mL) at room temperature and heated at 363 K. Benzylidene acetophenone (4.17 g, 0.02 mol) was added into the mixture. Subsequently, the mixture was refluxed for 6 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. Yield: 69.97%. (synthetic route is described as Scheme 1). Anal. Calcd. (%) for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.54; N, 8.51. Found (%): C, 80.95; H, 5.56; N, 8.59. Selected IR (KBr pellet, cm^{-1}): ν (C=C) 1 601; ν (C=O) 1 709; ν (C=N) 1 624; ν (C-N) 1 212.

1.3 Preparation of the complex 1 and 2

A methanol solution (10 mL) of 5-bromo-2-hydroxyphenyl benzophenone-4-methoxy benzoyl hydrazone (0.1 mmol, 0.038 9 g) was mixed with acetone solution (5 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 0.029 1 g). The mixture was stirred at 298 K for 2 h. and then filtered. A red precipitate was produced after about 30 days. A pyridine amount (5 mL) was used to dissolve the precipitate at 330 K. Red block-shaped crystals were obtained after one month. Anal. Calcd. (%) for $C_{26}H_{20}BrN_3NiO_3$: C, 55.72; H, 3.48; N, 7.46. Found: C, 55.65; H,

3.59; N, 7.49. Selected IR (KBr pellet, cm^{-1}): ν (C=C) 1 564; ν (C-N) 1 255; ν (N-H) 3 419; ν (C-O) 1 266.

A mixture of benzylidene acetophenone benzoyl hydrazone (0.032 6 g, 0.1 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.024 2 g, 0.1 mmol), pyridine (0.007 9 g, 0.1 mmol), and H_2O (5 mL), several drop of acetone solution was 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 blue crystals were obtained. Anal. Calcd. (%) for $C_{49}H_{39}CuN_5O_2$: C, 73.98; H, 4.98; N, 8.79. Found (%): C, 74.17; H, 4.95; N, 8.83. Selected IR (KBr pellet, cm^{-1}): ν (C=C) 1 556; ν (C-N) 1 210; ν (N-H) 3 239; ν (C-O) 1 278.

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 ($\lambda = 0.071\ 073$ nm) using an ω scan mode at (298 ± 2) K (compound **1** and **2**). Diffraction intensity data were collected in the θ range of $1.68^\circ \sim 25.05^\circ$ for compound **1** and **2**. The collected data were reduced using the SAINT program^[14], and empirical absorption corrections were performed using the SADABS program^[15]. Two structures were solved by direct methods and refined using full-matrix least square techniques on F^2 with the program SHELX-97^[16]. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. Some of hydrogen atoms were placed in their geometrically generated positions and other hydrogen atoms were located from the different Fourier map and refined isotropically. Crystallographic data are given in Table 1. Selected bond distances and angles are given in Table 2.

CCDC: 841410, **1**; 819584, **2**.

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

| Complex | 1 | 2 |
|-------------------|--------------------------|------------------------|
| Empirical formula | $C_{26}H_{20}BrN_3NiO_3$ | $C_{49}H_{39}CuN_5O_2$ |
| Formula weight | 561.07 | 793.39 |
| Temperature / K | 298(2) | 293(2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | Pc |
| a / nm | 0.789 1(18) | 0.855 2(2) |
| b / nm | 1.042 9(2) | 1.481 8(3) |
| c / nm | 1.457 6(3) | 1.741 7(4) |

Continued Table 1

| | | |
|---|-------------------------|--------------------------|
| $\beta / (^{\circ})$ | 103.890(4) | 115.733(9) |
| V / nm^3 | 1.131 3(4) | 1.988 3(8) |
| Z | 2 | 2 |
| $D_c / (\text{Mg} \cdot \text{m}^{-3})$ | 1.647 | 1.325 |
| $F(000)$ | 568 | 826 |
| θ rang for data collection / $(^{\circ})$ | 2.01~25.05 | 2.60~25.04 |
| Absorption coefficient / mm^{-1} | 2.659 | 0.597 |
| Reflections collected / unique (R_{int}) | 5 722 / 3 863 (0.027 8) | 10 110 / 4 500 (0.039 9) |
| Final R indices ($I > 2\sigma(I)$) | 0.045 9, 0.119 1 | 0.040 9, 0.104 1 |
| R indices (all data) | 0.057 1, 0.127 1 | 0.044 0, 0.106 4 |
| Largest diff. peak and hole / $(\text{e} \cdot \text{nm}^{-3})$ | 1 562 and -875 | 1 146 and -378 |

Table 2 Selected bond distances (nm) and bond angles ($^{\circ}$) for complex 1 and 2

| Complex 1 | | | | | |
|-----------------|------------|-----------------|------------|-----------------|------------|
| Ni(1)-O(1) | 0.180 5(3) | Ni(1)-N(1) | 0.183 2(3) | Ni(1)-N(2) | 0.191 4(3) |
| Ni(1)-O(2) | 0.183 4(2) | | | | |
| O(1)-Ni(1)-N(1) | 96.90(12) | N(1)-Ni(1)-N(2) | 174.67(13) | O(1)-Ni(1)-N(2) | 87.81(12) |
| N(1)-Ni(1)-O(2) | 84.38(11) | O(1)-Ni(1)-O(2) | 178.60(11) | O(2)-Ni(1)-N(2) | 90.93(11) |
| Complex 2 | | | | | |
| Cu(1)-O(1) | 0.192 2(3) | Cu(1)-N(5) | 0.230 2(4) | Cu(1)-N(4) | 0.208 7(3) |
| Cu(1)-N(2) | 0.207 9(3) | Cu(1)-O(2) | 0.192 4(3) | O(1)-C(7) | 0.128 5(5) |
| O(1)-Cu(1)-O(2) | 168.53(17) | N(2)-Cu(1)-N(5) | 96.38(14) | O(2)-Cu(1)-N(5) | 94.38(14) |
| O(2)-Cu(1)-N(2) | 99.26(15) | O(1)-Cu(1)-N(2) | 79.76(12) | N(4)-Cu(1)-N(5) | 97.57(14) |
| O(2)-Cu(1)-N(4) | 79.78(12) | O(1)-Cu(1)-N(4) | 98.39(15) | | |
| O(1)-Cu(1)-N(5) | 97.09(14) | N(2)-Cu(1)-N(4) | 166.05(16) | | |

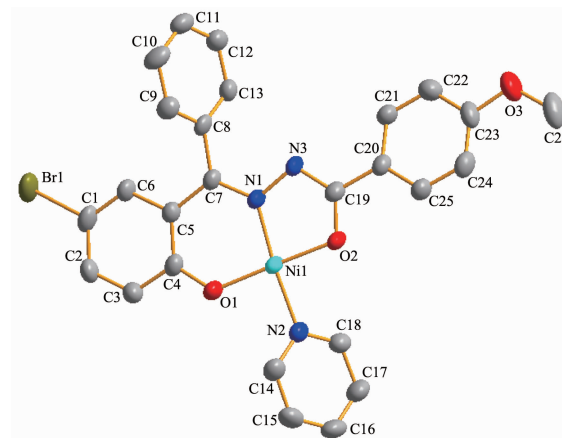
2 Results and discussion

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 four-coordinated nickel. The coordination environment of Ni is comprised of pyridine ligand and hydrazone ligand (two O atoms, N atom). The central Ni(II) atom in the title complex **1**, is in a square-planar trans- N_2O_2 environment defined by the NO_2 donor atoms of the tridentate hydrazone ligand and the monodentate pyridine ligand. The pyridine molecule forms a dihedral angle of $46.14(11)^{\circ}$ with the least squares plane through the NiN_2O_2 atoms.

The bond lengths of Ni(1)-N(1) and Ni(1)-N(2) are 0.183 2(3) nm and 0.191 4(3) nm, respectively, these data indicate the bonds are very close to the complex with identical coordination^[17-18]. The Ni(1)-O(1), Ni(1)-

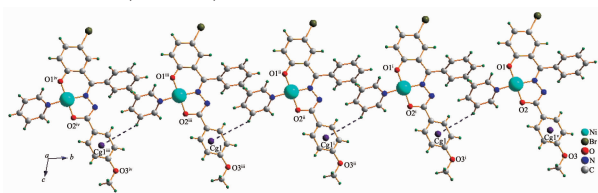
O(2) bond distances are 0.1805(3) nm and 0.183 4(2) nm, respectively, which are shorter than reported^[19]. C(7)-N(1) (0.132 6(5) nm) and C(19)-N(3) (0.130 6(5) nm)



H atoms are omitted for clarity

Fig.1 Molecular structure of compound **1** showing 40% probability displacement ellipsoids

are longer than the C=N double bond (0.130 nm), but shorter than the C-N single bond (0.144 3 nm). This is mainly affected by chelating with nickel ion. Different angles around the nickel atom and their sum of 360.02° indicate a nearly coplanar geometry of the metal environment. The bonds of [C(4)-O(1) (0.131 0(5)) nm], C(19)-O(2) (0.131 1(4) nm), C(7)-N(1) (0.132 6(5) nm), C(19)-N(3) (0.130 6(5) 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 enol coordination model for ligands. Bond lengths of C(5)-C(7) (0.145 1(5) nm) and C(19)-C(20) (0.146 8(5) nm) confirm the sp^2 hybridization of carbon atom^[20]. The mononuclear units in **1** are packed alongside with each other through weak C-H $\cdots\pi$ interactions. Along with this shortest interaction (distance H17 \cdots centroid of ring C20-C25: 0.179 2 nm; angle between C(17)-H(17) \cdots Cg1: 130.348° ; distance C(17) \cdots Cg1: 0.450 7 nm) propagating crystallographic a-axis with the formation of a 1D sheet structure (Fig.2). The distance of C-H $\cdots\pi$ contact is typical for this type of interactions (Table 3).



Symmetry code: ⁱ $x, -1+y, z$; ⁱⁱ $x, -2+y, z$; ⁱⁱⁱ $x, -3+y, z$; ^{iv} $x, -4+y, z$; ^v $x, 1+y, z$

Fig.2 A view of 1D sheet structure in **1** formed through C-H $\cdots\pi$ interactions

Table 3 C-H $\cdots\pi$ interactions existing in compound **1**

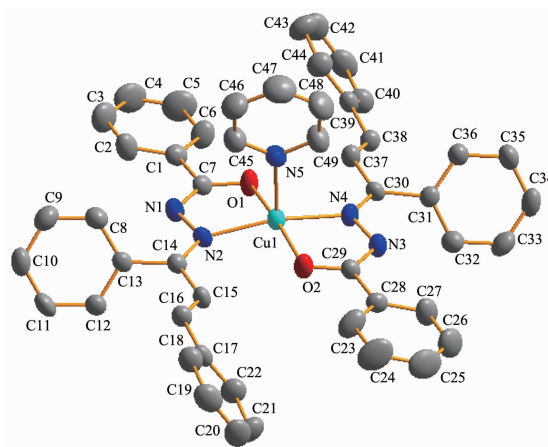
| | Central separation / nm | Angle / ($^\circ$) ^a |
|-------------------------------|-------------------------|-----------------------------------|
| C-H \cdots Cg1 | 0.405 5(6) | 127.816 |
| C-H \cdots Cg1 ⁱ | 0.384 9(6) ^b | 130.348 |

Symmetry code: ⁱ $x, -1+y, z$; ^a angle of C-H \cdots ring centroid in C-H $\cdots\pi$ interactions; ^b Separation of an H atom and π ring centroid.

2.2 Structure descriptions of the compound **2**

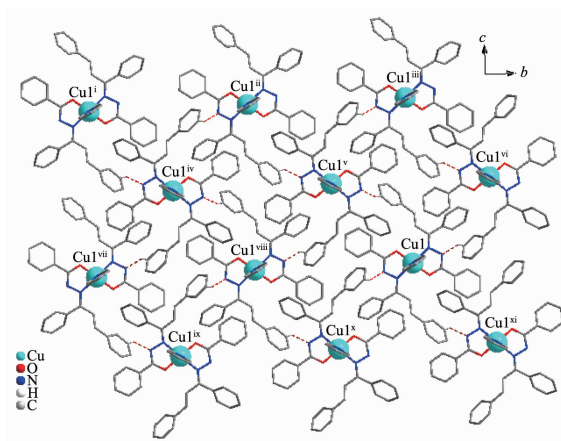
Compound **2** is mononuclear five-coordinated copper complex. The molecular structure is given in Fig. 3. The coordination environment of Cu is comprised of one pyridine ligand and two hydrazone ligands (two O atoms, two N atoms). The copper(II) center in **2** adopts a structure which is similar to pyramid configuration. O1, N2, O2 and N4 constitute a pyramid's bottom. N5

occupies the top position, which completes the coordination environment of Cu center. The bond lengths of Cu(1)-N(2), Cu(1)-N(4) and Cu(1)-N(5) are 0.207 9(3) nm, 0.208 7 (3) nm and 0.230 2 (4) nm. The bonds are very close to the complex with identical coordination^[21-22]. The Cu(1)-O(1), Cu(1)-O(2) bond distances are 0.192 2(3) nm, and 0.192 4(3) nm, respectively, which are shorter than reported^[23]. C(14)-N(2) (0.131 2(5) nm) and C(29)-N(3) (0.130 4 (6) nm) are longer than the C=N double bond (0.130 nm) and shorter than the C-N single bond (0.1443 nm). This is mainly affected by chelating with copper ion. Due to the existence of π - π stacking interactions, the bond angles of C(14)-N(2)-N(1), N(2)-



H atoms are omitted for clarity

Fig.3 Molecular structure of compound **2** showing 25% probability displacement ellipsoids



Symmetry code: ⁱ $x, -2+y, 1+z$; ⁱⁱ $x, -1+y, 1+z$; ⁱⁱⁱ $x, y, 1+z$; ^{iv} $0.5+x, -y, 0.5+z$; ^v $0.5+x, 1-y, 0.5+z$; ^{vi} $0.5+x, 2-y, 0.5+z$; ^{vii} $x, -2+y, z$; ^{viii} $x, -1+y, z$; ^{ix} $0.5+x, -y, -0.5+z$; ^x $0.5+x, 1-y, -0.5+z$; ^{xi} $0.5+x, 2-y, -0.5+z$

Fig.4 A view of 2D sheet structure in compound **2** formed through C-H \cdots N interactions

Table 4 Selected hydrogen bonds for compound **2**

| D-H...A | <i>d</i> (D-H) / nm | <i>d</i> (H...A) / nm | <i>d</i> (D...A) / nm | ∠DHA / (°) |
|-----------------------------|---------------------|-----------------------|-----------------------|------------|
| C19-H19...N3 ⁱ | 0.093 0 | 0.266 6 | 0.130 5 | 154.629 |
| C19-H19...N3 ⁱⁱ | 0.093 0 | 0.675 9 | 0.620 2 | 50.020 |
| C43-H43...N3 ⁱⁱ | 0.093 0 | 0.261 1 | 0.349 8 | 159.623 |
| C43-H43...N1 ⁱⁱⁱ | 0.093 0 | 0.659 2 | 0.601 4 | 48.308 |

Symmetry code: ⁱ *x*, -2+*y*, 1+*z*; ⁱⁱ 0.5+*x*, -*y*, 0.5+*z*; ⁱⁱⁱ *x*, -1+*y*, *z*.

C(14)-C(13), C(1)-C(7)-O(1) and C(1)-C(7)-N(1) are close to 120°. Bond lengths of C(1)-C(7) (0.150 4(5) nm) and C(14)-C(15) (0.145 6(5) nm) confirm the *sp*² hybridization of carbon atom^[20]. The mononuclear units in **2** are packed alongside with each other through weak C-H...N interactions (Fig.4, Table 4).

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 °C in N₂ at a heating rate of 10 °C·min⁻¹. The typical TG curves of the two compounds are shown in Fig.5.

The TG curve for **1** shows that it is stable up to 225 °C without any weight loss, which means the compound could retain structural integrity to 225 °C. From 225.31 to 241.48 °C, the total loss of 13.76% is consistent with the phenyl fragment. From 386.15 to 417.28 °C, the total loss of 30.83% is consistent with the pyrolysis of 4-methoxy benzene formyl fragment and the final residue was probably NiO (remaining weight: Found: 14.42%, Calcd. 13.31%).

The TG curve for **2** shows that it is stable up to 170 °C without any weight loss, which means the compound could retain structural integrity to 170 °C. From 170.3 to 720.1 °C, the total loss of 71.9% is

consistent with the pyrolysis of benzyl fragments and benzene-methyl phenylethyl fragments. The final residue was probably CuO (remaining weight: Found: 11.6%, Calcd. 10.0%).

3 Conclusions

In summary, two new mononuclear complexes, NiLPy (**1**) and Cu(babh)₂(Py) (**2**), have been synthesized and characterized by elemental analysis, IR, TG analysis and X-ray crystal structure analysis. Complex **1** is in a square-planar trans-N₂O₂ environment defined by the NO₂ donor atoms of the tridentate hydrazone ligand and the monodentate pyridine ligand. The copper (II) center in Complex **2** adopts a structure which is similar to pyramid configuration. O1, N2, O2 and N4 constitute a pyramid's bottom. N5 occupies the top position, which completes the coordination environment of Cu center. The TG analysis shows that the complex **1** and **2** are stable below 225 and 170 °C.

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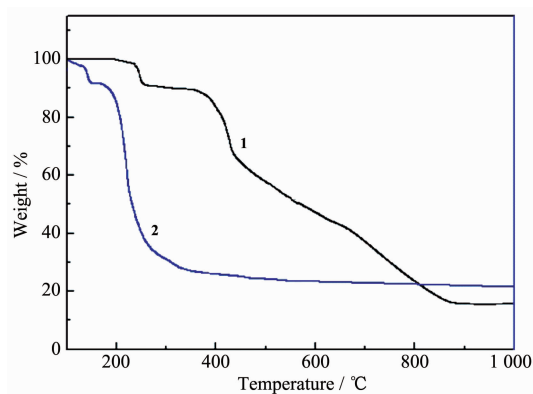


Fig.5 TG curves of complex **1** and **2**

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