

Hydrothermal Preparation and Photophysical Properties of a Ni(II) Complex Containing Quinoline Derivative and Phen Ligands^①

CHEN Hai-Hui YI Xiu-Guang^② PAN Chang-Wang

WEN Ji-Wu ZHANG Cong

(School of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an, Jiangxi 343009, China)

ABSTRACT A novel nickel complex $[\text{Ni}_2\text{L}_2\text{Phen}_3] \cdot 3\text{H}_2\text{O}$ (HL = 3-hydroxy-2-methylquinoline-4-carboxylic acid) has been synthesized by a hydrothermal approach and is structurally determined by single-crystal X-ray diffraction. The title complex crystallizes in triclinic space group $P\bar{1}$. Crystal data for the title complex: $\text{C}_{58}\text{H}_{44}\text{N}_8\text{Ni}_2\text{O}_9$, $M_r = 1108.35$, $a = 11.8648(4)$, $b = 12.7369(4)$, $c = 17.0728(5)$ Å, $\alpha = 97.694(3)$, $\beta = 96.702(2)$, $\gamma = 99.566(3)^\circ$, $V = 2495.66(14)$ Å³, $Z = 2$, $T = 293(2)$ K, $D_c = 1.475$ g/cm³, $\mu(\text{MoK}\alpha) = 0.824$ mm⁻¹, $F(000) = 1140$, $R = 0.0757$, $wR = 0.2129$ and $GOF = 1.017$. The nickel ions are surrounded by five oxygen and six nitrogen atoms to yield two slightly distorted octahedral geometries. Solid-state photoluminescence spectrum reveals that it shows blue purple emission. Solid-state UV/Vis diffuse reflectance spectroscopy exhibits that it has an optical band gap of 1.702 eV.

Keywords: hydrothermal preparation, crystal structure, photophysical properties;

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1 INTRODUCTION

The coordination complexes have a wide application prospect in the fields of fluorescent materials, semiconductor materials, magnetic materials solar cells and biomedicine^[1-4]. However, in the design process of coordination complexes, the selection of metal ions is relatively limited, while the selection of ligands is infinite. Especially in the aspect of ligands containing nitrogen and oxygen atoms at the same time, nitrogen and oxygen atoms have not only different coordination modes, but also different rigidity and flexibility.

Quinoline carboxylic acid derivatives are very interesting organic ligands. Many quinoline carboxylic acid derivatives possess a variety of biological activities, such as antibacterial activities, anti-inflammatory^[5, 6], and so on. Quinoline carboxylic acid derivatives also have luminescent properties based on the special structures of quinoline carboxylic acid derivative ligands. Quinoline carboxylic acid ligands have nitrogen and oxygen atoms at the same time, which can

produce a variety of coordination modes, such as single tooth, multi tooth, bridging^[7, 8], and so forth.

Base on the special interest in quinoline carboxylic acid derivatives, a series of metal complexes with the ligand were reported by our group^[9], such as mononuclear Zn(II)/Ni(II)/Pr(III) complexes with monodentate coordination and mononuclear Cu(II)/Zn(II) complexes with bidentate chelated coordination. In the continuing of our work, we report here the hydrothermal preparation and photophysical properties of a Ni(II) complex, which is a binuclear complex with both bridging and chelating modes.

2 EXPERIMENTAL

2.1 General procedure

All reactants of A.R. grade were commercially obtained and used without further purification. The infrared spectrum was measured on a PE Spectrum-One FT-IR spectrophotometer over the frequency range of 4000~400 cm⁻¹ by

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② Corresponding author. Yi Xiu-Guang, male, associate professor, majoring in inorganic chemistry. E-mail: jayxggchem@163.com

using the KBr pellet technique. ^1H NMR spectra were measured on a Bruker Avance 400 MHz instrument with DMSO- d_6 as the solvent. The solid state UV/Vis diffuse reflectance spectroscopy was investigated using TU-1901 UV/Vis spectrometer. The photoluminescence of solid state samples was investigated using the FX-97XP fluorescence spectrometer.

2.2 Preparation of quinoline derivative

(3-hydroxy-2-methyl-quinoline-4-carboxylic acid)

The synthesis of quinoline derivative was based on relevant references^[10, 11], which was briefly introduced as follows: firstly, indigo was oxidized by K_2CrO_7 to form the intermediate product isatin. Secondly, the ligand 3-hydroxy-2-methyl-quinoline-4-carboxylic acid was obtained by adding chloroacetone to the isatin in alkaline condition.

2.3 Preparation of the title complex

The title complex was prepared by mixing $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (2 mmol, 497.4 mg), 3-hydroxy-2-methyl-quinoline-4-carboxylic acid (2 mmol, 406 mg), phen (3 mmol, 540 mg), Et_3N (4 mL) and distilled water (15 mL) mixed in a 25 mL Teflon-lined stainless-steel autoclave. The mixture was heated to 393 K and kept at this temperature for one week. After cooling the mixture slowly down to room temperature, yellowish crystals suitable for X-ray analysis

were collected and washed. Yield: 75% (based on nickel). IR (KBr, cm^{-1}): 3432 (vs), 3061 (w), 1634 (w), 1584 (m), 1525 (m), 1476 (m), 1433 (m), 1309 (w), 1222 (m), 1143 (w), 851 (m), 764 (m), 730 (m), 634 (w).

2.4 X-ray structural determination

A carefully selected single crystal of the title complex was collected on a SuperNova CCD X-ray diffractometer equipped with a graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with an ω scan method. The reduction and empirical absorption correction of diffraction data were carried out with the SIR2004. Using Olex2^[12], the structure of the title complex was solved by ShelXH^[13] and refined by ShelXL^[14] refinement package with full-matrix least-squares. All of the non-hydrogen atoms were generated based on the subsequent Fourier difference maps and refined anisotropically. The hydrogen atoms, except for the lattice water, were located theoretically and ride on their parent atoms. Reflections measured are 19494; the final $R = 0.0780$ for 699 parameters and 9118 observed reflections with $I > 2\sigma(I)$ and $wR = 0.2318$, index ranges are $-14 \leq h \leq 14$, $-14 \leq k \leq 15$, $-20 \leq l \leq 20$, $S = 1.017$, $(\Delta\rho)_{\text{max}} = 1.488$ and $(\Delta\rho)_{\text{min}} = -1.135 \text{ e/\AA}^3$. The selected bond distances and bond angles are shown in Table 1.

Table 1. Selected Bond Lengths (\AA) and Bond Angles ($^\circ$)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ni(1)–N(3)	2.090(5)	Ni(1)–O(5)	2.042(3)	Ni(2)–O(4)	2.103(4)
Ni(1)–N(4)	2.110(4)	Ni(1)–O(6)	1.965(4)	Ni(2)–O(5)	2.232(4)
Ni(1)–N(5)	2.123(4)	Ni(2)–O(1)	1.974(4)	Ni(2)–N(1)	2.095(5)
Ni(1)–N(6)	2.073(4)	Ni(2)–O(2)	1.979(4)	Ni(2)–N(2)	2.075(4)
Angle	($^\circ$)	Angle	($^\circ$)	Angle	($^\circ$)
N(3)–Ni(1)–N(4)	78.7(2)	O(6)–Ni(1)–N(6)	93.1(2)	O(2)–Ni(2)–O(1)	93.03(16)
N(3)–Ni(1)–N(5)	93.19(17)	O(6)–Ni(1)–O(5)	85.08(17)	O(2)–Ni(2)–O(4)	94.90(15)
N(4)–Ni(1)–N(5)	97.64(16)	N(6)–Ni(1)–N(3)	96.2(2)	O(2)–Ni(2)–O(5)	154.98(15)
O(5)–Ni(1)–N(3)	94.61(17)	N(6)–Ni(1)–N(4)	173.7(2)	O(2)–Ni(2)–N(1)	96.53(18)
O(5)–Ni(1)–N(4)	91.52(16)	O(1)–Ni(2)–N(1)	95.01(18)	O(2)–Ni(2)–N(2)	88.31(15)
O(5)–Ni(1)–N(5)	169.00(16)	O(1)–Ni(2)–N(2)	173.43(17)	O(4)–Ni(2)–O(5)	60.14(12)
O(5)–Ni(1)–N(6)	92.63(17)	O(1)–Ni(2)–O(4)	92.28(16)	N(2)–Ni(2)–N(1)	78.44(16)
O(6)–Ni(1)–N(3)	170.0(2)	O(1)–Ni(2)–O(5)	86.65(13)	N(2)–Ni(2)–O(4)	94.01(15)
O(6)–Ni(1)–N(4)	91.72(18)	N(1)–Ni(2)–O(4)	166.08(16)	N(2)–Ni(2)–O(5)	94.86(13)
O(6)–Ni(1)–N(5)	85.06(16)	N(1)–Ni(2)–O(5)	108.43(15)		

3 RESULTS AND DISCUSSION

Single-crystal X-ray diffraction analysis revealed the title complex is a neutral molecule that crystallizes in the $P\bar{1}$ space group, triclinic system. The Ni^{2+} ions are located at the inversion center and are pentacoordinated by the two

3-hydroxy-2-methyl-quinoline-4-carboxylic acid molecules and three phen molecules, yielding two slightly deformed octahedral geometries. The Ni^{2+} (1) ion is coordinated by two oxygen and four nitrogen atoms, with the former from one 3-hydroxy-2-methyl-quinoline-4-carboxylic acid ligand and the latter from two phen ligands. The Ni^{2+} (2) ion is

coordinated by four oxygen atoms from two 3-hydroxy-2-methyl-quinoline-4-carboxylic acid ligands and two nitrogen atoms from one phen ligand, of which the O(5) acts a μ_2 -bridge, connecting the Ni(1) and Ni(2) ions. Quinolinecarboxylate and phen act as the bidentate ligands coordinated to the nickel metal center, as shown in Fig. 1. The bond distances of Ni–O are in the range of 1.967(4)~2.229(4) Å, while those of Ni–N vary from 2.065(4) to 2.123(4) Å. These are comparable with those reported in the literature^[15, 16]. Additionally, there are abundant offset

face-to-face π - π stacking interactions between $Cg1 \cdots Cg3$, $Cg2 \cdots Cg4$, $Cg2 \cdots Cg8$, $Cg3 \cdots Cg7$, $Cg5 \cdots Cg6$, and $Cg7 \cdots Cg7$, as shown in Fig. 2 and Table 2 ($Cg1$ is the ring consisting of N(1) and C(20) to C(24); $Cg2$ is N(2), C(13) to C(17); $Cg3$ is N(3), C(25) to C(29); $Cg4$ is N(4), C(32) to C(36); $Cg5$ is N(5), C(8) to C(12); $Cg6$ is C(4) to C(9); $Cg7$ is C(16) to C(21); $Cg8$ is C(28) to C(33)). There are π - π stacking interactions and van der Waals attraction, yielding the 1-D supramolecular structure.

Table 2. π - π Stacking Interactions of the Title Complex

$Cg \cdots Cg$	Symmetry codes	Centroid-centroid distance (Å)	Slippage distance (Å)	Dihedral angle (°)
$Cg1 \cdots Cg3$		3.811(4)	1.525	0.4(3)
$Cg2 \cdots Cg4$		3.909	1.869	4.8(3)
$Cg2 \cdots Cg8$		3.523(4)	0.520	2.9(3)
$Cg3 \cdots Cg7$		3.771(4)	1.356	1.3(3)
$Cg5 \cdots Cg6$	$-x, 1-y, 1-z$	3.936(4)	1.473	1.1(3)
$Cg7 \cdots Cg7$	$1-x, 2-y, 2-z$	3.736(4)	1.056	0.0(3)

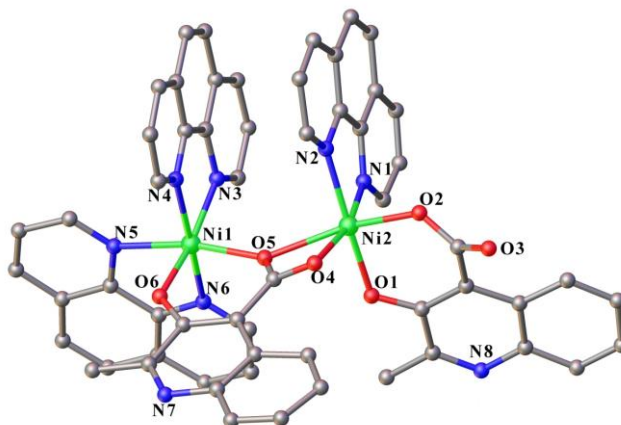


Fig. 1. Molecular structure of the title complex. Hydrogen atoms and lattice water molecules are omitted for clarity

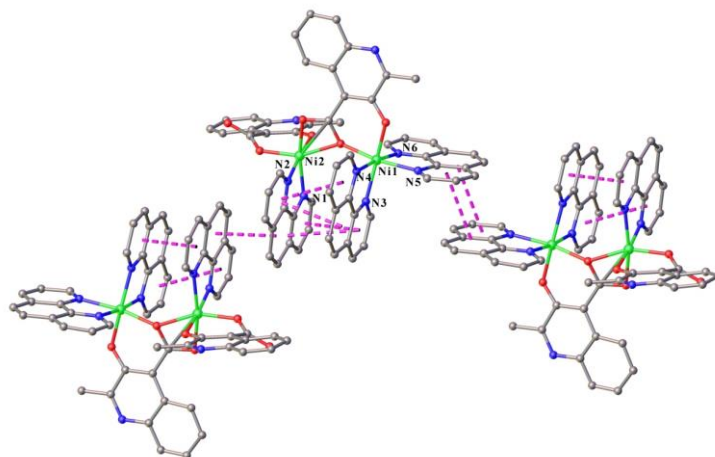


Fig. 2. π - π stacking interaction diagram of the title complex. Hydrogen atoms and three lattice water molecules are omitted for clarity

Based on consideration, increasing attention has been paid to the photoluminescence of coordination complexes. We conducted photoluminescence spectral analysis on solid state sample of the title complex at room temperature and the result is shown in Fig. 3. The photoluminescent spectra of the Ni(II) complex display effective energy absorption in the range of 225~350 nm. When the emission is 416 nm, the excitation spectra of the title complex show the band at 286 nm. Further, we measured the corresponding photolumi-

nescence emission spectra of the title complex. Upon excitation at 286 nm, the blue purple region of the spectra showed a similar peak of 449 nm. The Commission International De L'Eclairage (CIE) 1931 chromaticity coordinates under emission were calculated for the title complex. The estimated CIE values were found to be $x = 0.1691$ and $y = 0.007$, as shown in Fig. 4. Therefore, we deem that the title complex is a promising blue purple light emitting diode material.

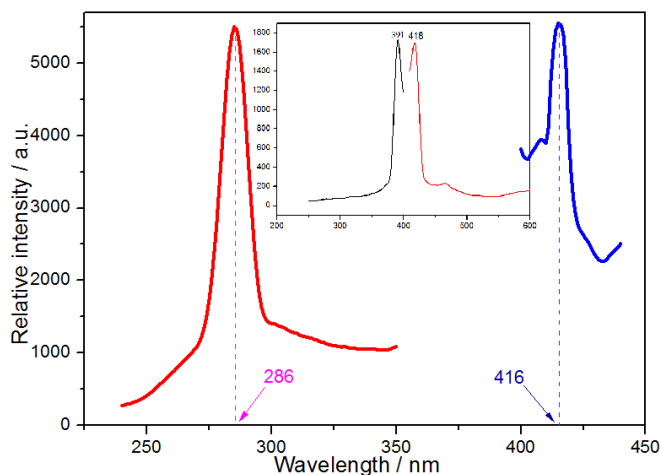


Fig. 3. Solid-state excitation and emission spectra of the title complex. The inset is the solid-state photoluminescence spectra of the title complex

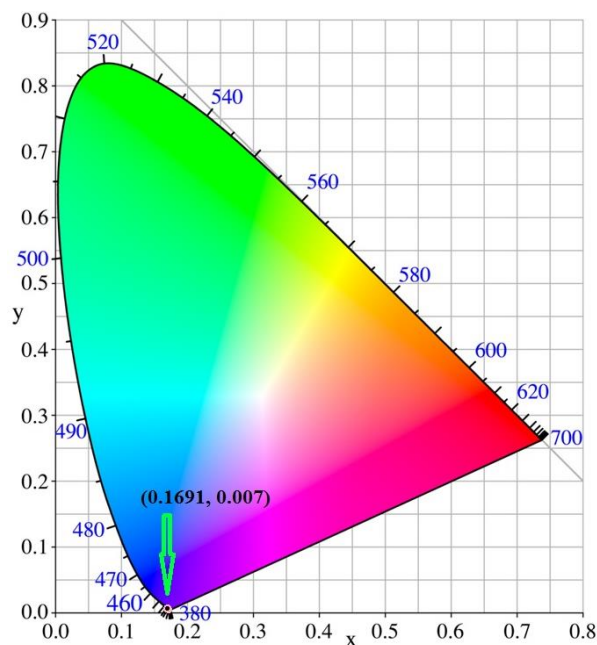


Fig. 4. CIE chromaticity diagram and chromaticity coordinates of the emission spectra of the title complex

As the diffuse reflectance spectroscopy (DRS) can be helpful to understand the conductance property of materials, UV-Vis DRS analysis on solid state sample of the title complex was carried out at room temperature on the basis of

barium sulfate as a reference giving 100% reflectivity, with the result shown in Fig. 5. The Kubelka-Munk function ($F = \alpha/S = (1 - R)^2/2R$) was used to process the data^[17] after measuring the DRS of solid state. The y-axis is transformed

from the Kubelka-Munk and the x -axis is transformed from the energy formula $E_g = hc/\lambda$. For this function, the parameters of α , S , R and λ stand for the absorption coefficient, the scattering coefficient, the reflection coefficient and the absorption wavelength, respectively. From the plot of α/λ vs E_g , we can obtain the value of the optical band gap, which can be extrapolated from the linear part of the absorption edge. The solid-state UV-Vis DRS shows the

band width of the title complex is 1.702 eV. The energy band gap of the title complex is obviously larger than those of GaAs (1.40 eV), CdTe (1.50 eV), and CuInS₂ (1.55 eV), which are well known as highly efficient band gap photovoltaic materials^[18-20]. Therefore, we deem that the title complex may represent highly efficient band gap photovoltaic materials.

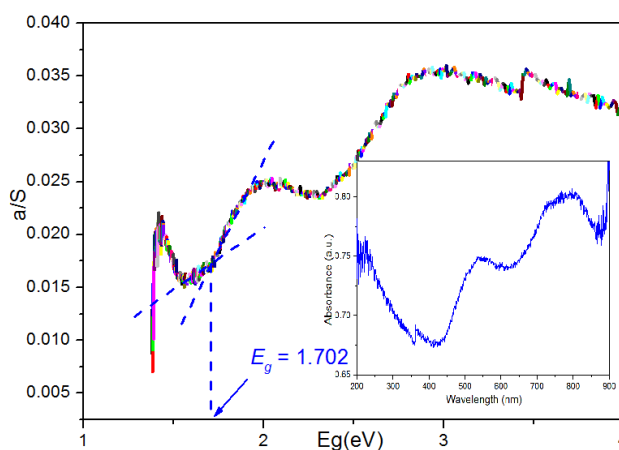


Fig. 5. Solid-state UV-Vis DRS of the title complex. The inset is the UV-Vis spectra of the title complex

4 CONCLUSION

In summary, a nickel compound has been prepared through a hydrothermal reaction and characterized by single-crystal X-ray diffraction. It is characterized by a 1-D chain-like structure. Solid-state photoluminescence reveals that the title complex shows blue purple emission. Solid-state DRS

revealed the presence of a narrow optical band gap of 1.702 eV, indicating that the title complex is a candidate for narrow optical band gap organic semiconductor material. Further investigations on the relationship between the structure and the properties of nickel crystalline complex are in progress in our laboratory.

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