Scientific paper

Preparation, Structure, Photoluminescent and Semiconductive Properties, and Theoretical Calculation of a Mononuclear Nickel Complex with 3-Hydroxy-2-Methylquinoline-4-Carboxylato Ligand

Xiao-Niu Fang,[1] Jia Li,[1,3] Xiu-Guang Yi,[1,2]* Qi Luo,[1] Jia-Yi Chen[1] and Yong-Xiu Li[2]*

[1] *Institute of Applied Chemistry, School of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an, Jiangxi, 343009, China*

[2] *School of Materials Science and Engineering & Chemistry, Nanchang University, Nanchang, Jinagxi, 330031, China*

[3] *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

* *Corresponding author: E-mail: jayxgggchem@163.com*
Tel: +86 (796)8100490; Fax: +86 (796)8100490

Abstract

A novel nickel complex with mixed ligands $[Ni(L)_2(EtOH)_2(MeOH)_2]$ (HL = 3-hydroxy-2-methylquinoline-4-carboxylic acid) has been synthesized through solvothermal reaction and its crystal structure was determined by single-crystal X-ray diffraction technique. Single-crystal X-ray diffraction analyses reveals that the title compound crystallizes in the triclinic system of the *P*–1 space group, and exists as isolated mononuclear complex. The intermolecular hydrogen bonds lead to the formation of chains, and the layered supramolecular structure is formed by the strong π···π stacking interactions. Solid-state photoluminescent characterization reveals that the title compound has an emission in the green region. Time-dependent density functional theory (TDDFT) calculation shows that the nature of the photoluminescence of the title compound originates from the ligand-to-ligand charge transfer (LLCT; from the HOMO of the p-orbital of ligand HMCA to the LUMO of the oxygen atoms). A wide optical band gap of 2.25 eV is found by the solid-state UV/vis diffuse reflectance spectrum.

Keywords: Nickel; photoluminescence; semiconductor; TDDFT; LLCT

1. Introduction

In recent years, metallo-organic coordination polymers have attracted considerable interest due to their diverse structures and potential applications in fluorescence, magnetic materials, gas adsorption, catalysis and medicine and so forth.[1–6] The synthesis of coordination polymers with specific functions has gradually become a research hotspot in the field of material chemistry.[7] From the perspective of crystal engineering, the most useful and facile way to construct coordination complexes is to adopt a suitable ligand to connect metal centers. The ligand is better to possess as much donor atoms as possible that enable it to bridge metal centers together to yield extended architectures. The important feature of metallo-organic coordination polymers is the extension of low dimensional building blocks to high dimensional networks through weak intermolecular interactions, including weak van der Waals force, hydrogen bonding, π-π stacking, etc.[8–10]

Selecting a good ligand is very important in the design and preparation of complexes. Nitrogen heterocyclic compounds have attracted much attention due to their flexible coordination modes and easy coordination with metal ions. They are commonly used ligands for building complexes. A series of complexes based on these ligands have been reported.[11–14] But carboxyl groups not only have many coordination modes such as monodentate coordination, symmetrical chelation coordination, asymmetrical

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chelation coordination, monoooxy bridging coordination and so on, but also have strong coordination ability. They can coordinate with almost all metals to form complexes, and have a large number of unique structures and excellent properties. Various metal carboxylate complexes have been reported.[15–20] If carboxyl groups are introduced into heterocyclic compounds, a series of heterocyclic carboxylic acids with more abundant coordination sites and patterns can be obtained. For example, 4,5-imidazoledicarboxylic acid, 2-pyridine-4,5-imidazoledicarboxylic acid, and corresponding complexes. Up to now, there are few reports on the complexes of quinolinecarboxylates.[21,22]

Quinolinecarboxylate ligands, as ligands containing nitrogen atoms and carboxyl oxygen atoms, are easy to coordinate with metal ions. The coordination modes of carboxyl oxygen atoms are diverse, and the degree of deprotonation of carboxyl groups varies under different pH values, bringing more coordination modes. The coordination mode can exhibit various structures and unique properties. A new nickel coordination polymer (the title compound) was synthesized by hydrothermal method with 3-hydroxy-2-methyl-quinoline-4-carboxylic acid (HL) as ligand and nickel acetate. Its structure and properties were investigated with infrared spectrum, elemental analysis, single-crystal X-ray, solid-state diffuse reflectance spectrum, photoluminescent and theoretical calculations.

2. Experimental

2. 1. Materials and Instrumentation

All reagents and chemicals were of reagent grade, commercially available and directly applied for the reaction. ^{1}H NMR of the ligand were performed on Bruker Avance 400 MHz based on deuterium DMSO as solvent. Infrared spectra were obtained with a PE Spectrum-One FT-IR spectrometer using KBr discs. Elemental microanalyses of carbon, hydrogen and nitrogen were performed on an Elementar Vario EL elemental analyser. Solid-state UV/Vis diffuse reflectance spectroscopy was acted on a computer-controlled TU1901 UV/Vis spectrometer, Finely-ground powder sample was coated on barium sulfate for a 100% reflectance. Photoluminescence characterization was performed on a F97XP photoluminescence spectrometer. Time-dependent density functional theory (TDDFT) calculation were carried out by virtue of the Gaussian09 suite of program packages.

2. 2. Synthesis of 3-hydroxy-2-methylquinoline-4-carboxylic acid (HL)

Synthesis of isatin: indigo (262 g, 1.0 mol) and $K_2Cr_2O_7$ (147 g, 0.50 mol) were added into 500 mL of water and stirred. After cooling, $K_2Cr_2O_7$ (147 g, 0.50 mol), 300 mL of water and 500 mL of 10 % H_2SO_4 were added and kept stirring at 43 °C for 1.5 h. Then, the mixture was

diluted with twice its volume of water, filtered off, dissolved in 10% KOH solution, filtered again, acidified with 10% HCl to pH = 7 and refiltered. Yield: 230 g (90%); m.p. 210 °C; HRMS *m/z* (ESI) calcd for $C_8H_5NO_2$ ([M+H]$^+$) 147.0320, found 147.0826.

Synthesis of HL: isatin (147 g, 1.0 mol) and KOH (56 g, 1.0 mol) were dissolved into a sufficient amount of water and filtered. The filtrate and KOH (56 g, 1.0 mol) were added into chloroacetone (184 g, 2.0 mol), and hydrochloric acid was added dropwise to adjust pH = 7, then filtered. Yield: 193 g (95%); m.p. 225 °C. IR peaks (KBr, cm^{-1}): 3433(vs), 3125(w), 3043(w), 2869(w), 2499 (m), 2040(m), 1621(m), 1553 (s), 1500 (m), 1462(m), 1410(m), 1242(vs), 1160(m), 1014(w), 906(m) and 686(s); HRMS *m/z* (ESI) calcd for $C_{11}H_9NO_3$ ([M+H]$^+$) 203.0582, found 203.0548; ^{1}H NMR (400MHz, DMSO) δ 9.15 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.60–7.52 (m, 1H), 2.70 (s, 3H).

2. 3. Synthesis of Complex 1

0.124 g Ni(CH$_3$COO)$_2$·4H$_2$O (0.50 mmol), 0.203 g HL (1.0 mmol), 5 mL methanol, 5 mL ethanol and 0.5 mL distilled water were added in turn into a 25 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 100 °C in an oven and kept there for one week, then let to cool down to room temperature. Light yellow block crystals were obtained and used to collect the single-crystal X-ray data. Yield 0.434 g **1** (70% based on HL). IR (KBr, cm^{-1}): 3421(s), 1610(s), 1558 (s), 1416(m), 1348(m), 1228(vs), 826(s), 659(w) and 636(s); Anal. Calcd for $C_{28}H_{36}N_2NiO_{10}$: C, 54.30; H, 5.86; N, 4.52; found: C, 54.39; H,5.81; N, 4.66%.

2. 4. X-ray Structure Determination

The single-crystal data of the title complex were collected on the SuperNova CCD X-ray diffractometer equipped with a graphite monochromated Mo-Kα radiation source (0.71073 Å) at 293(2) K. The reduction and empirical absorption correction of the diffraction data were carried out with CrystalClear software. The crystal structure was successfully solved by using the direct methods and Siemens SHELXTLTM Version 5 software package and refined with a full-matrix least-squares refinement on F^2.[23] All of the non-hydrogen atoms were generated based on the subsequent Fourier difference maps and refined anisotropically. The hydrogen atoms were located theoretically and ride on their parent atoms. Due to the problem of crystal quality and the week high-angle diffraction points, lead to the low completeness 0.806. Crystallographic data and structural refinements for the title complex are summarized in Table 1. Selected bond lengths and bond angles for the crystal structure are displayed in Table 2. The hydrogen bonding interactions are presented in Table 3.

Table 1. Crystallographic data and structural analysis for the title compound

Empirical formula	$C_{28}H_{36}N_2NiO_{10}$
M_r	619.30
Color	yellow
Crystal system	Triclinic
Space group	P–1
a (Å)	7.8897(9)
b (Å)	8.8950(14)
c (Å)	10.4485(16)
α (°)	75.433(14)
β (°)	87.129(12)
γ (°)	70.233(12)
V (Å^3)	667.38(17)
Z	1
Reflections collected	5646
Independent, Observed reflections (R_{int})	1895, 1686 (0.0464)
$d_{calcd.}$(g/cm^3)	1.541
μ(mm^{-1})	0.791
$F(000)$	326
R_1, wR_2	0.0944, 0.2312
S	1.059
Largest and mean Δ/σ	0,0
Δ/σ(max, min)(e. Å^3)	1.147, –0.541

Table 2. Selected bond lengths (Å) and bond angles (°) for the title compound

Distance	(Å)	Distance	(Å)
Ni1–O1	2.044(5)	Ni1–O3	2.088(6)
Ni1–O4	2.052(5)	O1–C11	1.298(10)
O2–C11	1.248(10)	O3–C14	1.393(14)
O4–C13	1.412(10)	O5–C8	1.346(12)
N1–C9	1.307(10)	N1–C1	1.362(10)

Angle	(°)	Angle	(°)
O1–Ni1–O4	93.0(2)	N1–C1–C6	121.3(6)
O1–Ni1–O3	91.4(2)	N1–C9–C10	117.5(7)
O4–Ni1–O3	88.9(3)	N1–C9–C8	122.7(7)
C11–O1–Ni1	130.1(5)	O2–C11–O1	122.4(6)
C14–O3–Ni1	127.8(8)	O2–C11–C7	120.2(7)
C13–O4–Ni1	129.3(5)	O1–C11–C7	117.5(7)
C9–N1–C1	120.3(6)	O4–C13–C12	83.4(7)

Table 3. Hydrogen bonding interactions

D–H⋯A	D–H, Å	H⋯A, Å	D⋯A, Å	D–H⋯A, °
O4–H4B⋯N1^i	0.93	1.94	2.728(7)	141
O5–H5B⋯O1	0.82	1.89	2.605(10)	145
C5–H5A⋯O2	0.93	1.97	2.647(10)	128

Symmetric code: (i) *x*, *y*, 1 + *z*.

3. Results and Discussion

The 3-hydroxy-2-methylquinoline-4-carboxylic acid (HL) was prepared by the reaction of isatin with chloroacetone in alkali condition, and the isatin was obtained by the oxidation of indigo, as shown in Scheme 1. The experimental procedure was improved according to the basis of literature.[24,25]
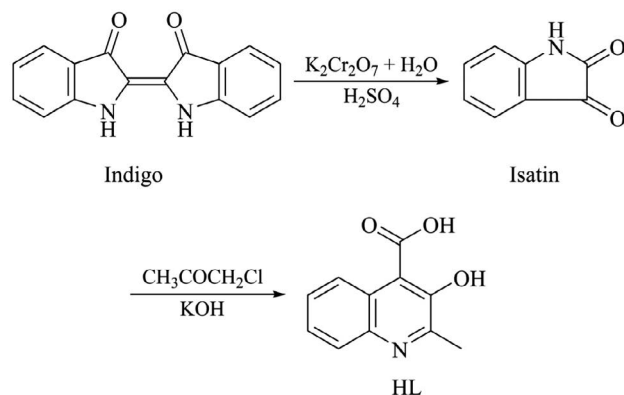
Scheme 1. Synthetic route of HL

In the first step, the amount of oxidant and temperature control is the key factors to the success of the oxidation. In the second progress, the amount of KOH and the feeding mode of chloroacetone make the important effects on reactions.

Single-crystal X-ray diffraction measurement revealed that the title compound crystallizes in the space group *P*–1 of the triclinic system. In the crystal structure of title compound **1**, the metal Ni atom is sitting at the inversion center. The nickel (II) ion is hexacoordinated octahedron by the doubly deprotonated HL, two methanol and two ethanol molecules, yielding an octahedral geometry, as presented in Fig. 1. The bond distance of Ni–O1 is 2.044(5) Å, for is Ni^{ii}–O3 2.088(6) Å, while that of Ni–O4 is 2.052(5) Å [ii = –*x*, –*y*, 1 – *z*]. These are comparable with that reported in the references.[26,27] Quinolinecarboxylate (L$^-$) acts as the monodentate ligand coordinated to the nickel metal center, and two such ligands occupy both axial positions. The four O atoms of methanol and ethanol are located in the equatorial plane with the good coplanarity. The intramolecular hydrogen bond can be found between the phenolic hydroxyl group and carboxylate group (O5–H5B⋯O1), and another week intramolecular hydrogen bond exist between the carbon atom and the carboxyl oxygen atom (C5–H5A⋯O2). The intermolecular hydrogen bond O4–H4B⋯N1^i can be found between ethanol oxygen and aromatic N atom of quinoline moiety, forming a one-dimensional supramolecular structure extending along the *c*-axis, as presented in Fig. 2. In the complex, there are strong offset face-to-face π⋯π stacking interactions between *Cg*1⋯*Cg*1^{iii} and *Cg*2⋯*Cg*1^{iv} [*Cg*1 and *Cg*2 are

N1/C1/C6–C9 and C1–C6 ring centroids; iii = –*x*, –*y*, –*z*; iv = 1 – *x*, –*y*, –*z*]. The centroid-centroid distance of *Cg*1⋯*Cg*1[iii] is 3.6528(4) Å with the shift distance 1.3372(7) Å and the twist angle of 0.00(4)°. The centroid-centroid distance of *Cg*2⋯*Cg*1[iv] is 3.5966(4) Å with the shift distance 1.0197(8) Å and the twist angle of 2.387(5)°. These π⋯π stacking interactions yield the two-dimensional supramolecular layers along the *ac*-axis plane, then *via* van der Waals attraction complete a crystal packing as presented in Fig. 3.
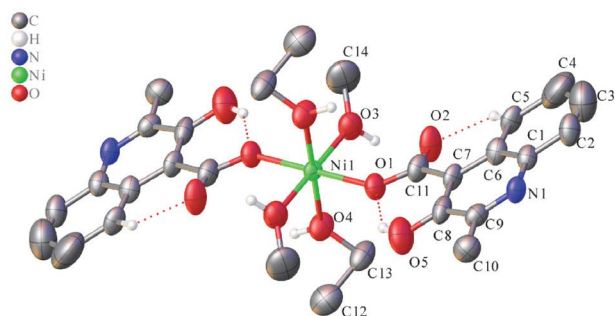
Figure 1. The molecular structure of the title compound. Hydrogen atoms not involved in the motif shown were removed for clarity.
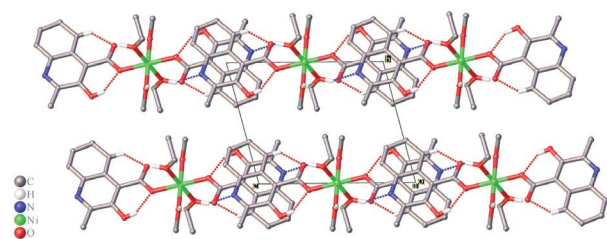

Figure 2. The 1-D chain structure of the title compound. Hydrogen atoms not involved in the motif shown were removed for clarity. The intramolecular hydrogen bond is shown as red stipple line, the intermolecular hydrogen bond is shown as blue stipple line.
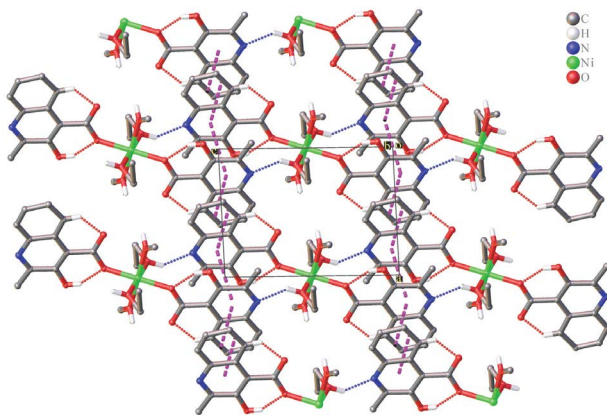
Figure 3. Packing diagram of the title compound viewed along the *b* axis. Hydrogen atoms not involved in the motif shown were removed for clarity. The intramolecular hydrogen bond is shown as red stipple line, the intermolecular hydrogen bond is shown as blue stipple line, and the magenta stipple line represent the π⋯π stacking interactions.

In recent years, the photoluminescence properties of coordination complexes have gained increasing interest. Generally, coordination complexes containing lanthanide and transition elements can exhibit photoluminescence behavior because they possess rich 4*f*-orbit and 3/4*d*-orbit electron configurations. Many studies about the photoluminescence performance of lanthanide and transition compounds have been conducted so for.[28–30] The title compounds contain Ni^{2+} ions; therefore, we deemed that nickel and HL complexes can possibly exhibit interesting photoluminescence performance. Based on the above considerations and in order to reveal its potential photoluminescent properties, we carried out the photoluminescence spectra with solid state samples at room temperature and the result is presented in Figs. 4. It is obvious that the photoluminesent spectrum of the title compound displays an effective energy absorption residing in the wavelength range of 350–450 nm. Upon the emission of 544 nm, the excitation spectrum shows a band at 408 nm. We further measured the corresponding photoluminescence emission spectrum of the title compound. Upon excitation at 408 nm, the emission spectrum is characterized by a sharp band at 544 nm in the blue region of the spectrum. The emission band of the title compound is located in the green light region with the CIE (Commission Internationale de l'Éclairage) Chromaticity coordinate (0.3551, 0.634) (Fig. 5). As a result, the title complex is a potential green photoluminescent material.
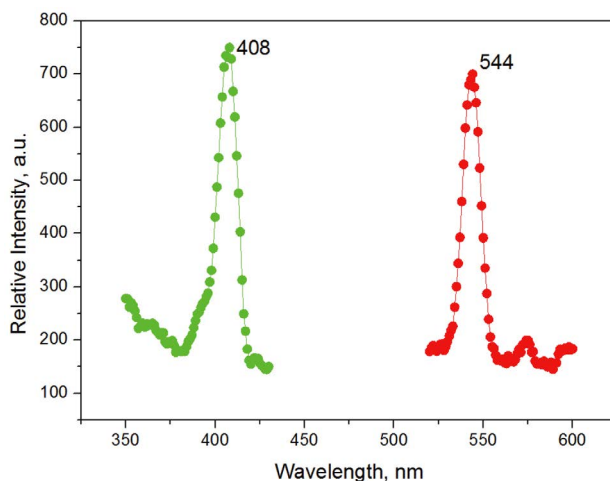
Figure 4. Solid-state photoluminescence spectra of the title compound measured at room temperature (green curve: excitation; red curve: emission).

In order to reveal the nature of the photoluminescence emission of the title compound, we truncated ground state geometry from its single-crystal X-ray diffraction data set (without optimization) and carried out its theoretical calculation in light of the time-dependent density functional theory (TDDFT) based on this ground state
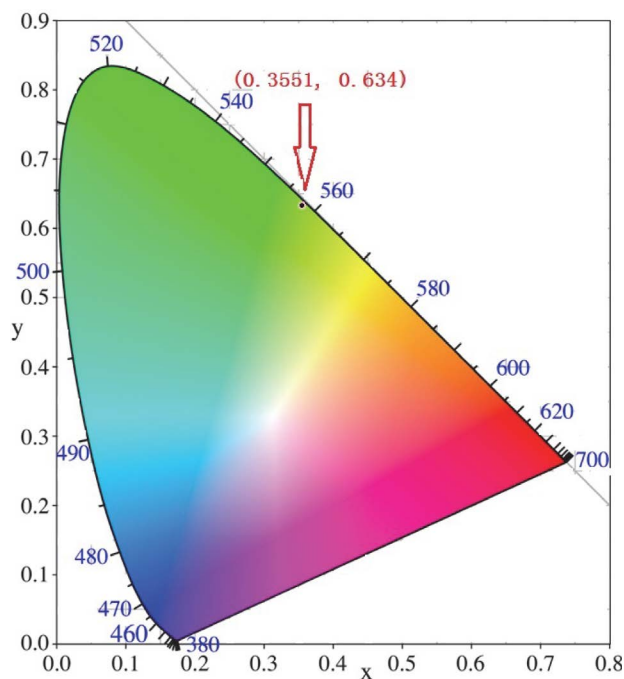
Figure 5. The CIE chromaticity diagram and chromaticity coordinates of the emission spectrum of the title compound.

could be assigned to the ligand-to-ligand charge transfer (LLCT; from the HOMO of the p-orbital of ligand HL to the LUMO of the oxygen atoms).

To investigate the semiconductive properties of the title complex, the solid-state UV/vis diffuse reflectance spectra was measured on a powder sample at room temperature, using barium sulfate as the reference for 100% reflectivity, its surface was coated with finely-ground powder samples for measurement. After measuring, the data were treated with the Kubelka-Munk function which is known as $\alpha/S = (1 - R)^2/2R$. With regard to this function, the parameter α means the absorption coefficient, S means the scattering coefficient, and the R means the reflectance, which is actually wavelength independent when the size of the particle is larger than 5 μm. From the α/S vs. energy gap diagram, we can obtain the value the optical band gap, which can be extrapolated from the linear portion of the absorption edges. In the way, the solid-state UV/vis diffuse reflectance spectrum reveals that the title compound has a wide optical energy band gap of 2.25 eV, as shown in Fig. 7. As a result, the title compound is a possible candidate for wide band gap semiconductors. The gentle slope of the optical absorption edge of title compound indicates that it must be an indirect transition.[34] The energy band gap of 2.25 eV is obviously larger than those of GaAs (1.4 eV), CdTe(1.5 eV) and CuInS$_2$

geometry. The TDDFT calculations were performed using the B3LYP function[31,32] and carried out by means of the Gaussian09 suite of programs,[33] with SDD for Ni and 6-31G* basis for other atoms. The characteristics of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the title compound is shown in Fig. 6. It is easy to find out that the electron-density distribution of HOMO is totally resided at the coordinating the p-orbital of ligand HL with an energy being of –0.21787 Hartrees; however, the electron-density population of LUMO is mainly distributed on the oxygen atoms and the energy of the LUMO is calculated to be –0.19871 Hartrees. The energy difference between LUMO and HOMO is 0.01916 Hartrees that is small enough to allow the charge transfer from HOMO to LUMO. In light of this observation, it is proposed that the essence of the photoluminescence of the title compound
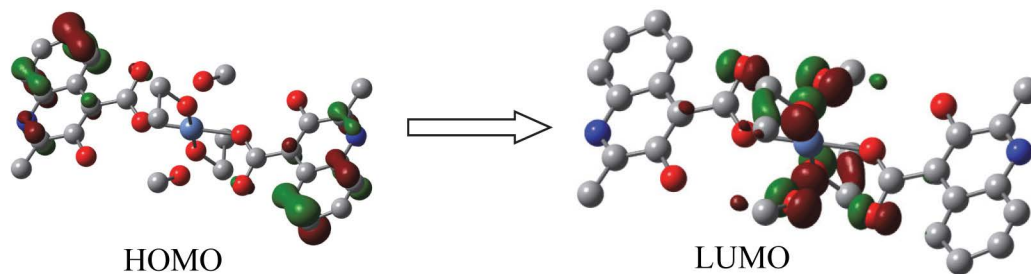

Figure 7. Solid-state UV/vis diffuse reflectance spectrum for the title compound.

Figure 6. B3LPY predicted frontier molecular orbital of the title compound. The isovalue of 0.04 is used for plotting isosurfaces.

(1.55 ev),[35,36] all of them are well known as highly efficient band gap photovoltaic materials.

4. Conclusions

A novel nickel(II) complex [Ni(L)$_2$(EtOH)$_2$(MeOH)$_2$] with the ligands of 3-hydroxy-2-methylquinoline-4-carboxylic acid (HL), MeOH and EtOH was synthesized by solvothermal synthesis, its structure and properties were investigated with infrared spectrum, elemental analysis, single-crystal X-ray, solid-state diffuse reflectance spectrum, photoluminescent and theoretical calculations. The title compound crystallizes in the triclinic system of the *P*–1 space group as isolated mononuclear complex. The intermolecular hydrogen bonds lead to the formation of chains, and the layered supramolecular structure is formed by the offset face-to-face π···π stacking interactions. Solid-state photoluminescence spectrum reveals that it shows an emission in the green region of the light spectrum. Time-dependent density functional theory (TDDFT) calculations reveal that this emission can be attributed to ligand-to-ligand charge transfer (LLCT). Solid-state diffuse reflectance data shows there is a narrow optical band gap of 2.25 eV.

5. Acknowledgements

6. Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1876986. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Povzetek

Sintetizirali smo nov nikljev kompleks s prisotnimi različnimi ligandi $[Ni(L)_2(EtOH)_2(MeOH)_2]$ (HL = 3-hidroksi-2-metilkinolin-4-karboksilna kislina) s solvotermalno tehniko in določili kristalno strukturo z monokristalno rentgensko difrakcijo. Monokristalna rentgenska analiza je razkrila, da spojina kristalizira v triklinskem sistemu v prostorski skupini *P*–1 kot izoliran enojedrni kompleks. Intermolekularne vodikove vezi sodelujejo pri tvorbi verig, plastovita supramolekularna struktura pa nastane zaradi močnih π···π interakcij. Fotoluminiscentne lastnosti v trdnem stanju kažejo, da ima spojina emisijo v zelenem območju. Izračuni na podlagi časovno odvisne teorije gostotnostnih funkcionalov (TDDFT) kažejo, da fotoluminiscenca spojine izvira v prenosu naboja ligand-ligand (LLCT; iz HOMO p-orbitale liganda L v LUMO kisikovega atoma). Široka razlika med optičnima pasovoma 2.25 eV je bila ugotovljena z UV/vis difuzno reflektanco v trdnem stanju.