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Synthesis, X-ray structure, spectroscopic characterization and nonlinear optical properties of Nickel (II) complex with picolinate: A combined experimental and theoretical study

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ABSTRACT

A novel Nickel (II) complex with picolinate was prepared and its structural characterization was carried out by X-ray diffraction method. Its vibration spectra (FT-IR and Raman) were recorded to investigate the vibrational wavenumbers and the coordination environment of Ni(II) ion. In order to demonstrate electronic transitions and molecular charge transfers within complex **1**, UV–vis spectrum was measured in ethanol solvent. Furthermore, the density functional theory (DFT) calculations were performed to both support the experimental results and convert this study to more advanced work. The geometry optimization and calculations of vibration spectra and electronic transitions were performed by using DFT level. Obtained small HOMO–LUMO energy gap displayed that complex **1** can be easily polarized and molecular charge transfer occurs within complex **1**. Molecular stability and hyperconjugative interactions were investigated by applying natural bond orbital (NBO) analysis. The nonlinear optical properties of complex **1** were determined, and obtained results showed that complex **1** can be considered as a potential candidate for NLO material.

1. Introduction

The synthesis of new metal-organic frameworks which have potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and material chemistry remains as a fundamental research field for the study of structure-property correlations and finding novel structural motifs [1–4]. Meanwhile, the chemistry of nickel (II) ion have gathered great attention due to biological properties of nickel that lead to several structural and biochemical models [5,6]. For the complexation of nickel (II), picolinic acid (Hpic) has been chosen as the coordination ligand in the present study. Picolinic acid, which is also known as pyridine-2-carboxylic acid has a reputation for binding to metal ions as a bidentate N,O-donor forming a stable five-membered chelate ring. Picolinic acid is an interesting ligand due to the different nature of two donor sites, one is pyridine nitrogen and the other is carboxylate oxygen. The carboxylate oxygen which is a hard donor is recognized to stabilize transition metals in their higher oxidation states, while the pyridine nitrogen which is a soft donor is known as stabilizer of the lower oxidation states of transition metals. Picolinic acid ligand is of particular interest to medicinal chemists because of their wide range of physiological effects exhibited by natural and synthetic acids. Moreover, Hpic is a versatile ligand and its complexes with transition metal ions have found use in medicine and in quantitative analysis [7–9]. Furthermore, picolinic acid have been extensively studied in view of their interesting magnetic properties [10,11].

Considering the above mentioned facts, picolinic acid has been studied extensively, both structurally and spectroscopically for many years [10–12]. On the other hand, the investigation of nonlinear optical properties of picolinic acid complexes is neglected up to now. In recent years, the nonlinear optical materials have received remarkable interest due to advances in optical, electro-optical laser and opto-electronic technology [12–14]. It is well known that the NLO properties of molecular systems can be improved by the coordination of metal ion as well as the modifying the donor and acceptor capacity and extending the π-conjugated bridge. Furthermore, in most cases, the D–π–A structure is designed to enhance the intramolecular charge transfer (ICT) transitions, leading to more active NLO properties.

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Having all above mentioned facts in mind, we have performed this study in order to investigate molecular structure, spectroscopic (IR, Raman and UV–vis) and electronic properties, bonding properties, nonlinear optical properties and molecular surfaces of complex **1**.

2. Experimental and theoretical methods

2.1. Synthesis of the complex 1

All chemical reagents were analytical grade commercial products. Solvents were purified by conventional methods. To an ethanol/water (40 mL, ca 1:1 (v/v)) containing $NiCl_2 \cdot 6H_2O$ (1 mmol), picolinic acid (2 mmol) was slowly added with continuous stirring. The resulting solutions were refluxed for 4 h and then filtered. The green filtrates were allowed to stand for five days at room temperature, and then the green crystals adequate for X-ray diffraction studies were obtained.

2.2. Instrumentation

FT-IR spectra for complex **1** were recorded on a Perkin–Elmer FT-IR spectrophotometer, where samples were dispersed in KBr at the region of 4000–600 cm^{-1}. Raman spectroscopy analyze of complex **1** was performed at the region of 3500–400 cm^{-1} by Kaiser RAMANRXN1. The UV–vis absorption spectrum of the complex was examined in the range 200–900 nm using an Agilent Model 8453 diode array spectrophotometer in ethanol solvent.

2.3. X-ray data collection and structure refinement

The solid-state structure of complex **1** was confirmed by X-ray diffraction analysis. Data were obtained with Bruker APEX II QUAZAR three-circle diffractometer. Indexing was performed using APEX2 [15]. Data integration and reduction were carried out with SAINT [16]. Absorption correction was performed by multi-scan method implemented in SADABS [17]. The Bruker SHELXTL [18] software package was used for structure solution and structure refinement. All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. Aromatic C-bound H atoms were positioned geometrically and refined using a riding mode. H atoms of water molecules were located in a difference Fourier map and the O–H distances restrained to be 0.84 Å from O atom using DFIX command and their positions were constrained to refine on their parent O atoms with $U_{iso}(H) = 1.5U_{eq}(O)$. Crystallographic data and refinement details of the data collection for complex **1** are given in Table 1. The selected bond lengths and bond angles are given in Table 2. Final geometrical calculations were performed using PLATON software [19]. MERCURY software [20] was used for visualization of the cif files. The important conditions for the data collection and the structure refinement parameters of complex **1** are given in Table 1.

2.4. Computational details

The molecular modeling of complex **1** was performed at GAUSSIAN 09 Rev: D.01 program [21], and the obtained results were visualized via GaussView 5 program [22]. The optimized structure and vibrational wavenumbers were calculated by using B3LYP level (Becke's three parameter hybrid model using the Lee-Yang Parr correlation functional) [23,24] of density functional theory (DFT). The effective core potential (ECP) of Hay and Wadt and the concomitant LanL2DZ basis set was used [25–27] for Ni(II) ion, while 6-311++G(d,p) [28] basis set was used for other atoms (C, O, N and H). The electronic absorption spectrum and frontier molecular orbitals were simulated by using time dependent DFT (TD-DFT) method at the same level and basis sets. Natural bond orbital (NBO) calculation [29] was performed to understand various second order interaction between the filled orbital of one subsystem and vacant orbital of another subsystem which is measure of the molecular delocalization or hyperconjugation using NBO 3.1 program. The nonlinear optical properties were evaluated by the determining of dipole moment, polarizability and hyperpolarizability parameters by using B3LYP level and 6-311++G(d,p)/LanL2DZ basis sets. Finally, molecular surfaces such as molecular electrostatic potential (MEP), electrostatic potential (ESP) and contour plot of ESP were simulated at the same level and basis sets.

Table 1
Crystal data and refinement parameters for complex **1**.

CCDC	1061065
Empirical formula	$C_{12}H_{16}N_2NiO_8$
Formula weight ($g.mol^{-1}$)	374.98
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.6830(7)
b (Å)	5.1640(5)
c (Å)	14.4171(12)
α (°)	90
β (°)	90.092(4)
γ (°)	90
Crystal size (mm)	0.187 × 0.319 × 0.400
V ($Å^3$)	720.90(11)
Z	2
Density (g/cm^3)	1.727
μ (mm^{-1})	1.392
F(000)	388
θ range for data collection (°)	2.53–25.67
h/k/l	−6/11, −6/6, −16/17
Reflections collected	4795
Independent reflections	1359 [R(int) = 0.0304]
Absorption correction	multi-scan
Data/restraints/parameters	1359/6/118
Goodness-of-fit on F^2 (S)	1.111
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0224$, $wR_2 = 0.0622$
R indices (all daTa)	$R_1 = 0.0239$, $wR_2 = 0.0630$
Largest diff. peak and hole ($e.Å^{-3}$)	0.261 and −0.362

3. Results and discussion

3.1. Molecular geometry

Complex **1** crystallizes in the monoclinic P21/n space group with

Table 2
Selected experimental and theoretical geometric parameters for complex **1**.

Bond lengths	X-ray	B3LYP		X-ray	B3LYP
Ni1–N1	2.0641 (14)	2.092	C3–C2–C1	119.12 (17)	118.77
Ni1–N1#1	2.0640 (14)	2.077	C2–C3–C4	119.12 (17)	119.11
Ni1–O2	2.0463 (11)	2.034	C5–C4–C3	118.16 (16)	118.71
Ni1–O2#1	2.0463 (11)	2.055	N1–C5–C4	123.04 (16)	121.85
Ni1–O1	2.0882 (12)	2.173	N1–C5–C6	115.51 (15)	116.64
Ni1–O1#1	2.0881 (12)	2.195	C4–C5–C6	121.46 (15)	121.47
C1–N1	1.334 (2)	1.338	O3–C6–O2	125.14 (16)	126.26
C1–C2	1.385 (2)	1.391	O3–C6–C5	118.56 (15)	119.26
C2–C3	1.379 (3)	1.393	O2–C6–C5	116.30 (14)	114.42
C3–C4	1.387 (3)	1.391	C1–N1–C5	118.27 (15)	116.60
C4–C5	1.380 (2)	1.391	C1–N1–Ni1	129.10 (12)	128.66
C5–C6	1.508 (2)	1.526	O2–Ni1–O2#1	180.00 (7)	176.79
C5–N1	1.344 (2)	1.344	N1–Ni1–N1#1	180.00 (8)	177.45
C6–O3	1.238 (2)	1.222	O1–Ni1–O1#1	180.00 (4)	175.50
C6–O2	1.276 (2)	1.298	O2–Ni1–N1	80.63 (5)	80.83
Bond angles			O2–Ni1–O1	90.56 (5)	92.79
N1–C1–C2	122.28 (16)	121.94	N1–Ni1–O1	84.71 (5)	85.04