



# A molecular butterfly: Self-assembly of an imidazolate bridged tetranuclear nickel(II) compound from Ni(II) and 3-(4-methylimidazol-5-yl)methylenehydrazonobutan-2-one oxime

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## ABSTRACT

Reaction of the Schiff-base ligand, 3-(4-methylimidazol-5-yl)methylenehydrazonobutan-2-one oxime ( $H_2L$ ) with nickel(II) perchlorate hexahydrate in 1:1 molar proportion in methanol gives rise to a tetranuclear nickel(II) compound,  $Ni_4L_4$  (**1**) in moderate yield. The compound has been characterized by C, H, N microanalyses, FT-IR, UV-Vis spectra and room temperature magnetic susceptibility measurements. The X-ray crystal structure of the title compound has been determined. The structure reveals that it is an imidazolate bridged neutral tetranuclear nickel(II) compound. The nickel(II) centers in **1** adopt a rare 'butterfly-like' topology. The compound crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 17.648$  (4),  $b = 23.209$  (5),  $c = 14.418$  (3) Å,  $\beta = 108.708$  (2)°,  $V = 5593$  (2) Å<sup>3</sup> and  $Z = 4$ . Individual nickel(II) center is in square-planar 'N<sub>4</sub>' coordination chromophore. Electrochemical studies show Ni(II) to Ni(III) oxidation along with Ni(II) to Ni(I) reduction in dichloromethane solution. Bond-Valence Sum (BVS) model calculation was performed to assign the oxidation state of each nickel center in **1**.

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## 1. Introduction

Metal ions occurring usually in metalloproteins are bound to a specific amino acid residue of the peptide backbone like the imidazole group of the amino acid histidine. This forms all or part of the binding sites of various transition metal ions like nickel(II), copper(II) or zinc(II) in a good number of metalloproteins [1–4]. Copper-imidazole interactions are well known in biological systems [5,6]. One of the most widely studied systems is the Cu–Zn superoxide dismutase (Cu–Zn SOD) [7–11]. The conjugate base ( $Im^-$ ) of imidazole ( $ImH$ ) is present as a bridging ligand between copper(II) and zinc(II) in Cu–Zn SOD that catalyses the disproportionation of the lethal superoxide radical anion. In order to mimic them many model compounds have been synthesized [12–16]. Attempts have been taken to synthesize low molecular weight copper complexes with imidazole and imidazolate ( $Im^-$ ) containing tailored ligands. It appears from the model studies that imidazole can bind metal centers through different modes. The most common is the pyrrole-like monodentate mode via N<sup>3</sup> (IUPAC convention) nitrogen [17,18]. This has been extensively studied with histidine/histamine containing di-, tri-, or oligopeptide in presence of copper(II),

nickel(II), cobalt(II) and zinc(II) ions [17,18]. In some rare cases it acts as a bidentate bridging ligand between a pair of metal centers via N<sup>3</sup> and deprotonated N<sup>1</sup> (pyrrole-like) nitrogens<sup>1</sup>. Herein we report the synthesis, characterization, structure and redox behavior of a cyclic tetrameric neutral nickel(II) compound having bridging bidentate imidazole moiety via N<sup>3</sup> and deprotonated N<sup>1</sup> nitrogens. A Bond-Valence Sum (BVS) model calculation was also performed to assign the oxidation state of each nickel center in the present compound.

## 2. Experimental

### 2.1. Materials and measurements

All chemicals were of analytical reagent grade and used without further purification. 4-Methylimidazole-5-carboxaldehyde and diacetyl-monoxime were procured from Sigma–Aldrich Chemicals Pvt. Ltd., C, H and N microanalyses were performed by a Perkin–Elmer 2400II elemental analyser. FTIR spectra (KBr disc) were recorded in the range 4000–400 cm<sup>-1</sup> on a Shimadzu FTIR-8400S spectrophotometer. UV-Vis spectra (in dichloromethane) were recorded on a Shimadzu UV-160A spectrophotometer. Nickel was estimated gravimetrically as its dimethylglyoximate complex. Cyclic voltammetric (CV) experiments were performed under nitrogen in dry and degassed dichloromethane on a BAS Epsilon electrochemical

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workstation at 293 K. The conventional three-electrode assembly is comprised of a BAS Glassy Carbon (GC) working electrode, a platinum-wire auxiliary electrode and an Ag/AgCl reference electrode. The supporting electrolyte is *n*-Et<sub>4</sub>NClO<sub>4</sub> (0.1 M). Magnetic susceptibility was determined at 305 K with a PAR 155 vibrating sample magnetometer. The magnetometer was calibrated with Hg[Co(SCN)<sub>4</sub>].

**Caution!** Perchlorate salts of metal complexes can be explosive [19]. Although no detonation tendencies have been observed, care is advised and handling of only small quantities recommended.

### 2.1.1. Preparation of ligand 3-(4-methylimidazol-5-yl) methylene hydrazonobutan-2-one oxime (H<sub>2</sub>L)

The above ligand was prepared and characterized following a procedure reported earlier by us [20].

### 2.1.2. Synthesis of Ni<sub>4</sub>L<sub>4</sub> (1)

Fifty milligram (0.24 mmol) of H<sub>2</sub>L was dissolved in 15 ml methanol to get a clear yellow solution. Then 20 mg (0.24 mmol) of solid sodium acetate was added to dissolve in it. After this 89 mg (0.24 mmol) of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolved in 3 ml methanol was added dropwise to this solution. The yellow solution gradually turned into deep reddish brown and the resulting reaction mixture was left in air for slow evaporation. After 48 h the precipitated brown compound so formed was filtered and washed thoroughly with diethyl ether. Then it was dried in a vacuum desiccator over fused CaCl<sub>2</sub>. The crude product was recrystallized from dichloromethane. The compound was soluble in dichloromethane, methanol but insoluble in petroleum ether (40–60 °C), *n*-hexane, propane and diethyl ether. Yield: 26 mg (42%). *Anal. Calc.* for C<sub>36</sub>H<sub>44</sub>N<sub>20</sub>Ni<sub>4</sub>O<sub>4</sub>: C, 40.94; H, 4.20; N, 26.54; Ni, 22.23. Found: C, 40.89; H, 4.26; N, 26.48; Ni, 22.31%. FTIR (KBr) ν[cm<sup>-1</sup>]: 3422 (br) [ν(OH)], 1607 (s) [ν(C=N)], 1342 (s) [ν(N–O)]. UV–Vis (DCM): λ<sub>max</sub> [nm] (ε<sub>max</sub> [dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]): 568 (5, 394), 403 (19, 033), 320 (68, 911), 231 (66, 333). μ<sub>eff</sub>/μ<sub>B</sub>: Diamagnetic.

### 2.2. Crystal structure determination

Shining red rectangular single crystals suitable for X-ray crystallography were grown by direct diffusion of a moderately concentrated dichloromethane solution of the compound in *n*-hexane. Single crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Intensity data were collected at 298 (2) K for **1** on a Bruker Smart Apex II diffractometer equipped with 1 K CCD instrument by using a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Cell parameters were determined using SMART software [21]. Data reduction and corrections were performed using SAINTPLUS [21]. Absorption corrections were made via SADABAS [22]. The structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least-squares methods on all F<sup>2</sup> data with SHELXL-97 [22]. The non-H atoms were refined anisotropically. Hydrogen atoms attached with C atoms were added theoretically and treated as riding on the concerned atoms. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Large void spaces with this account in total for 1745.2 Å<sup>3</sup> per unit cell, i.e. some 31.2% of the total volume, were examined using PLATON [23]. The reflection data were subjected to the SQUEEZE routine in PLATON before the final refinement and this suggested the presence of 150 electrons per unit cell within the voids, but we failed to define some solvent molecules. A summary of data collection, structure refinement for **1** is given in Table 1. Selected bond lengths, bond angles and hydrogen-bond geometry are given in Tables 2 and 3 (supplementary data).

## 3. Results and discussion

### 3.1. Synthesis and formulation

The ligand employed for the present work is H<sub>2</sub>L, a Schiff-base condensate (Scheme 1). It is prepared from a 1:1 molar condensation of diacetyl-monoxime monohydrazone with 4-methylimidazole-5-carboxaldehyde in methanol. For quite some time we were working to develop the copper(II) chemistry with this ligand [20].

In our attempt to generate polynuclear nickel(II) compound out of this ligand, we have reacted equimolar proportion of H<sub>2</sub>L with nickel(II) perchlorate hexahydrate in methanol in presence of a base, sodium acetate to isolate the title Ni(II) compound (**1**) in moderate yield (Scheme 1). The imidazolate bridged tetranuclear nickel(II) compound, Ni<sub>4</sub>L<sub>4</sub> is neutral. The ligand acts in a tetradentate and bianionic mode.

Convincing support for the presence of a bridged imidazolate moiety between any two nickel centers is given by the absence of a ν(N–H) stretching band in the IR spectrum of **1**. However, the NH-stretching vibration is discernable at 3250 cm<sup>-1</sup> in the IR spectrum of the free ligand, H<sub>2</sub>L.

### 3.2. Molecular structure of Ni<sub>4</sub>L<sub>4</sub> (1)

The molecular structure and the atom labeling scheme for **1** is shown in (Fig. 1), which provides confirming evidence in support of their imidazolate (Im<sup>-</sup>) bridged discrete tetranuclear structure. Selected metrical parameters of this structure is summarized in Table 2. The neutral Ni complex in **1**, crystallizes in the monoclinic space group with four molecular weight units accommodated per cell.

**Table 1**  
Crystal data and structure refinement for the complex Ni<sub>4</sub>L<sub>4</sub> (**1**).

CCDC No.	835052
Empirical formula	C <sub>36</sub> H <sub>44</sub> N <sub>20</sub> O <sub>4</sub> Ni <sub>4</sub>
Color/shape	red/rectangular
Formula weight	1055.75
T (K)	298 (2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Crystal size (mm)	0.26 × 0.21 × 0.17
Space group	P2 <sub>1</sub> /c
<i>Unit cell dimensions</i>	
a (Å)	17.648 (4)
b (Å)	23.209 (5)
c (Å)	14.418 (3)
β (°)	108.708 (2)
V (Å <sup>3</sup> )	5593 (2)
Z	4
P <sub>calcd.</sub> (g/cm <sup>3</sup> )	1.254
Absorption coefficient (mm <sup>-1</sup> )	1.376
F(000)	2176
θ Range for data collection	1.22° < θ < 25.00°
Index ranges	−19 < h < 20; −27 < k < 27; −17 < l < 17
Reflections collected	75334
Independent reflections	9859 [R <sub>int</sub> = 0.1351]
Completeness to θ	100% (θ = 25.00)
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.7997 and 0.7161
Refinement method	full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	9859/0/589
Goodness-of-fit on F <sup>2</sup>	0.978
R <sub>1</sub> , all data, R <sub>1</sub> [I > 2σ(I)]	0.0705, 0.1161
wR <sub>2</sub> , all data, wR <sub>2</sub> [I > 2σ(I)]	0.2076, 0.2304
Largest difference peak and hole (e Å <sup>-3</sup> )	1.374 and −0.546

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