

两个单核镍含氮配体配合物的合成、晶体结构及荧光性质

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摘要: 采用回流法在水溶剂中合成了 2 个含氮配体单核镍配合物 $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](1,6\text{-nds}) \cdot 2\text{H}_2\text{O}$ (**1**) 和 $[\text{Ni}(\text{phen})_3](1,6\text{-nds}) \cdot 10\text{H}_2\text{O}$ (**2**) (1,6-nds=1,6-萘二磺酸根离子, phen=1,10-邻菲罗啉)。配合物 **1** 中, 镍离子与 2 个 1,10-邻菲罗啉和 2 个水分子配位, 形成 $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ 阳离子。2 个没有配位的水分子通过氢键与 $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ 和 1,6-萘二磺酸根离子相互连接形成二维层状结构。配合物 **2** 中, 镍离子与 3 个 1,10-邻菲罗啉配位, 形成 $[\text{Ni}(\text{phen})_3]^{2+}$ 阳离子。大量的氢键将自由的水分子和 1,6-萘二磺酸根离子连接形成三维网状结构。2 个配合物中 1,6-萘二磺酸根离子均没有与镍离子配位, 只是起到平衡电荷的作用。室温下, 配合物显示了较大的荧光发射峰, 其最大发射峰分别在 443 和 438 nm。

关键词: 镍配合物; 荧光性质; 晶体结构

中图分类号: O614.81+3

文献标识码: A

文章编号: 1001-4861(2014)05-1187-08

DOI: 10.11862/CJIC.2014.139

Synthesis, Crystal Structures and Luminescent Properties of Two Nickel Mononuclear Complexes Containing N-donor Ligands

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Abstract: The synthesis of the two Ni(II) mononuclear complexes containing N-donor ligands $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](1,6\text{-nds}) \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{phen})_3](1,6\text{-nds}) \cdot 10\text{H}_2\text{O}$ (**2**) (1,6-nds=1,6-naphthalene-disulfonate anion, phen=1,10-phenanthroline) was conducted in water by the reflux method. For the complex **1**, the nickel ion coordinates with two 1,10-phenanthroline ligands and two water molecules, respectively, forming the $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation, and the two uncoordinated water molecules connect to the $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cations and 1,6-nds anions to form a two-dimensional layered structure via the hydrogen bonds. For the complex **2**, the nickel ion coordinates with three 1,10-phenanthroline ligands to form the $[\text{Ni}(\text{phen})_3]^{2+}$ cation. There are abundant hydrogen bonds between free water molecules and 1,6-nds anions, leading to a three-dimensional network structure. In the two complexes, the 1,6-nds anions don't coordinate with the nickel ions, only balance the charges. The complexes exhibit strong luminescence with emission maximum at 443 and 438 nm at room temperature, respectively. CCDC: 947688, **1**; 960245, **2**.

Key words: nickel complex; luminescent property; crystal structure

收稿日期: 2013-09-16。收修改稿日期: 2013-10-25。

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0 Introduction

Recently, the synthesis of coordination polymers have attracted enormous attentions, not only because of their versatile structural topologies, but also because of their special potential applications in the fields of porous materials, catalysis, gas storage, fluorescent and magnetic science, and so on^[1-3]. The organic ligands possessing sulfonate groups exhibit various coordination models. So far, the coordination polymers have been reported, which were interlinked by hydrogen bonds to form one-dimensional chain, two-dimensional layer or three-dimensional network structures^[7-16]. In our efforts to investigate the coordination behavior with transition metals, we have chosen pyridine as auxiliary ligand to react with transition metals (Co(II), Ni(II), or Zn(II)) and 1,5-naphthalene-disulfonate, resulting in three novel coordination molecules. Song et al. used the naphthalene-2,6-disulfonate and 1,3-bis (4-pyridyl) propane to synthesis the complex containing N-donor ligand. The 2,6-naphthalene-disulfonate does not coordinated to the Zn(II). The cations link the free 2,6-naphthalene-disulfonate to form two-dimensional network via hydrogen bonds^[16]. In this paper, we report the synthesis, structures and luminescent properties of the two-dimensional layered coordination polymer $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](1,6\text{-nds}) \cdot 2\text{H}_2\text{O}$ and three-dimensional network coordination polymer $[\text{Ni}(\text{phen})_3](1,6\text{-nds}) \cdot 10\text{H}_2\text{O}$ interlinked by hydrogen bonds (1, 6-nds=1, 6-naphthalene-disulfonate anion, phen=1, 10-phenanthroline).

1 Experimental

1.1 Material

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 1,6-naphthalenedisulfonic acid and 1,10-phenanthroline were of reagent grade and were used without further purification.

1.2 Synthesis of the complexes

Synthesis of the complex **1**: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.263 g, 1 mmol), 1,6-naphthalenedisulfonic acid (0.288 g, 1 mmol), 1,10-phenanthroline (0.198 g, 1 mmol) were added into 20 mL H_2O and stirred for 2 h to afford a

blue solution. The solution of sodium hydroxide ($1 \text{ mol} \cdot \text{L}^{-1}$) was dropwise added adjusting pH value to 4~5. The resulting solution was allowed to stand at ambient temperature for 12 d, yielding blue single crystals. The single crystals for X-ray diffraction analysis were obtained in ca. 50% yield based on Ni(II). Elemental Anal. Calcd. for $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_{10}\text{S}_2\text{Ni}$ (%): C, 52.48; N, 7.20; H, 3.86. Found (%): C, 52.55; N, 7.37; H, 3.98.

Synthesis of the complex **2**: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.263 g, 1 mmol), 1,6-naphthalenedisulfonic acid (0.576 g, 2 mmol), 1,10-phenanthroline (0.396 g, 2 mmol) were added into 20 mL H_2O and stirred for 2 h to afford a blue solution. The solution of sodium hydroxide ($1 \text{ mol} \cdot \text{L}^{-1}$) was dropwise added adjusting pH value to 5~6. The resulting solution was allowed to stand at ambient temperature for 5 d, yielding red single crystals. The single crystals for X-ray diffraction analysis were obtained in ca. 59% yield based on Ni(II). Elemental Anal. Calcd. for $\text{C}_{46}\text{H}_{50}\text{N}_6\text{NiO}_{16}\text{S}_2$ (%): C, 51.79; N, 7.88; H, 4.69. Found (%): C, 52.55; N, 8.35; H, 4.96.

1.3 Physical measurements

The elemental analyses were performed on a Perkin-Elmer 240C element analyzer. Thermogravimetric analysis experiment was carried out on a TA Q50 unit at a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under N_2 atmosphere. The luminescence analyses were performed on a Perkin Elemer LS55 fluorescence spectrometer. X-ray single crystal diffraction data were collected at 298(2) K from a single crystal mounted atop a glass fiber with a Bruker Apex-II diffractometer using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.071\ 073 \text{ nm}$) radiation. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELX-97^[17-19]. The crystal data and structure refinement are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC: 947688, **1**; 960245, **2**.

2 Results and discussion

2.1 Structure descriptin of the complex **1**

The complex **1** crystallizes in the triclinic with

Table 1 Crystal data and structure refinement

Complex	1	2
Empirical formula	C ₃₄ H ₃₀ N ₄ O ₁₀ S ₂ Ni	C ₄₆ H ₅₀ N ₆ O ₁₆ S ₂ Ni
Formula weight	777.45	1 065.75
Temperature / K	298(2)	298(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Unit cell dimensions	$a=1.115\ 69(9)\ \text{nm}$; $\alpha=70.613\ 0(10)^\circ$ $b=1.178\ 00(10)\ \text{nm}$; $\beta=86.958(2)^\circ$ $c=1.588\ 71(13)\ \text{nm}$; $\gamma=71.246\ 0(10)^\circ$	$a=1.381\ 80(12)\ \text{nm}$ $b=1.922\ 89(17)\ \text{nm}$; $\beta=124.843(2)^\circ$ $c=2.1817(2)\ \text{nm}$
Volume / nm ³	1.861 7(3)	4.757 6(7)
Z , D_c / (g·cm ⁻³)	2, 1.387	4, 1.488
Absorption coefficient / mm ⁻¹	0.693	0.574
$F(000)$	804	2 224
Crystal size / mm	0.38×0.28×0.04	0.35×0.32×0.20
Theta range for data collection	2.43° to 25.02°	2.20° to 25.02°
Limiting indices	$-11 \leq h \leq 13$, $-14 \leq k \leq 13$, $-18 \leq l \leq 18$	$-9 \leq h \leq 16$, $-22 \leq k \leq 22$, $-25 \leq l \leq 21$
Reflections collected / unique	9 338/6 429 ($R_{\text{int}}=0.048\ 8$)	23 933/8 387 ($R_{\text{int}}=0.085\ 3$)
Completeness to $\theta=25.02^\circ$	97.9%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.972 8 and 0.778 8	0.893 8 and 0.824 3
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6 429/0/461	8 387/0/640
Goodness-of-fit on F^2	0.985	1.076
Final R indices [$I > 2\sigma(I)$]	$R_1=0.071\ 6$, $\omega R_2=0.153\ 8$	$R_1=0.061\ 3$, $\omega R_2=0.137\ 3$
R indices (all data)	$R_1=0.145\ 5$, $\omega R_2=0.171\ 2$	$R_1=0.164\ 3$, $\omega R_2=0.157\ 9$
Largest diff. peak and hole / (e·nm ⁻³)	751 and -448	644 and -542

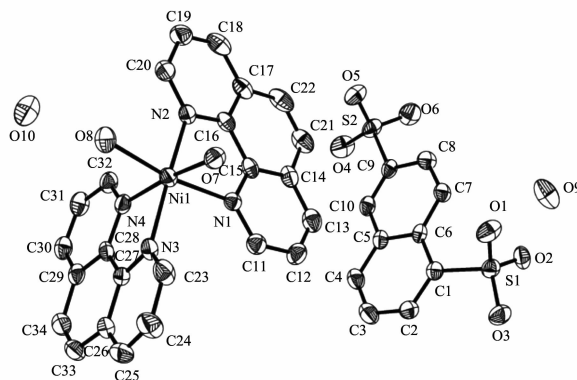
Table 2 Selected bond lengths (nm) and bond angles (°) for complexes 1 and 2

Complex 1					
Ni(1)-N(1)	0.209 0(5)	Ni(1)-N(2)	0.207 8(4)	Ni(1)-N(3)	0.207 8(4)
Ni(1)-N(4)	0.208 2(5)	Ni(1)-O(7)	0.208 0(4)	Ni(1)-O(8)	0.207 8(4)
N(4)-Ni(1)-N(1)	92.95(17)	O(7)-Ni(1)-N(1)	88.33(16)	N(2)-Ni(1)-N(4)	93.82(17)
O(8)-Ni(1)-N(1)	170.81(16)	O(8)-Ni(1)-N(2)	91.78(18)	N(2)-Ni(1)-O(7)	94.29(15)
N(3)-Ni(1)-O(8)	93.74(17)	N(3)-Ni(1)-N(2)	171.8(2)	N(3)-Ni(1)-O(7)	91.89(16)
O(8)-Ni(1)-O(7)	88.81(16)	N(3)-Ni(1)-N(4)	80.03(18)	O(8)-Ni(1)-N(4)	91.11(17)
O(7)-Ni(1)-N(4)	171.89(16)	N(3)-Ni(1)-N(1)	95.08(18)	N(2)-Ni(1)-N(1)	79.72(19)
Complex 2					
Ni(1)-N(1)	0.209 3(5)	Ni(1)-N(2)	0.208 3(4)	Ni(1)-N(3)	0.208 8(5)
Ni(1)-N(4)	0.210 9(5)	Ni(1)-N(5)	0.207 3(5)	Ni(1)-N(6)	0.208 3(5)
N(5)-Ni(1)-N(6)	79.8(2)	N(5)-Ni(1)-N(2)	96.85(19)	N(5)-Ni(1)-N(3)	169.5(2)
N(6)-Ni(1)-N(3)	94.3(2)	N(5)-Ni(1)-N(1)	96.87(18)	N(6)-Ni(1)-N(1)	92.88(19)
N(3)-Ni(1)-N(1)	92.0(2)	N(5)-Ni(1)-N(4)	91.9(2)	N(2)-Ni(1)-N(4)	93.67(18)
N(3)-Ni(1)-N(4)	79.8(2)	N(6)-Ni(1)-N(2)	171.62(19)	N(2)-Ni(1)-N(1)	79.8(2)
N(2)-Ni(1)-N(3)	90.14(17)	N(6)-Ni(1)-N(4)	94.14(17)	N(1)-Ni(1)-N(4)	169.6(2)

space group $P\bar{1}$. The asymmetric unit contains one Ni(II) ion, one 1,6-nds anion, two 1,10-phenanthroline ligands, two coordinated water molecules and two uncoordinated water molecules, as shown in Fig.1. The nickel ion coordinates with two 1,10-phenanthroline ligands and two water molecules, forming $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation. The 1,6-nds anion uncoordinates with the nickel ion, just balances the charge. The Ni-N distances are in the range of 0.207 8(4) to 0.209 0(5) nm, and the Ni-O distances are 0.207 8(4) and 0.208 0(4) nm, respectively. The angles of cis O-Ni-N are between $91.11(17)^\circ$ and $171.89(16)^\circ$. The structure is similar to the result reported in the Ref.[16]. The ligand containing N-donor does not improve the coordination ability of the 2,6-naphthalene disulfonate to the metal center. The anion uncoordinates with the metal center, just balances the charge.

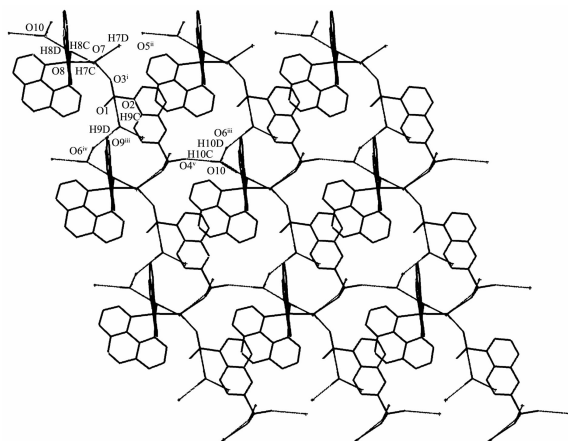
The hydrogen bonds O7-H7C \cdots O3ⁱ, O7-H7D \cdots O5ⁱⁱ, O8-H8C \cdots O9ⁱⁱⁱ and O8-H8D \cdots O10 can be seen

between the coordinated water molecules and 1,6-nds anion, and between the coordinated water molecules and free water molecules. The hydrogen atoms (H9C, H9D, H10C and H10D) in the uncoordinated water molecules form hydrogen-bondings with the O2, O4 and O6 atoms of the sulfonate groups, such as O9-H9C \cdots O2, O9-H9D \cdots O6^{iv}, O10-H10C \cdots O4^v and O10-H10D \cdots O6ⁱⁱⁱ. Consequently, $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$, 1,6-nds anion and the two uncoordinated water molecules are interlinked by the hydrogen bonds, respectively. A view of the two-dimensional layer of the complex **1** along the *c* axis with the hydrogen bonds are shown in Fig.2. The two uncoordinated water molecules extend the layered structure through extensive hydrogen-bonding interactions. The hydrogen bonds play important roles in stabilizing the crystal structure. The hydrogen-bonding details of the complex **1** are listed in Table 3.



Ellipsoids are displayed at 50% probability level

Fig.1 Molecular structure of the complex **1**



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

Fig.2 A view of the two-dimensional layer of the complex **1** along the *c* axis with the hydrogen bonds

Table 3 Hydrogen bond lengths and bond angles for the complexes 1 and 2

Complex 1				
D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O7-H7C...O3 ⁱ	0.085	0.197 5	0.282 3	175.85
O7-H7D...O5 ⁱⁱ	0.085	0.188 2	0.273 1	175.64
O8-H8C...O9 ⁱⁱⁱ	0.085	0.182 6	0.266 7	170.35
O8-H8D...O10	0.085	0.196 9	0.281 1	170.65
O9-H9C...O2	0.085	0.205 2	0.290 2	178.08
O9-H9D...O6 ^{iv}	0.085	0.202 6	0.287 5	177.92
O10-H10C...O4 ^v	0.085	0.208 8	0.293 7	176.30
O10-H10D...O6 ⁱⁱⁱ	0.085	0.193 9	0.278 8	175.78
Complex 2				
D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O7-H7D...O11 ⁱ	0.085	0.188 9	0.273 9	178.03
O7-H7C...O8	0.085	0.196 4	0.281 3	178.33
O7-H7B...O7 ⁱ	0.085	0.209 9	0.275 5	133.63
O8-H8C...O10 ⁱ	0.085	0.199 5	0.284 5	177.89
O8-H8D...O12 ⁱⁱ	0.085	0.190 0	0.275	178.06
O8-H8A...O7	0.085	0.202 9	0.281 3	153.11
O9-H9C...O1 ⁱⁱⁱ	0.085	0.191 5	0.276 4	177.62
O9-H9D...O6 ^{iv}	0.085	0.195 3	0.280 2	177.75
O10-H10C...O5	0.085	0.213 4	0.294 1	158.44
O10-H10D...O9 ^{iv}	0.085	0.220 5	0.301 4	159.1
O11-H11C...O5	0.085	0.190 7	0.273 5	164.51
O11-H11D...O2 ⁱⁱ	0.085	0.223 2	0.306 1	165.08
O12-H12C...O14	0.085	0.190 1	0.275 1	177.45
O12-H12D...O4 ^v	0.085	0.199 2	0.284 2	177.95
O13-H13C...O9 ⁱ	0.085	0.202 6	0.287 2	173.51
O13-H13D...O13 ^{vi}	0.085	0.172 8	0.257 4	173.34
O14-H14C...O2	0.085	0.211 8	0.295 5	167.97
O14-H14D...O13	0.085	0.209 9	0.293 3	167.07
O15-H15C...O1 ⁱⁱⁱ	0.085	0.206 5	0.290 0	167.37
O15-H15C...O3 ⁱⁱⁱ	0.085	0.256 4	0.315 4	127.44
O15-H15D...O4 ⁱⁱ	0.085	0.241 1	0.324 5	167.35
O16-H16C...O6 ^{vii}	0.085	0.221 3	0.306 1	175.28
O16-H16D...O14 ⁱⁱⁱ	0.085	0.183 7	0.268 4	174.31

Symmetry codes for complex 1: ⁱ $-x+1, -y+1, -z+1$; ⁱⁱ $-x+1, -y, -z+1$; ⁱⁱⁱ $x, y, z-1$; ^{iv} $-x+1, -y, -z+2$; ^v $-x, -y, -z+1$. For complex 2: ⁱ $-x+1, -y+1, -z+1$; ⁱⁱ $x, -y+3/2, z+1/2$; ⁱⁱⁱ $x, y, z+1$; ^{iv} $-x, y+1, -z+1$; ^v $x+1, y, z$; ^{vi} $-x+1, -y+1, -z$; ^{vii} $x+1, y, z+1$

2.2 Structure descriptin of the complex 2

The complex **2** crystallizes in the monoclinic with space group $P2_1/c$. The Ni (II) lies on a slightly distorted octahedral geometry. The nickel ion is coordinated with three 1,10-phenanthroline ligands to form $[\text{Ni}(\text{phen})_3]^{2+}$ cation. The 1, 6-nds anion uncoordinates with the nickel ion, just balances the

charge, as shown in Fig.3. The Ni-N distances are in the range of 0.207 3(5) to 0.210 9(5) nm. The angles of cis N-Ni-N are between 79.8(2)° and 171.62(19)°.

The hydrogen bonds can be seen between the uncoordinated water molecules or between the free water molecules and 1, 6-nds anions, as shown in Fig. 4. They include O7-H7D...O11ⁱ, O7-H7C...O8, O7-

out to characterize the thermal stability of the complexes. The experiments were performed under the flowing nitrogen gas with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The TGA curves of the complexes are shown in Fig.6. For complex **1**, the weight-loss step of 9.66% (Calcd. 9.26%) below $179\text{ }^{\circ}\text{C}$ are attributed to the release of the two coordinated and two free water molecules. And then a obvious weight-loss step of 25.20% (Calcd. 25.47%) observed between 179 and $515\text{ }^{\circ}\text{C}$ was attributed to the decomposition of one 1,10-phenanthroline ligand. Above the $515\text{ }^{\circ}\text{C}$, the weight of the remainder gradually makes a loss. The TGA curve of the complex **2** shows that the weight loss of 15.92% below $264\text{ }^{\circ}\text{C}$ corresponds to the loss of the ten water molecules (Calcd. 16.89%). Then it remains stable up to $393\text{ }^{\circ}\text{C}$. The weight loss step of 26.20% that occurs between 393 and $520\text{ }^{\circ}\text{C}$ corresponds to

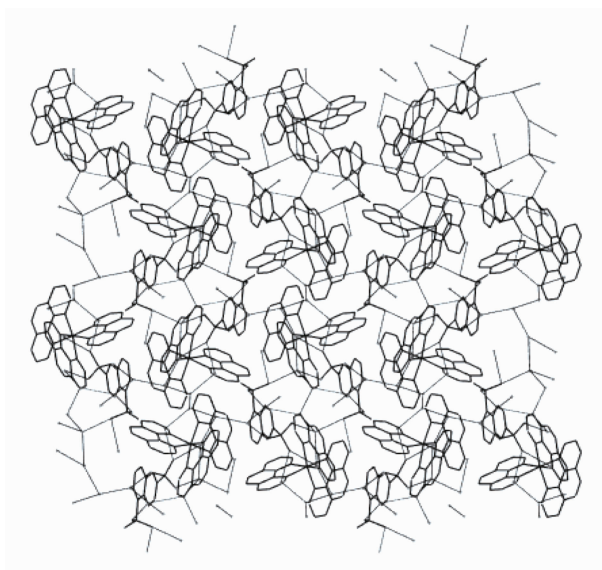


Fig.5 A view of the three-dimensional network of the complex **2** along the *a* axis with the hydrogen bonds

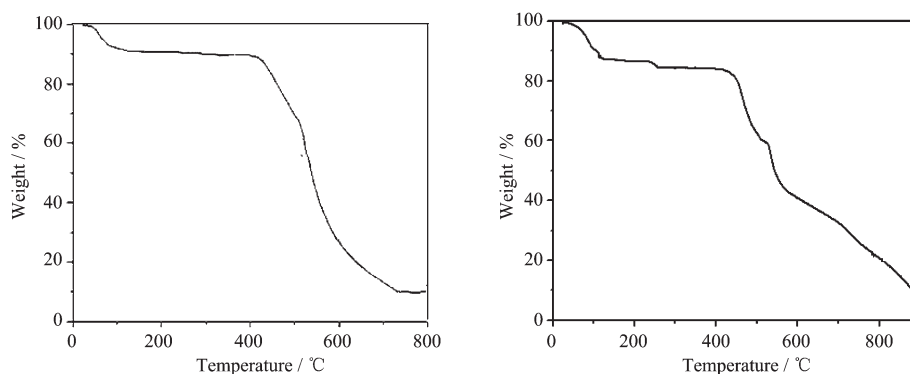


Fig.6 TGA curves of the complexes **1** and **2**

the decomposition of 1,6-naphthalenedisulfonate anion (Calcd. 26.84%). The framework collapses in the temperature range of 520 to 900 °C before the final formation of a nickel oxide.

2.4 Luminescent properties

The solid-state fluorescent spectra of the complexes **1** and **2** at room temperature are depicted in Fig.7. The complex **1** displays the fluorescent emission maximum at 443 nm upon an excitation at 315 nm and the strongest excitation peak at 334 nm upon emission at 340 nm. The complex **2** shows the fluorescent emission maximum at 438 nm upon an excitation at 315 nm and the strongest excitation peak at 316 nm upon emission at 340 nm. The main emission peaks of the 1,6-nds and 1,10-

phenanthroline are at 400 and 380 nm, respectively. Compared with them, the fluorescence spectra of the complexes show that the emission peaks happen red shift. The removal of a proton from 1,6-nds and the coordination of the 1,10-phenanthroline to the nickel ion play important roles in the red shift of the emission. The luminescence of the complexes should depend on the transitions between the energy levels of sulfonate anion and 1,10-phenanthroline. It belongs to both deprotonation of the sulfonic acid and the coordination action of the neutral ligand to nickel ion. The strong blue luminescence properties of the complexes at room temperature suggest that the complexes could have potential application, such as in the luminescent materials.

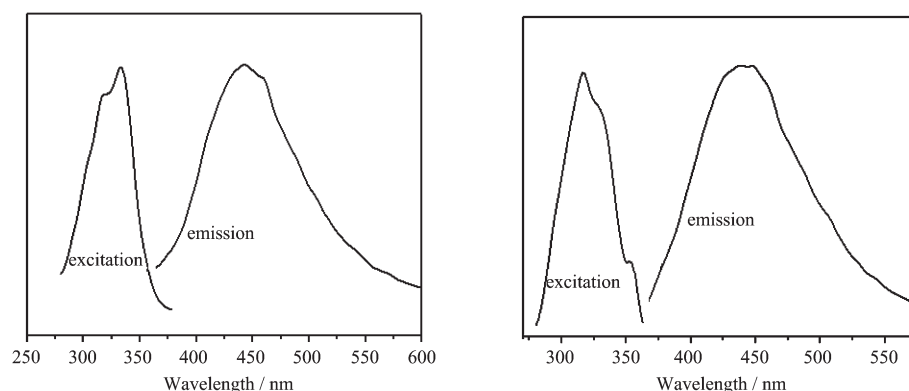


Fig.7 Solid-state excitation and emission spectra of the complexes **1** and **2** at room temperature

3 Conclusion

In summary, the two nickel mononuclear complexes $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](1,6\text{-nds}) \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{phen})_3](1,6\text{-nds}) \cdot 10\text{H}_2\text{O}$ were synthesized in water by the reflux method. For the complex **1**, the nickel ion coordinates with two 1,10-phenanthroline ligands and two water molecules to form $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation. The both of the uncoordinated water molecules connect to the $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cations and 1,6-nds anions to form the two-dimensional layered structure by the hydrogen bonds. For the complex **2**, the nickel ion coordinates with three 1,10-phenanthroline ligands to form $[\text{Ni}(\text{phen})_3]^{2+}$ cation. The uncoordinated water molecules connect to the free 1,6-nds anions to form the three-dimensional network structure via the hydrogen bonds. Compared with 1,6-nds and 1,10-phenanthroline, the fluorescence spectra of the complexes show that the emission peaks happen red shift. They show strong emission maximum at 443 and 438 nm at room temperature, respectively.

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