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Synthesis, characterization, crystal structure determination, computational study, and thermal decomposition into NiO nano-particles of a new $Ni^{II}L_2$ Schiff base complex (L = 2-{(E)-[2-chloroethyl)imino]methylphenolate)

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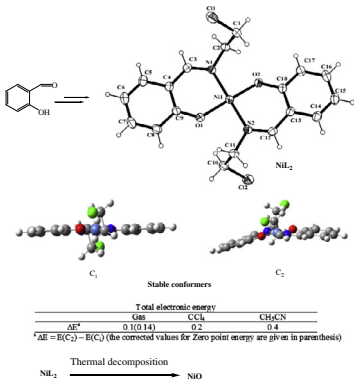
HIGHLIGHTS

- A new NiL_2 Schiff base complex was prepared.
- It was characterized by X-ray crystallography, CHN analysis and FT-IR spectra.
- The conformational analysis and molecular structures of NiL_2 were investigated.
- The results showed a small difference between the stability of them.
- Thermal decomposition of NiL_2 resulted in formation of the NiO nano-particles.

GRAPHICAL ABSTRACT



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ABSTRACT

The Nickel (II) Schiff base complex of NiL_2, (L = 2-{(E)-[2-chloroethyl) imino]methylphenolate) have been synthesized and characterized by elemental (CHN) analysis, UV–vis and FT-IR spectroscopy. The molecular structure of [NiL_2] was determined by single crystal X-ray diffraction technique. The Schiff base ligand HL acts as a chelating ligand and coordinates via one nitrogen atom and one oxygen atom to the metal center. The nickel (II) center is coordinated by two nitrogen and two oxygen atoms from two Schiff base ligands in an approximately square planar trans-[MN_2O_2] coordination geometry. Thermogravimetric analysis of NiL_2 showed that it decomposed in three stages. In addition, complex NiL_2 thermally decomposed in air at 660 °C and the XRD pattern of the obtained solid showed the formation of NiO nanoparticles with an average size of 43 nm. In addition, the conformational analysis and molecular structures of NiL_2 were investigated by means of density functional theory (DFT) calculations at B3LYP/6-311G* level and the calculated geometrical parameters were compared with the experimental results.

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Introduction

Schiff base complexes derived from substituted salicylaldehydes and various amines have been widely investigated because of versatility of their properties and functionalities, by choosing the appropriate amine precursors and ring substituent and their wide applicability [1–4]. Recently a large number of publications and studies, describing the synthesis of nickel (II) complexes with salicylaldehyde substituted Schiff-base ligands, are reported for their interesting structural applications and properties [5–10]. Schiff base ligands and complexes derived from substituted salicylaldehydes and amines containing alkyl halide pendant group are very rare. Recently we described the synthesis, characterization, crystal structure determination of some of them and their metal complexes [4,11–14]. In those researches we described the structural features of some of these ligands and their vanadyl complexes and the catalytic activity of complexes. The other activities such as medicinal and biological activities of the ligands and their complexes can be investigated. In this research we describe the synthesis, characterization, crystal structure determination, thermal study of a new nickel(II) Schiff base complex of [NiL_2] (Scheme 1), and improve understanding of conformational and structural information of the mentioned complex by means of density functional theory (DFT) studies. The calculated conformational analysis and geometrical parameters are compared with those observed experimentally.

Experimental

Physical techniques and materials

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and the results agreed with calculated values. UV–vis spectra were recorded by Perkin Elmer Spectrometer Lambda 25. The TG analysis was performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in air atmosphere with a heating rate of 20 °C/min in the temperature range 30–660 °C.

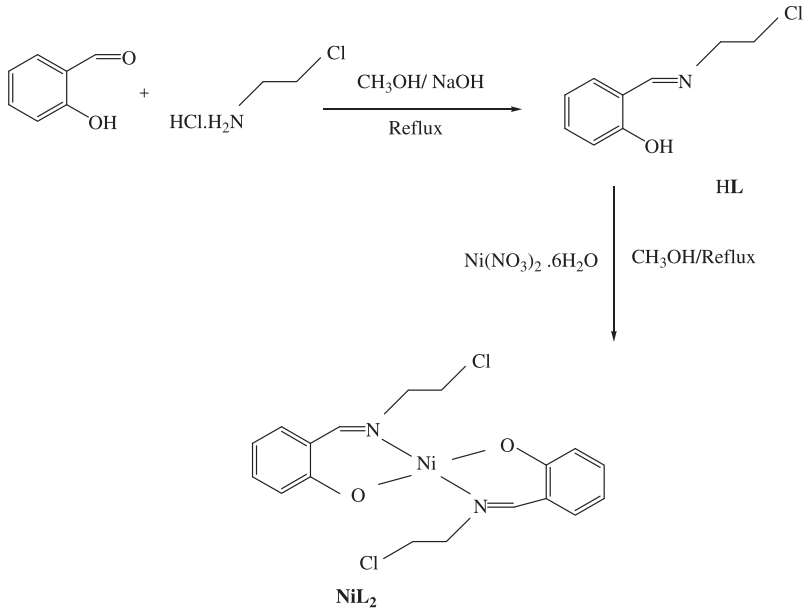
Table 1
Crystallographic data and experimental details for NiL_2.

	1
Chemical formula	$C_{18}H_{18}Cl_2NiN_2O_2$
Formula weight	423.95
Crystal system	Monoclinic
Space group	$P2_1/c$
T, K	296
a, Å	9.2030(12)
b, Å	10.6192(13)
c, Å	18.680(2)
β, deg	96.017(7)
V, Å^3	1815.5(4)
Z	4
μ, mm^{-1}	1.377
Measured reflections	64359
Independent reflections	3966
R_{int}	0.010
GOF on F^2	1.048
Number of parameters	226
F(000)	872
Theta range for data collection	2.19–27.00 deg
Limiting indices	$-11 \leqslant h \leqslant 11$ $-13 \leqslant k \leqslant 13$ $-23 \leqslant l \leqslant 23$
Goodness-of-fit on F^2	1.048
$R[F^2 > 2\sigma(F^2)]$	0.0301
$wR(F^2)$	0.0846
Largest diff. peak and hole	0.298 and −0.383 e.A^{-3}

Method of analysis

In this study, the conformational analysis and molecular structure of NiL_2 complex were computed with the Gaussian 09 W software system [15]. The stability of four possible conformers, their relative stability, the optimized geometrical parameters of the stable conformers (with C_i and C_2 symmetry) were calculated at the B3LYP level [16,17] of theory with the 6-311G* basis set. The zero point vibrational energy, ZPE, corrections were obtained at the B3LYP/6-311G* level, without applying any scaling.

Acetonitrile and carbon tetrachloride, as solvents with different polarities, were selected for studying the relative energy studying of two C_i and C_2 stable conformers of NiL_2 complex in solution



Scheme 1. Synthesis of NiL_2.