



Synthesis, crystal structure, DFT study and photocatalytic property of a new Ni(II) complex of a symmetric N₂O₄-donor bis-Schiff base ligand



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ARTICLE INFO

Article history:

Received 7 September 2015
Received in revised form
16 November 2015
Accepted 18 November 2015
Available online 25 November 2015

Keywords:

1,2-bis(2-Methoxy-6-formylphenoxy)ethane
2-aminoethanesulfonic acid
Ni(II) complex
DFT study
Photocatalytic activity

ABSTRACT

A new complex, Ni(C₂₂H₂₆N₂O₁₀S₂)·2CH₃OH, with a sexidentate (N₂O₄) symmetric bis-Schiff base ligand (C₂₂H₂₆N₂O₁₀S₂ = 1,2-bis(2-methoxy-6-formylphenoxy)ethane-2-aminoethane-sulfonic acid) has been synthesized and characterized by physico-chemical and spectroscopic methods. The X-ray crystal structure shows that the Ni(II) atom of the complex is six-coordinated by two nitrogens from C=N groups, two oxygens from ether groups and two hydroxyl oxygens from sulfonic acid groups in the mono-ligand, forming a distorted octahedral geometry. Theoretical study of the complex is carried out by density functional theory (DFT) method and the B3LYP method employing the 6-31+G^{*} basis set. Moreover, the complex proved to be good candidate for the photocatalytic degradation of methylene blue.

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1. Introduction

Schiff base ligand, which can be easily synthesized by condensation of primary amine and carbonyl compound, have high coordination capability and can form stable complexes with transition metal ions [1–3]. In addition, due to the good anticancer activity [4–6], heterogeneous or homogeneous catalysis ability [7–9] and magnetism property [10,11], Schiff base complexes derived from amino acids have attracted enough attention [12,13]. A lot of complexes with open-chain and macrocyclic multidentate ligand have been investigated to study their synthetic, thermodynamic and structural properties [14–16]. Recently, extensive work has been done on the photocatalytic degradation of organic dyes using Schiff base complexes due to their good photocatalytic performance, non-toxicity, low production costs [17–19]. The release of organic dyes via waste waters is an important source of pollution, leading to eutrophication and perturbation of aquatic life [18]. The photocatalytic process is based on the generation of the hydroxyl radicals (·OH) that can oxidize common organic dyes non-selectively or selectively in a short period of time.

To the best of our knowledge, there is rare report on the

systematic investigation on synthesis of sexidentate N₂O₄-donor bis-Schiff base Ni(II) complex and the dyes photocatalytic degradation using the complex. In view of these observations, in this work, a new sexidentate N₂O₄-donor bis-Schiff base Ni(II) complex, namely Ni(C₂₂H₂₆N₂O₁₀S₂)·2CH₃OH, has been synthesized and characterized. Additionally, based on crystal data, density functional theory (DFT) study of the complex is performed using the Gaussian 03 program suite. The natural atomic charges distribution, molecular total energy, frontier molecular orbital energies and components, and molecular electrostatic potential of the complex are discussed. At last, photocatalytic property for decomposition of methylene blue (MB), rhodamine B (RhB) and methyl violet (MV) are considered.

2. Experimental section

2.1. Materials and methods

All chemical reagents were of analytical grade and were used as received without further purification. 2-aminoethanesulfonic acid, methylene blue, rhodamine B and methyl violet were purchased from Aladdin. The other chemicals were produced in China. IR spectra were recorded as KBr pellets on a Nicolet 170SX spectrophotometer in the 4000–400 cm⁻¹ region. UV spectra were

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recorded on a Unicam UV2 spectrometer. Elemental analyses (C, H and N) were obtained with a model 2400 Perkin–Elmer analyzer. ^1H NMR spectra was obtained on a Bruker DRX-400 spectrometer. X-ray diffraction data were collected on an Enraf-nonius CAD-4 diffractometer. Powder X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation at room temperature. Thermal gravimetric analyses (TGA) were performed on a Perkin–Elmer Pyris 1 TGA analyzer from room temperature to 1000 °C with a heating rate of 20 °C min $^{-1}$ under nitrogen.

2.2. Computational procedure

Becke's three-parameter hybrid (B3LYP) level [20,21] was selected for DFT [22] calculations by the basis set of 6-311G* (d, p) for the H, C, N, O and S atoms, while valence double- ζ LANL2DZ [23] basis set was used for Ni atom. Atom coordinates used in the calculations were from crystallographic data, and a molecule in the unit cells was selected as the initial model. All calculations were conducted on a Pentium IV computer using Gaussian 03 program [24].

2.3. Synthesis of the Ni(II) complex

2-aminoethanesulfonic acid (0.125 g, 1.0 mmol) and potassium hydroxide (0.056 g, 1.0 mmol) were dissolved in methanol (30 mL) and then 1,2-bis(2-methoxy-6-formylphenoxy)ethane (0.165 g, 0.5 mmol) [25] was added to the solution. The mixture was heated to 50 °C with stirring and then refluxed for 5 h to give a bright yellow solution. After that, a methanol solution (10 ml) of Ni(CH $_3$ COO) $_2$ ·4H $_2$ O (0.124 g, 0.5 mmol) was added to the solution of the ligand. The resulting mixture was stirred and refluxed at 50 °C for 5 h. The resulting solution was cooled at room temperature and then filtered. The filtrate was left for slow evaporation at room temperature. The dark green block-shaped crystals were formed after about two weeks. Yield: 71% based on 2-aminoethanesulfonic acid. Elemental Anal Calc (%) for Ni(C $_{22}$ H $_{26}$ N $_2$ O $_{10}$ S $_2$)·2CH $_3$ OH: C, 43.32; H, 5.15; N, 4.21; S, 9.64. Found: C, 43.33; H, 5.13; N, 4.22; S, 9.64%. IR (KBr cm $^{-1}$): 1637 vs, 1588 vs, 1450 s, 1270 s, 1201 vs, 1047 vs, 785 w, 742 w, 600 m, 503 m.

2.4. X-ray crystallography

Single crystals were mounted on an Enraf-Nonius CAD-4 X-ray single-crystal diffractometer. All data were collected at 293(2) K with graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) in ω -2 θ scan mode. The structure was solved by direct methods using SHELXS-97 [26]. Nonhydrogen atoms were defined by the Fourier synthesis method. Positional and thermal parameters were refined by full matrix least-squares (on F^2) to convergence. A summary of the key crystallographic information is given in Table 1. The selected bond lengths and bond angles are listed in Table 2. The molecular structure and two-dimensional layer structure of the complex is shown in Fig. 1.

2.5. Catalysis experiment

Methylene blue (MB), rhodamine B (RhB) and methyl violet (MV) were selected as model organic dyes pollutants to investigate the photocatalytic activity of the Ni(II) complex at ambient temperature (298 K). A sample of the required complex (50 mg) was dispersed to a solution of MB, RhB, or MV in water (150 mL, 6 mg/L). Prior to irradiation, the solution containing organic dye and the complex was magnetically stirred in the dark for 30 min till an adsorption–desorption equilibrium was established. Then, the

Table 1
Crystal and X-ray experiment data details for the Ni(II) complex.

Parameter	Value
Empirical formula	C $_{24}$ H $_{34}$ N $_2$ O $_{12}$ S $_2$ Ni
Formula weight	665.36
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
a (Å)	9.2325(9)
b (Å)	17.2205(19)
c (Å)	18.6194(17)
α (°)	90
β (°)	100.697(2)
γ (°)	90
Volume (Å 3)	2908.8(5)
Z	4
Calculated density (g/cm 3)	1.519
Absorption coefficient (mm $^{-1}$)	0.875
$F(000)$	1392
Crystal size (mm)	0.45 × 0.40 × 0.33
θ range for data collection (°)	2.54 to 25.01
Limiting indices	$-10 \leq h \leq 10$ $-16 \leq k \leq 20$ $-22 \leq l \leq 22$
Reflections collected/unique	9816/2567 [$R_{\text{int}} = 0.0791$] 0.999
Completeness to $\theta = 25.02$	0.999
Max. and min. transmission	0.7612 and 0.6943
Data/restraints/parameters	2567/0/189
Goodness of fit on F^2	1.079
$R_1^a, wR_2^b [I > 2\sigma(I)]$	$R_1 = 0.0678$, $wR_2 = 0.1597$
R_1^a, wR_2^b (all data)	$R_1 = 0.0924$, $wR_2 = 0.1755$
Largest diff. peak and hole (e. Å 3)	0.618 and -0.442

Notes: $^a R = \sum(|F_o| - |F_c|) / \sum|F_o|$ $^b wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)]^{1/2}$.

Table 2
The selected bond length (Å) and angle (°) for the Ni(II) complex.

Bond	d, Å
Ni(1)–O(1)	2.024(3)
Ni(1)–O(1)#1	2.024(3)
Ni(1)–N(1)	2.048(4)
Ni(1)–N(1)#1	2.048(4)
Ni(1)–O(4)	2.084(4)
Ni(1)–O(4)#1	2.084(4)
C(3)–N(1)	1.287(6)
Angle	ω , deg
O(1)–Ni(1)–O(1)#1	93.2(2)
O(1)–Ni(1)–N(1)	97.15(15)
O(1)#1–Ni(1)–N(1)	88.08(15)
O(1)–Ni(1)–N(1)#1	88.08(15)
O(1)#1–Ni(1)–N(1)#1	97.15(15)
N(1)–Ni(1)–N(1)#1	172.04(15)
O(1)–Ni(1)–O(4)	172.04(15)
O(1)#1–Ni(1)–O(4)	93.99(15)
N(1)–Ni(1)–O(4)	86.42(15)
N(1)#1–Ni(1)–O(4)	87.72(15)
O(1)–Ni(1)–O(4)#1	93.99(15)
O(1)#1–Ni(1)–O(4)#1	172.04(15)
N(1)–Ni(1)–O(4)#1	87.72(15)
N(1)#1–Ni(1)–O(4)#1	86.42(15)
O(4)–Ni(1)–O(4)#1	79.0(2)

Symmetry transformations used to generate equivalent atoms:
#1 $-x+1, y, -z+1/2$.

mixture was illuminated under a 400 W Hg lamp and stirred continuously using a magnetic stirrer. The distance between the light source and reaction vessel was 30 cm. At given intervals, 5 mL of reaction solution was periodically taken from the reactor and

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