



# Synthesis, structural characterization and DFT calculation on a square-planar Ni(II) complex of a compartmental Schiff base ligand



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## ABSTRACT

Reaction of a symmetric compartmental Schiff-base ligand, (H<sub>2</sub>L) with nickel(II) perchlorate hexahydrate in 1:1 M ratio in methanol gives rise to a mononuclear nickel(II) compound, NiL (**1**). The compound has been characterized by C, H, N microanalyses and UV–Vis spectra. The single crystal X-ray diffraction studies reveal a square planar geometry around the Ni(II) center. The compound crystallizes in monoclinic system with space group C2/c with  $a = 21.6425(6)$ ,  $b = 9.9481(3)$ ,  $c = 13.1958(4)$  Å,  $\beta = 107.728(2)^\circ$ ,  $V = 2706.16(14)$  Å<sup>3</sup> and  $Z = 4$ . Ground state DFT optimization and TDDFT calculations on the ligand and complex were performed to get their UV–Vis spectral pattern.

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## 1. Introduction

Multidentate Schiff base ligands play a pivotal role in the development of coordination chemistry as they readily form sufficiently stable complexes with most of the transition metal ions [1–3]. For many years, Schiff base–transition metal complexes have received great attention of chemists [4] due to important roles they play in catalytic and enzymatic reactions, in magnetism, and also in therapeutic applications [5,6]. They are, once again, typical in connection with the self-assembled clusters [7]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [8,9] because of their ability to possess unusual configurations, structural lability and their sensitivity to molecular environments [10]. Amongst them, compartmental Schiff base ligands are enduring much more popularity due to their wide-range versatility and complexing ability [11].

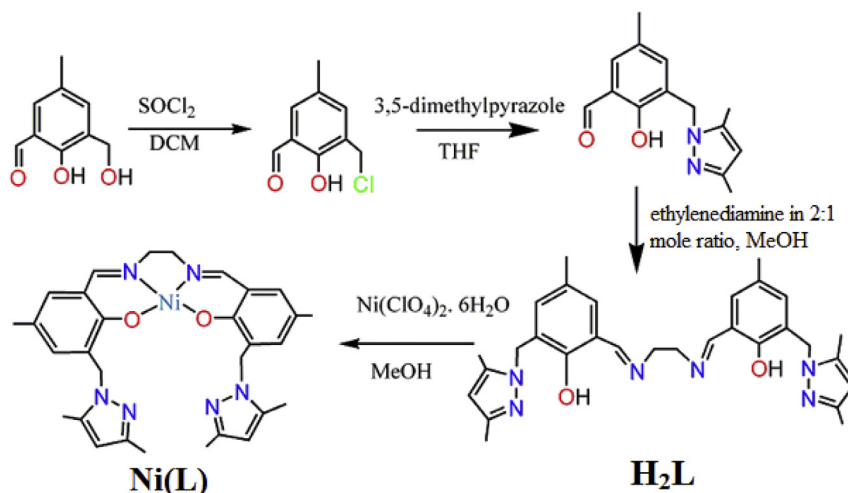
On the other hand, the chemistry of nickel complexes with multidentate Schiff base ligands has attracted much attention due to its ability to exhibit several oxidation states. Such complexes also play important roles in bioinorganic chemistry and redox enzyme

systems and provide the basis of modeling the active sites of biologically relevant systems or catalysts [12,13].

Metal-based supramolecular networks with different kind of non-covalent interactions like hydrogen bond,  $\pi$ – $\pi$  stacking etc. have prospective applications in the fields of host–guest chemistry, crystal engineering, biochemistry, electronics, optics, gas absorbent, catalysis and molecular recognition [14–20]. A large numbers of one-, two- and three-dimensional self-assembled metal–organic supramolecular solids were prepared by the careful selection of the building blocks and organic ligands with appropriate functional groups for supramolecular interactions [21–25]. The structural characteristics of organic ligands highly influence the self-assembly process in the supramolecular frameworks [26] and towards this end, metal complexes of Schiff bases derived from diformyl-*p*-cresol (dfc) with pendant pyrazole units have ample possibilities to form such supramolecular networks [27–31]. The pyrazole nitrogen, the oxygen atoms of phenol groups can act as hydrogen bond acceptors, and the  $\pi$  electron system of the pyrazole ring can participate in CH $\cdots$  $\pi$  interaction between ethylene hydrogen and  $\pi$ -electrons of pyrazole ring (CH $\cdots$ Cg). Having all the above mentioned potentials of the ligand in mind we have now synthesized and characterized the corresponding nickel(II) complex (**1**) of a two pyrazole appended highly symmetrical Schiff base ligand. In the present article we are describing the synthesis and structural

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Scheme 1. Synthesis of H<sub>2</sub>L and complex 1.

characterization of complex 1. It is interesting to note that there are some interesting non-covalent interactions that lead to 3D supra-molecular architecture.

## 2. Experimental

### 2.1. Materials and measurements

2-(chloromethyl)-6-carbaldehyde-4-methyl phenol was prepared by the reported method [32]. All reagents and solvents are commercially available. THF was dried using sodium metal and benzophenone and other solvents were used without further purification. Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. <sup>1</sup>H NMR were recorded in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> on a Bruker 300 MHz NMR Spectrophotometer using tetramethylsilane ( $\delta = 0$ ) as an internal standard. Electronic spectra were recorded on Agilent-8453 diode array UV–Vis spectrophotometer.

Table 1

Crystal data and structure refinement for the complex NiL (1).

CCDC No.	942787
Formula	C <sub>30</sub> H <sub>34</sub> N <sub>6</sub> O <sub>2</sub> Ni
Formula weight	569.32
Crystal system	Monoclinic
Space group	C2/c (No. 15)
a [Å]	21.6425 (6)
b	9.9481 (3)
c	13.1958 (4)
$\alpha$ [°]	90
$\beta$	107.728 (2)
$\gamma$	90
V [Å <sup>3</sup> ]	2706.16 (14)
Z	4
D(calc) [g/cm <sup>3</sup> ]	1.397
$\mu$ (MoK $\alpha$ ) [1/mm]	0.757
F(000)	1200
Temperature (K)	273
Radiation [Å] MoK $\alpha$	0.71073
$\theta$ Min–Max [°]	1.98, 25.76
Dataset	–26: 26; –12: 12; –16: 16
Tot., Uniq. Data, R(int)	19615, 2595, 0.028
Observed data [I > 2.0 $\sigma$ (I)]	2284
N <sub>ref</sub> , N <sub>par</sub>	2595, 188
R, wR <sub>2</sub> , S	0.0383, 0.1666, 0.959

**Caution!** Perchlorate salts of metal complexes can be explosive. Although no detonation tendencies have been observed, care is advised and handling of only small quantities is recommended.

### 2.1.1. Preparation of ligand

**2.1.1.1. Synthesis of pro-ligand 2-formyl-4-methyl-6-[3, 5-dimethyl pyrazole]phenol.** 2-chloromethyl-6-carbaldehyde-4-methyl phenol (1.52 g, 8.2 mmol) was dissolved in 15 ml dry THF in a round bottom flask. 0.7883 g (8.2 mmol) 3,5-dimethyl pyrazole and 1.659 g (16.4 mmol) triethylamine (Et<sub>3</sub>N) were dissolved in 5–10 ml dry THF separately. Then later solution was added to the previous one and this mixture was further added dropwise to the 2-chloromethyl-6-carbaldehyde-4-methyl phenol solution. An instant precipitation of Et<sub>3</sub>NHCl was observed and the color of the solution turned bright yellow. After 24 h of stirring the precipitate was filtered off. The solvent (THF) was removed from the filtrate under reduced pressure. After few days under vacuum a light yellow coloured solid was obtained [Scheme 1]. <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 300 MHz):  $\delta$  in ppm 2.23–2.28 (9 H, m, -CH<sub>3</sub>), 5.27 (2H, s, -CH<sub>2</sub>), 5.88 (1H, s, -pyH), 7.09 (1H, s, -ArH), 7.27 (1H, s, -ArH), 7.28 (1H, s, -ArH), 9.88 (1H, s, -CHO), 11.23 (1H, brs, -ArOH) (Fig. S2).

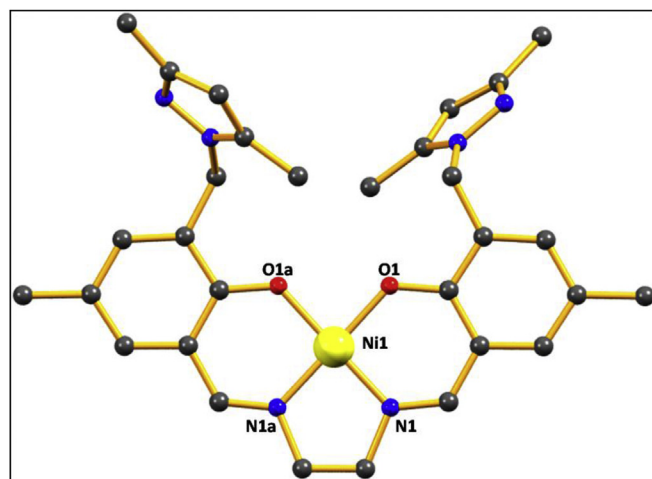


Fig. 1. Molecular view of complex 1, H-atoms are omitted for clarity.

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