



# 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 ‘ $N_4$ ’ 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  $N^3$  (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  $N^3$  and deprotonated  $N^1$  (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  $N^3$  and deprotonated  $N^1$  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  $cm^{-1}$  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)  $\nu$ [cm<sup>-1</sup>]: 3422 (br) [ $\nu$ (OH)], 1607 (s) [ $\nu$ (C=N)], 1342 (s) [ $\nu$ (N–O)]. UV–Vis (DCM):  $\lambda_{\text{max}}$  [nm] ( $\epsilon_{\text{max}}$  [dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]): 568 (5, 394), 403 (19, 033), 320 (68, 911), 231 (66, 333).  $\mu_{\text{eff}}/\mu_{\text{B}}$ : 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 K $\alpha$  radiation ( $\lambda$  = 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  $\nu$  (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.

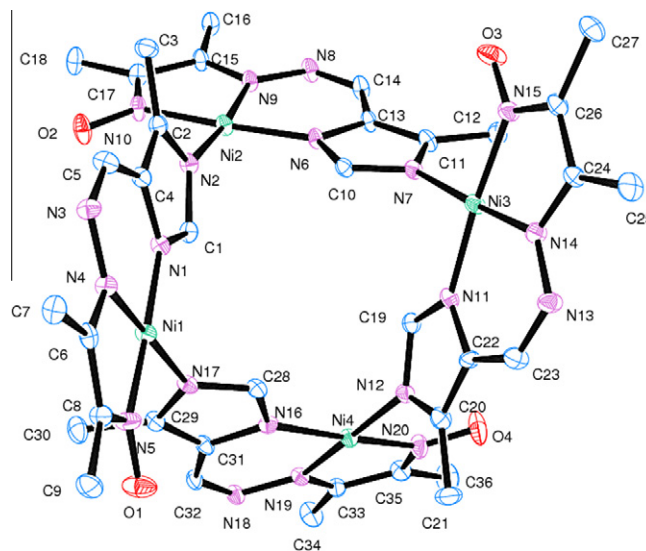
**Table 1**  
Crystal data and structure refinement for the complex Ni<sub>4</sub>L<sub>4</sub> (**1**).

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
<i>T</i> (K)	298 (2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Crystal size (mm)	0.26 × 0.21 × 0.17
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	17.648 (4)
<i>b</i> (Å)	23.209 (5)
<i>c</i> (Å)	14.418 (3)
$\beta$ (°)	108.708 (2)
<i>V</i> (Å <sup>3</sup> )	5593 (2)
<i>Z</i>	4
<i>P</i> <sub>calcd.</sub> (g/cm <sup>3</sup> )	1.254
Absorption coefficient (mm <sup>-1</sup> )	1.376
<i>F</i> (000)	2176
$\theta$ Range for data collection	1.22° < $\theta$ < 25.00°
Index ranges	−19 < <i>h</i> < 20; −27 < <i>k</i> < 27; −17 < <i>l</i> < 17
Reflections collected	75334
Independent reflections	9859 [ <i>R</i> <sub>int</sub> = 0.1351]
Completeness to $\theta$	100% ( $\theta$ = 25.00)
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.7997 and 0.7161
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	9859/0/589
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.978
<i>R</i> <sub>1</sub> , all data, <i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0705, 0.1161
<i>wR</i> <sub>2</sub> , all data, <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.2076, 0.2304
Largest difference peak and hole (e Å <sup>-3</sup> )	1.374 and −0.546

**Table 2**  
Selected bond distances (Å) and angles (°) for **1**.

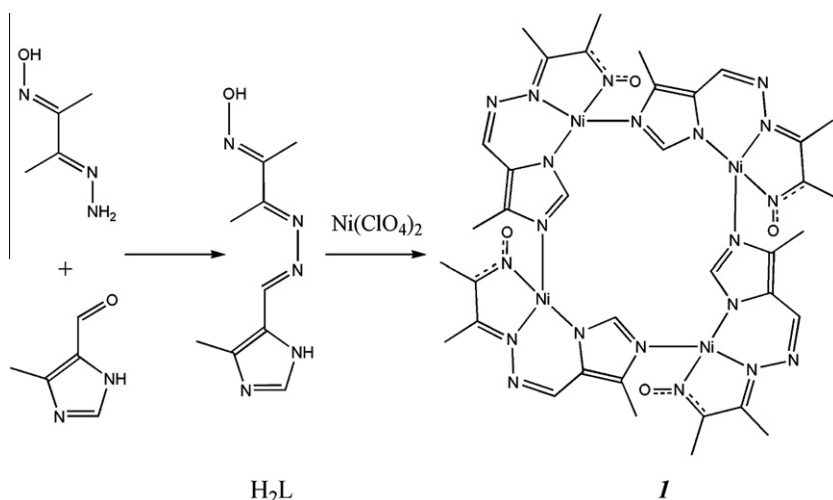
Ni1–N5	1.864 (6)	Ni1–N4	1.869 (5)
Ni1–N1	1.871 (5)	Ni1–N17	1.912 (5)
Ni2–N9	1.876 (5)	Ni2–N10	1.885 (6)
Ni2–N6	1.880 (5)	Ni2–N2	1.903 (5)
Ni3–N15	1.882 (6)	Ni3–N11	1.883 (5)
Ni3–N14	1.874 (6)	Ni3–N7	1.918 (5)
Ni4–N19	1.879 (5)	Ni4–N20	1.872 (6)
Ni4–N12	1.882 (5)	Ni4–N16	1.896 (5)
N1–C1	1.330 (7)	N1–C4	1.392 (8)
N3–C5	1.278 (8)	N3–N4	1.390 (7)
N4–C6	1.339 (8)	N5–O1	1.258 (7)
C2–C4	1.389 (9)	C4–C5	1.435 (8)
C6–C8	1.394 (9)	C6–C7	1.499 (8)
C8–C9	1.462 (9)	C1–N2	1.335 (8)
C2–N2	1.387 (8)	C2–C3	1.451 (9)
Ni1–Ni4	5.8238 (16)	Ni1–Ni2	5.8445 (15)
Ni1–Ni3	6.5938 (17)	Ni2–Ni3	5.7886 (15)
Ni2–Ni4	6.6808 (17)	Ni3–Ni4	5.7834 (15)
N5–Ni1–N4	83.2 (2)	N4–Ni1–N1	92.9 (2)
N5–Ni1–N1	176.1 (2)	N4–Ni1–N17	174.1 (2)
N5–Ni1–N17	92.3 (2)	N1–Ni1–N17	91.6 (2)
N9–Ni2–N6	92.5 (2)	N10–Ni2–N2	91.8 (2)
N10–Ni2–N6	175.5 (2)	N9–Ni2–N2	173.1 (3)
N6–Ni2–N2	92.6 (2)	N9–Ni2–N10	83.1 (2)
N15–Ni3–N11	175.0 (3)	N14–Ni3–N7	174.4 (3)
N11–Ni3–N14	92.6 (3)	N15–Ni3–N7	92.8 (3)
N11–Ni3–N7	91.5 (2)	N15–Ni3–N14	83.4 (3)
N19–Ni4–N20	83.2 (3)	N19–Ni4–N12	175.2 (2)
N20–Ni4–N12	93.0 (3)	N20–Ni4–N16	173.3 (3)
N19–Ni4–N16	92.3 (2)	N12–Ni4–N16	91.3 (2)
C1–N1–C4	103.7 (6)	C1–N1–Ni1	132.0 (5)
C4–N1–Ni1	124.3 (4)	C1–N2–C2	107.1 (5)
C5–N3–N4	118.1 (5)	C6–N4–N3	115.0 (5)
C6–N4–Ni1	113.1 (5)	O1–N5–C8	119.7 (6)
O1–N5–Ni1	124.7 (5)	C8–N5–Ni1	115.7 (5)

The complex in **1** contains four tetradentate bianionic ligands,  $L^{2-}$  and four Ni(II) centers. The individual metal centers are planar, tetra-coordinated with  $N_4$  donor sites. Each bianionic form of the oxime based ligand ( $H_2L$ ) offers four N atoms as donors to a Ni center – two N (each of oximino and imino), one imine nitrogen from the imidazolate moiety ( $N^3$  as per IUPAC convention)<sup>1</sup> and the remaining from the rarely deprotonated amine nitrogen ( $N^1$  as per IUPAC convention) of the imidazolate residue. The tetraaza-coordination around each Ni center is satisfied from the donation of three nitrogens (oximino, imino and  $N^1$ ) from a ligand while a  $N^3$  atom from an adjacent ligand molecule completes the fourth



**Fig. 1.** The structure of  $Ni_4L_4$  (**1**) with ellipsoids at 30% probability.

coordination. The bond lengths of all the Ni–N bonds (Table 2) are nearly equal and are in the range of 1.864 (6)–1.918 (5) Å. The average Ni–N (oximino), Ni–N (imino), Ni– $N^1$  (deprotonated imidazolate amino) and Ni– $N^3$  (imino nitrogen of the imidazolate moiety of the adjacent ligand) bond lengths are 1.876, 1.875, 1.883 and 1.904 Å, respectively. Individual Ni centers have square-planar geometry. For example, the trans angles N1–Ni1–N5 [176.1 (2)°] and N4–Ni1–N17 [174.1 (2)°] are close to linearity (Table 2) and the Ni1 atom is also displaced marginally by 0.036 (3) Å (0.036 (3), 0.010 (3) and 0.066 (3) Å for Ni2, Ni3 and Ni4, respectively) from the least-square plane through N5, N17, N1 and N4 atoms. Corresponding metrical parameters are almost the same around the Ni2, Ni3 and Ni4 centers. Again, the sum of all four bond angles around each Ni(II) center is almost 360°. For Ni4, the four angles around it are N16–Ni4–N12 = 91.3 (2)°, N16–Ni4–N19 = 92.3 (2)°, N19–Ni4–N20 = 83.2 (2)° and N20–Ni4–N12 = 93.0 (3)°. Here, the sum of the four bond angles is 359.8°, a value quite close to 360°. Equivalent is the situation for Ni1 (360°), Ni2 (360°) and Ni3 (360.3°). This also hints at the square-planar coordination disposition around individual Ni(II) center. In order to estimate the geometric shape of individual nickel center in **1**, the Addison angular



**Scheme 1.** Synthesis of  $H_2L$  and complex **1**.

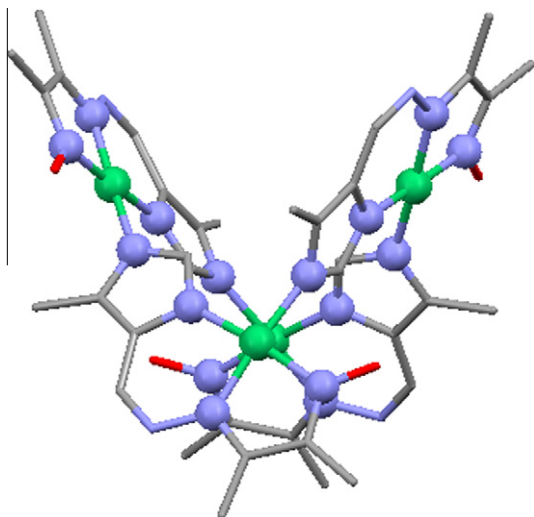


Fig. 2. View of **1** highlighting the 'butterfly-like' topology of the four nickel centers.

structural parameter ( $\tau$ ) has also been calculated [24,25]. For four-coordinate complexes the parameter,  $\tau_4$  is defined as  $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$ , where  $\alpha$  and  $\beta$  are the largest bond angles in the complex. For four-coordinated complexes a perfect square-planar geometry leads to  $\tau_4 = 0$  and a tetrahedral geometry to  $\tau_4 = 1$  [25]. For example, taking  $\text{Ni1} \cdots \text{Ni2} = 175.2^\circ$  ( $\alpha$ ) and  $\text{Ni2} \cdots \text{Ni4} = 173.3^\circ$  ( $\beta$ ), the  $\tau_4$  parameter for Ni4 center comes out to be 0.081. This value is close to 0. Thus Ni4 center adopts a square-planar disposition around the coordinating nitrogen atoms. Similar calculations on Ni1, Ni2 and Ni3 give rise to  $\tau_4$  values of 0.069, 0.081 and 0.075 respectively. The adoption of this geometry is also reflected in the magnetic susceptibility measurements of the bulk compound at 305 K. The compound is essentially diamagnetic. The C–N and N–O distances for the oxime moieties are in the ranges 1.324 (8)–1.339 (8) and 1.258 (7)–1.277 (6) Å, respectively. The Ni centers in **1** are separated by ( $\text{Ni1} \cdots \text{Ni2}$ , 5.8445 (15);  $\text{Ni2} \cdots \text{Ni3}$ , 5.7886 (15);  $\text{Ni3} \cdots \text{Ni4}$ , 5.7834 (15) and  $\text{Ni4} \cdots \text{Ni1}$ , 5.8238 (16) Å), and the included angles are [ $\text{Ni1} \cdots \text{Ni2} \cdots \text{Ni3}$ ,  $69.95^\circ$ ;  $\text{Ni2} \cdots \text{Ni3} \cdots \text{Ni4}$ ,  $68.97^\circ$ ;  $\text{Ni3} \cdots \text{Ni4} \cdots \text{Ni1}$ ,  $70.54^\circ$ ; and  $\text{Ni4} \cdots \text{Ni1} \cdots \text{Ni2}$ ,  $60.09^\circ$ ]. The four nickel centers are arranged likely in the form of a “butterfly” with the  $\text{Ni1} \cdots \text{Ni2} \cdots \text{Ni4}$  and  $\text{Ni2} \cdots \text{Ni3} \cdots \text{Ni4}$  planes forming the ‘wings’ of the butterfly (Fig. 2). The dihedral angle between these two planes is  $87.8 (1)^\circ$ . The topology of a  $\text{Ni}_4$  cluster can be manifold. The most common topology of the metal ions in  $\text{Ni(II)}$  complexes is cubane [26–31]. Face-shared distorted dicubanes having one missed corner from each cubane, however, are also known [32–34]. There are few  $\text{Ni}_4$  clusters in which the metal ions adopt less common topologies like linear [35], rectangular [36–38] and chair or butterfly-like ‘out-of-plane’ [39,40]. Our situation can be compared to a diamagnetic square-planar  $\text{Ni}_4$  cluster where the bridging ligand is also a deprotonated imidazolate ( $\text{Im}^-$ ) moiety [1]. Here also the neutral tetranuclear  $\text{Ni(II)}$  assembly assumes a rare ‘butterfly-like’ topology like ours. The distance between the centroids of any two imidazolate rings in **1** lie in the range 4.3–6.0 Å. For imidazole-imidazole ( $\pi \cdots \pi$ ) stacking interactions to be significant, the maximum limiting distance between the two aromatic moieties is set to be 3.6 Å [41]. Thus based on the distance criterion alone, this type of interaction is said to be non-operative here. Again, a classic H-bond is not present here; only weak  $\text{C} \cdots \text{N}(\text{O})$  H-bond can be observed (Fig. 3).

In dichloromethane, **1** displays a medium intensity band at 403 nm in the form of a shoulder due to the spin-allowed transition  $^1A_1 \rightarrow ^1A_2$ , typical of a square-planar  $d^8$  species [41]. The second ligand-field band at 568 nm is designated as  $^1A_{1g} \rightarrow ^1B_{1g}$ . Neutral nickel(II) complexes with square-planar geometry exhibit relatively weak features in the region 500–650 nm expected for ligand-field transitions of planar  $\text{Ni(II)}$  chromophore [42].

### 3.3. Electrochemistry

The electrochemical properties of the tetranuclear  $\text{Ni(II)}$  compound, **1**, have been studied in dichloromethane at GC electrodes under  $\text{N}_2$  atmosphere. On the positive side of the Ag–AgCl reference electrode, **1**, exhibits one anodic wave in dichloromethane with an  $E_{1/2}$  value of +1.06 V versus Ag–AgCl (Fig. 4). The corresponding cathodic response is absent in the subsequent reverse cycle. Thus this process is irreversible [43]. The ligand,  $\text{H}_2\text{L}$ , is electrochemically inert in the potential range of interest here. Thus this oxidation can safely be assigned as metal centered. Comparison of the voltammetric peak current with those of the ferrocene–ferrocenium couple (0.44 V versus Ag/AgCl) under the same experimental condition establishes that the present oxidative response in **1** involves four electrons. So, the oxidation at +1.06 V versus Ag–AgCl corresponds to  $\text{Ni}^{2+} \cdots \text{Ni}^{3+}$  oxidation. This observed value of the  $\text{Ni}^{3+} \cdots \text{Ni}^{2+}$  electrode potential is comparable to those reported for  $\text{Ni(II)}$  tetraazamacrocyclic complexes with mixed N(amide) N(amine) environments [44].

Our nickel compound, **1**, again exhibits one electrochemical response on the negative side of the Ag–AgCl electrode at  $-1.37$  V versus Ag–AgCl. This can be assigned as  $\text{Ni(II)}$  to  $\text{Ni(I)}$  reduction.

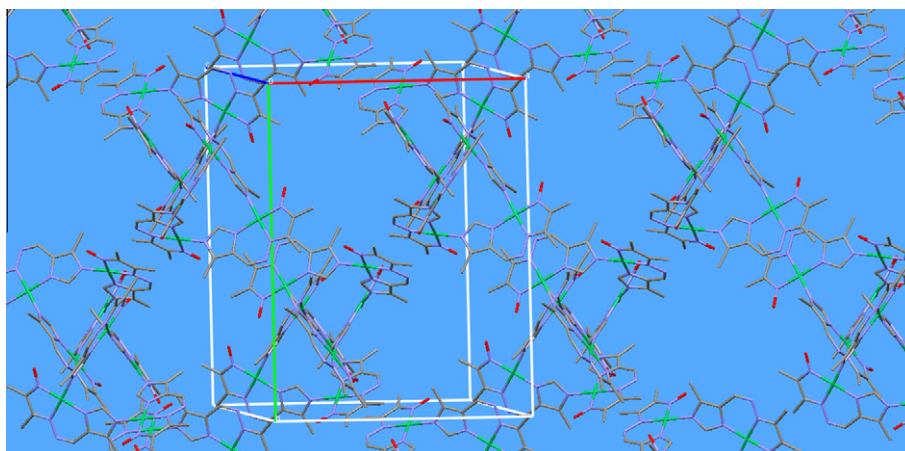
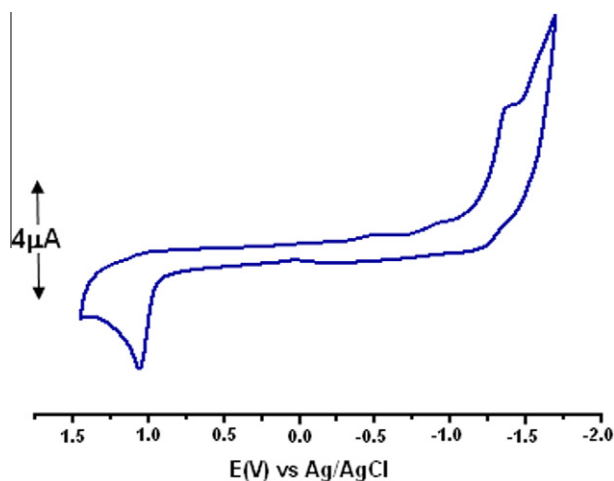


Fig. 3. Packing of  $\text{Ni}_4\text{L}_4$  (**1**) with large voids (31.2%).





**Fig. 4.** CV of  $\text{Ni}_4\text{L}_4$  (**1**) in dichloromethane at a scan rate of  $100 \text{ mV s}^{-1}$ . Analyte concentration was  $0.57 \times 10^{-3} \text{ (M)}$ .

**Table 4**  
Cyclic voltammetric data for **1**.

Ni(II) → Ni(III)				Ni(II) → Ni(I)		
Compound	$E_{\text{pa}}$	$E_{\text{pc}}$	$E_{1/2}$	$E_{\text{pa}}$	$E_{\text{pc}}$	$E_{1/2}$
$\text{Ni}_4\text{L}_4$	+1.06	0	+1.06(i)	−1.35	−1.37	−1.36(qr)
$[\text{Ni}_2\text{L}'](\text{PF}_6)_4^{\text{a}}$	+1.43	+1.30	+1.37(qr)	−1.33	−1.38	−1.36(r)
$[\text{Ni}_2\text{L}''](\text{PF}_6)_4^{\text{a}}$	+1.49	0	+1.49(i)	−1.27	−1.35	−1.31(qr)

i = irreversible, qr = quasi-reversible, r = reversible,  $E_{\text{pa}}$  = anodic peak potential in V,  $E_{\text{pc}}$  = cathodic peak potential in V,  $E_{1/2} = 0.5 (E_{\text{pa}} + E_{\text{pc}})$  V vs. Ag/AgCl.

<sup>a</sup> Ref. [44].

The corresponding cathodic peak current,  $i_{\text{pc}}$  is  $46.9 \mu\text{A}$ . Subsequent anodic response in the reverse cycle can be discernable at  $-1.35 \text{ V}$  versus Ag–AgCl with an anodic peak current,  $i_{\text{pa}}$  of  $10.6 \mu\text{A}$ . The electrochemical data are tabulated in Table 4. The ratio of  $i_{\text{pc}}$  to  $i_{\text{pa}}$  is 4.42. This value is in considerable deviation from unity. The cathodic peak current,  $i_{\text{pc}}$ , increases with the square root of the scan rate ( $v^{1/2}$ ), but not in proportionality. Again, the cathodic peak potential,  $E_{\text{pc}}$ , shifts more negatively with the increase in sweep rate,  $v$ . Judged on these criteria, the metal centered reduction for **1** is said to be quasi-reversible in nature [43].

### 3.4. BVS analysis

In order to delve into the oxidation state of each nickel center, we have taken recourse to the calculation based on Bond-Valence Sum (BVS) method [45–49]. In this method, the valences of a bond between two atoms  $i$  and  $j$  is related by an empirical expression (1).

$$S_{ij} = \exp[(r_0 - r_{ij})/0.37] \quad (1)$$

where  $r_{ij}$  is the length of the bond (expressed in Å), and  $r_0$  is a parameter, characteristic of the bond. This  $r_0$ , known as bond valence parameter, is however geometry and coordination number specific. The oxidation number  $N_i$  of the atom  $i$  is simply the algebraic sum of these 's' values of all the bonds ( $n$ ) around the atom,  $i$  (2)

$$N_i = \sum_{j=1}^n S_{ij} \quad (2)$$

This  $N_i$  is known as the BVS of the  $i$ th atom. Thus if  $r_0$  is known for a particular bond type, the BVS can be calculated from the crystallo-

graphically determined  $r_{ij}$  values. To find out  $r_0$ , earlier Datta et al. [50] in 1995 had solved Eq. (3) for  $r'_0$  akin to (2).

$$N_i = \sum_{j=1}^n S_{ij} = \sum_{j=1}^n \exp[(r'_0 - r_{ij})/0.37] \quad (3)$$

To find out  $r'_0$ , a good number of crystallographically determined structures were considered for an atom environment where the chemically equivalent ligands are attached to the target atom. In doing so, steric strain arising due to bulky groups around the donor atoms were carefully excluded. The  $r'_0$  values thus obtained were then averaged to get the best fit value of  $r_0$ . It is pertinent to note that a reliable  $r_0$  value is the outcome of the large number of such judiciously selected structures employed for averaging  $r'_0$ . In this endeavor, a value of  $1.673 \text{ Å}$  for  $r_0$  comes out for a  $\text{Ni}^{2+}$ –N bond [50]. We have taken this value for  $r_0$  to find out the BVS values of all the four nickel centers employing Eq. (1) in our present calculation. Taking the crystallographically determined bond lengths in Å of four Ni–N bonds for each nickel center, the BVS comes out as 2.294, 2.250, 2.232 and 2.272 valence units for Ni1, Ni2, Ni3 and Ni4 respectively (Table 5 as supplementary data). The calculated average BVS value for nickel in our compound **1** is 2.262 valence units. This result is close to the error limit of  $\pm 0.250$  as proposed earlier by Thorp [51,52]. Thus an oxidation number of +2 can safely be assigned to each nickel center in (**1**) computationally.

## 4. Conclusions

Here we have synthesized and structurally characterized a neutral tetranuclear nickel(II) compound from an oxime based ligand, 3-(4-methylimidazol-5-yl)methylenehydrazonobutan-2-one oxime ( $\text{H}_2\text{L}$ ). The X-ray crystal structure of the cyclic tetrameric nickel(II) compound,  $[\text{Ni}_4\text{L}_4]$  (**1**), reveals that imidazolate bridged individual nickel(II) centers in **1** is in square-planar 'N<sub>4</sub>' coordination chromophore. The nickel(II) centers in **1** assume a rare 'butterfly-like' topology. The compound is essentially diamagnetic. BVS method of calculations also corroborate with the oxidation state of each nickel in **1**.

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## Appendix A. Supplementary data

The cif file of **1** was deposited with the Cambridge Crystallographic Data Center (CCDC835052). The data can be obtained free of charge from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2012.05.033>.

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