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Research Article

SYNTHESIS, CRYSTAL STRUCTURES, HYDROGEN BONDING GRAPH-SETS AND THEORETICAL STUDIES OF NICKEL (+II) CO-ORDINATIONS WITH PYRIDINE-2,6-DICARBOXAMIDE OXIME

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ABSTRACT

The pyridine-2,6-dicarboxamide oxime, $C_7H_9N_5O_2$, was Synthesis and characterises with ^{1}H NMR and FTIR spectroscopy . The reaction of this ligand with nickel (II) perchlorate yielded green crystals of formula $[Ni(C_7H_9N_5O_2)_2]^{2+}$,$2[ClO_4]^-$, which crystallized in the monoclinic space group *C2/c* with *a* = 14.915(2), *b* = 0.895(2), *c* = 8.205(1) Å, β = 114.69(1), and *Z* = 4. The complex consists of discrete cations (+II) and one perchlorate anion, the cations existing in a slightly distorted octahedral complex with bonding through the heterocyclic and oxime nitrogen atoms. The structure is held together through N-H…O, O-H…O and C-H...O hydrogen bonds occurring between the coordinated oxime molecules and the perchlorate counter-ion. Computational investigations of nickel(II) complex are done by using M062X method with 6-31+G(d)(LANL2DZ) basis set in vacuo.

Keywords: Oxime complexe; Crystal structure; Hydrogen-bonding graph-set; DFT; M062X method; 6-31+G(d)(LANL2DZ) basis.

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1. INTRODUCTION

The study of the coordination transition metal ions to different types of ligands has been amplified by the recent developments in the fields of adsorption, catalysis, luminescence, nonlinear optics, magnetism and ion exchange. [1–6], bioinorganic chemistry and medicine [7, 10]. Judicious choice of metal ions and organic ligands are of great importance in preparation of novel transition metal complexes with different structures and functional properties [6].

The chemistry of oxime-based ligand is diverse [11]. Introduced first in 1905 by Tschugaeff [12], dimethylglyoxime as a reagent for nickel, the oximes as potential ligands have been increasingly expanding its horizon in coordination chemistry. Structure, stability and reactivity of molecules, biochemical models, analytical and organometallic chemistry and particularly syntheses of molecules with unusual electronic properties are the aspects that kindled the interest for the oxime-based ligands [13–17]. Due to the marked ability to form bridges with metal ions, oxime ligands may be used to obtain polynuclear compounds with molecular magnetism and supramolecular structure [18, 19]. Also, oxime-containing ligands are strong donors, and therefore, they were found to efficiently stabilize high oxidation states of metal ions such as CuII and NiII [20, 21]. The presence of additional donor groups together with the oxime group in the ligand molecule may result in a significant increase in chelating efficiency and ability to form polynuclear complexes [22].

The literature contains reports of the structure of amide oximes (amidoximes) which can co-ordinate as bi-,tri-tetra-and hexa-dentate ligands[23-28]. The majority of these amidoximes are aliphatic compounds which form five-membered rings utilizing the diimine moiety, -N=C-C=N-, involving oxime and imine nitrogens as the co-ordination sites with transition-metal atoms [29].

Pyridine-2,6-dicarboxamide oxime (pyridine-2,6-diamidoxime), $C_7H_9N_5O_2$ **(L)**, possesses the structural requirements to react as a tridentate ligand with the heterocyclic and two oxime nitrogen atoms forming five-membered rings with transition-metal ions.

This research was carried out with the specific purpose of determining the structures of nickel (+II) co-ordination with pyridine-2,6-dicarboxamide oxime. We report here the synthesis and the single crystal X-ray structure of the complex. Optimized structures of mentioned complex are performed at B3LYP/6-31++G(d,p)(LANL2DZ) level in vacuo. IR spectrum of this complex is calculated at same level of theory and examined in detail. NMR spectra of Ni(II) complex are calculated by using gauge-including-atomic-orbital (GIAO) method and frontier molecular orbitals (FMOs) of this complexes are examined.

2. RESULTS AND DISCUSSION

The crystal structure of $[Ni(OX)_2{}^{+2},2(ClO4)^-]$ is explored with a discussion about the hydrogen-bonding networks and graph sets. The results of the electronic computations on the geometrical parameters of the compound are reported and discussed with respect to the X-ray data. This is followed by theorical studies.

2.1. Synthesis

The ligand pyridine-2,6-diamidoxime **(L)** was prepared as well as [29] by the reaction of an ethanolic solution of 2,6-dicyanopyridine with a neutralized aqueous solution of hydroxylamine hydrochloride . The infrared spectrum of **(L)** shows the bands at 3482 and 3414 cm^{-1} absorptions are assigned as the σ (asym) and σ (sym) NH stretching frequencies, Respectively; the band at 3352 cm^{-1} can be assigned to σ (sym) OH stretching, at 1653cm^{-1} assigned σ(sym) C=N and finally the band at 958 cm^{-1} can be assigned σ(sym) NO. The ^{1}H NMR shifts are listed in the Experimental section, however it should be noted that the NH and OH peaks are both concentration dependent. In addition both peaks disappear upon shaking the sample with 1 drop of D_2O, showing the lability of these hydrogens.

Reaction of (L) with the metal perchlorates in alcohol gave the corresponding coordination complex in 95 % yield.

2.2 Structure

A summary of crystal data and parameters for structure refinement details are given in Table 1. The atomic coordinates and equivalent thermal parameters are also given in Table 2, 3 and 4. The molecular structure of the compound showing the atom numbering scheme is shown in Figure. 1. All other refinement details are available in the CIF (CCDC: 1401464).

Table 1. Crystal data and parameters for structure refinement

Crystal data	Complex
Empirical formula	$NiC_{14}H_{18}Cl_2N_{10}O_{12}$ (a)
Formula weight (g mol^{-1})	$Mr = 647.99$
Temperature (K)	293
Crystal system	Monoclinic
Space group C2/c	*C2/c*
Hall symbo	-C 2yc
Unit cell dimensions (A°)	
a	14.915(3)
b	20.895(2)
c	8.2058(12)
β°	114.691(19)
Volume (A^3)	2323.6(6)
Z^a	4
Calculated density (g/cm3)	1.852
Absorption coefficient (mm^{-1})	1.151
F(000)	1320
Crystal size (mm3)	0.01 × 0.02 × 0.04 mm
Color	green
Shape	Block
Cell parameters from	5825 reflections
Wavelength (Mo Ka) (A)	0.71073
θ_{max} - θ_{min}	29.5°- 3.6°
Measured reflections 8144	5825
Independent reflections 2741	2770.
reflections with $I > 2\sigma(I)$	1874
Rint	0.0439
Limiting indices	
h	$-20 \rightarrow 19$
k	$k = -27 \rightarrow 18$
l	$l = -10 \rightarrow 8$
Refinement method	Full-matrix Least-squares on F2
Final R indices ^{b} [$F2 > 2\sigma(F2)$] R1, wR2	0.0747, 0.1317
Goodness-of-fit on F2^c Data/restraints/parameters	1.077
2548/0/106	2770/0/184
H atoms	a constrained refinement
Largest difference peak and hole (e A_3)	
$\Delta\rho$max, $\Delta\rho$min	0.670e , -0.592e

(a) The asymmetric unit contains 0.5 of the chemical formula.

(b) R1 =P|Fo -Fc|/Fo. wR2 = {P[w(Fo2 - Fc2)2]/P[w(Fo2)2]}1/2.

(c) S = {P[w(Fo2 - Fc2)2]/(Nobs - Nvar)}1/2.

Table 2. Atomic coordinates and thermal parameters (A^2)

Atom	x	y	z	Ueq
NiL_2				
Ni1	1/2	0.21975(2)	1/4	0.0347(2)
O1	0.32460(19)	0.23513(12)	-0.1423(3)	0.0610(9)
O2	0.3720(2)	0.20438(13)	0.4796(4)	0.0680(10)
N1	0.3843(2)	0.19684(13)	0.0034(3)	0.0434(8)
N2	1/2	0.12503(17)	1/4	0.0383(11)
N3	0.3169(2)	0.11410(17)	-0.2022(4)	0.0657(11)
N4	0.4117(2)	0.24268(13)	0.3853(3)	0.0423(9)
N5	1/2	0.31456(17)	1/4	0.0382(11)
N6	0.3702(3)	0.32419(17)	0.5335(5)	0.0769(16)
C1	0.3753(2)	0.13690(17)	-0.0396(4)	0.0458(11)
C2	0.4368(2)	0.09383(15)	0.1054(4)	0.0429(10)
C3	0.4344(3)	0.02778(17)	0.1024(5)	0.0567(14)
C4	1/2	-0.0049(3)	1/4	0.069(3)
C5	0.4109(2)	0.30161(17)	0.4251(4)	0.0459(10)
C6	0.4552(2)	0.34589(15)	0.3372(4)	0.0433(10)
C7	0.4527(3)	0.41171(17)	0.3379(5)	0.0598(11)
C8	1/2	0.4442(3)	1/4	0.0631(18)
Cl1	0.21041(7)	0.07618(4)	0.19648(11)	0.0467(3)
O3	0.2971(2)	0.08589(13)	0.3574(3)	0.0784(10)
O4	0.1266(2)	0.07083(13)	0.2364(4)	0.0745(11)
O5	0.2201(2)	0.01899(13)	0.1113(4)	0.0786(11)
O6	0.1989(2)	0.12993(12)	0.0827(3)	0.0675(10)

Table 3. Experimental and calculated bond lengths (Å) of Ni(II) complex at same level of theory

Bond	Experimental (X-ray)	Calculated	Bond	Experimental (X-ray)	Calculated
Ni1-N1	2.094(2)	2.179	N4-C5	1.275(4)	1.309
Ni1-N2	1.979(4)	2.083	N5-C6_a	1.337(4)	1.371
Ni1-N4	2.102(3)	2.12	N5-C6	1.337(4)	1.334
Ni1-N5	1.981(40	2.155	N6-C5	1.354(5)	1.358
Ni1-N1_a	2.094(4)	2.202	N3-H1N3	0.8300	1.013
Ni1-N4-a	2.102(3)	2.118	N3-H2N3	1.0600	1.023
Cl1-O6	1.424(3)	1.527	N6-H1N6	0.9400	1.006
Cl1-O3	1.425(3)	1.512	N6-H2N6	0.9400	1.011
Cl1-O4	1.423(4)	1.494	C1-C2	1.468(4)	1.488
Cl1-O5	1.422(3)	1.481	C2-C3	1.381(5)	1.398
O1-N1	1.405(3)	1.401	C3-C4	1.379(5)	1.394
O2-N4	1.405(4)	1.401	C5-C6	1.487(5)	1.492
O1-H1O	0.8200	0.968	C6-C7	1.376(5)	1.391
O2-H2O	0.8200	0.967	C7-C8	1.380(5)	1.432
N1-C1	1.293(4)	1.299	C3-H3	0.9300	1.082
N2-C2_a	1.337(4)	1.339	C4-H4	0.9300	1.085
N2-C2	1.337(4)	1.337	C7-H7	0.9300	1.084
N3-C1	1.340(4)	1.363	C8-H8	0.9300	1.086

Table 4. Experimental and calculated bond angles (deg.) of Ni(II) complex at same level of theory

Angle	Exp.	Calc.	Angle	Exp.	Calc.
N1-Ni1-N2	76.78(8)	75.03	Ni1-N4-C5	115.5(2)	118.69
N1-Ni1-N4	96.74(11)	96.29	O2-N4-C5	111.0(3)	111.08
N1-Ni1-N5	103.22(8)	104.61	Ni1-N5-C6_a	119.33(19)	117.37
N2 -Ni1-N4	103.18(8)	104.56	C6 -N5 -C6_a	121.4(3)	123.21
N2 -Ni1-N5	180.00(2)	178.52	Ni1-N5-C6	119.33(19)	119.34
N1_a -Ni1 -N2	76.78(8)	73.92	C1-N3-H2N3	126.00	113.42
N2 -Ni1 -N4_a	103.18(8)	107.9	H1N6 -N6 -H2N6	115.00	118.69
N4 -Ni1 -N5	76.82(8)	73.76	C5-N6 -H2N6	116.00	116.55
N1_a -Ni1 -N4	89.25(11)	93.38	C5-N6-H1N6	123.00	120.06
N4 -Ni1 -N4_a	153.65(11)	147.19	N1-C1-N3	124.5(3)	125.99
N1_a -Ni1 -N5	103.22(8)	106.48	N1-C1-C2	114.5(3)	114.43
N4_a -Ni1-N5	76.82(8)	73.82	N3-C1 -C2	121.0(3)	119.57
N1_a-Ni1-N4_a	96.74(11)	91.07	N2-C2-C1	113.0(3)	114.25
O3-Cl1-O6	108.03(17)	106.57	C1-C2-C3	126.6(3)	124.72
O4-Cl1-O5	109.06(18)	108.6	N2-C2-C3	120.5(3)	121.02
O4-Cl1-O6	109.63(18)	109.72	C2-C3-C4	118.4(4)	118.11
O5-Cl1-O6	110.46(17)	109.72	C3-C4-C3_a	118.4(4)	120.28
O3-Cl1-O4	110.01(18)	109.94	N6-C5-C6	120.9(3)	120.68
N1-O1-H1O	109.00	103.51	N4-C5-C6	115.0(3)	116.29
O1-N1-C1	111.3(2)	112.24	N4-C5-N6	124.0(3)	123.01
Ni1-N2-C2_a	119.19(19)	120.04	N5-C6-C5	112.2(3)	111.53
C7-C8-C7_a	121.1(5)	121.14	N5-C6-C7	120.8(3)	121.53
C2-C3-H3	121.00	120.7	C6-C7-C8	118.0(4)	116.91
C4-C3-H3	121.00	121.18	C6-C7-H7	121.00	122.51
C3_a-C4-H4	120.00	119.89	C8-C7-H7	121.00	120.57
C3 -C4 -H4	120.00	119.82	C7_a-C8-H8	119.00	119.64
Ni1-N2-C2	119.19(19)	120.04	C7-C8-H8	119.00	119.22
Ni1-N4-O2	131.5(2)	129.01	-	-	-

The Valance bond sum (1.995 A°) [30-32] confirms that the nickel ion in our complex is as Ni^{II+} . The crystal structure of **(1)** confirms the 1: 2 Ni^{II+} ligand co-ordination where the anions are not involved in the co-ordination. The nickel (II) ion is six-co-ordinated through the imine and heterocyclic nitrogens of the two oxime molecules.

The complex crystallizes in the monoclinic space group C2/c with four molecules in the unit cell (one-half per asymmetric unit) and a centro-symmetric molecule in the asymmetric unit, formed by a half Ni^{2+} metal ion located on a center of symmetry at (1/2, 0.21975(2) ,1/4), two crystallographically independent oxime ligands and perchlorate counter-ion located on general positions (figure .1).

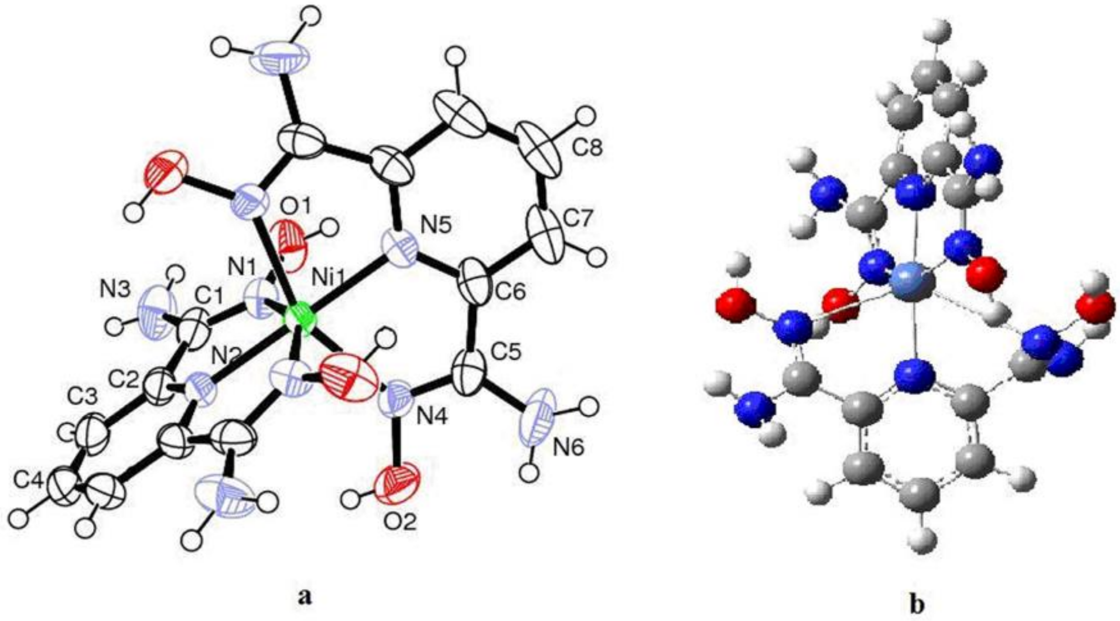

Fig.1. (a) Ortep diagram of $[Ni(OX)_2.(ClO_4)_2]$ **(1)** Showing 50% probability thermal ellipsoids. Only the asymmetric unit and those H-atoms whose positions were refined are labelled.The counter anion have been omitted for clarity. (b) Optimized structure of the complex at M062X/6-31+G(d)(LANL2DZ) level in vacuo.

The nickel (II) ions are surrounded by a slighty elangated N6 octahedral environnement, formed by two N atoms from to equivalent Imines (N1 and N1i), two N atoms of two equivalent imines crystallographically independent from the first two (N4 and N4i) with i:(-x, y, -z+1/2) and two coordinated pyridine nitrogen. The four equatorial coordination sites are occupied by four atoms belonging to the monodentately coordinated nitrogen oximes [Ni-N1= 2.094 (2) and Ni-N4= 2.102 (3)]. These atoms define the equatorial plane and because of the centro-symmetry, the nickel ion lies in this plane. The Ni-ligand distance (average: 2.098 (3) A°) is comparable to$[Ni(C_7H_9N_5O_2)][SO_4].5H_2O$ of 2.1272 (2)A°[29]. The two heterocyclic nitrogen are more strongly linked to the nickel (+II) center in the apical positions, with a $Ni-N_{pyridine}$ distance slightly shorter than the equatorial ones [Ni-N2=1.979(4)A° and Ni-N5= 1.981(4)A°]. The apical Ni-N distances are in agreement with those found in $[Ni(C_7H_9N_5O_2)][SO_4].5H_2O$ [29]. This short bond length is explained by the difference in type of hybridization between equatorials nitrogen (SP^3) and the apical pyridine nitrogens (SP^2).

The two co-ordinated oximes are at 80.94° (approximately orthogonal to each other) . A comparison of the same bond lengths and angles for the free ligand and the nickel(II) complex shows little change in (L) and **(1)**[29].

Bond lengths and angles within the aromatic rings are unremarkable and compare well with literature values [29, 33-36].

The (L) ligands in (1) are approximately S-shaped (see Figure. 2). Each of them is nearly planar (mean deviation from the plane comprising all non-H atoms: for the N1-ligand molecule, 0.056 A ˚; and for the N4-ligand molecule, 0.063 A ˚).

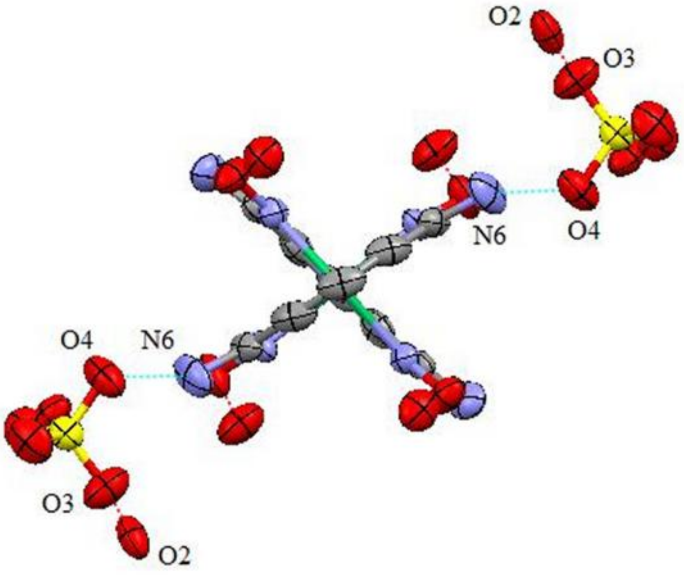

Fig.2. Diagram showing the twisting of the two (OX) rigs in (1). Dashed lines (…) indicate H-bonds

The perchlorate anion is not disordered at 293 K, and it is stabilized by strong interactions with its environment. The average Cl-O bond distances and O-Cl-O bond angles are 1.4232 (3) A°and 109.47° (17), respectively, confirming a tetrahedral configuration (Table 3 and 4), similar to other perchlorates studied at low temperature) [37-39].

2.3 Graph-sets of hydrogen bonding

The crystal pickings of (1) are mainly consolidate by N-H…O, O-H…O and C-H…O intramolecular hydrogen bonds due of the presence of perchlorate (ClO_4^-) counter ion. Therefore, a total of nine counter-ion-ligand hydrogen bonds are present in the unit (Table.5) (figure.3). Each oxygen perchlorate counter-ion is hydrogen bended to the hydroxide oxime (OH) or amine group (NH2) of the complex yilded to intramolecular contacts.

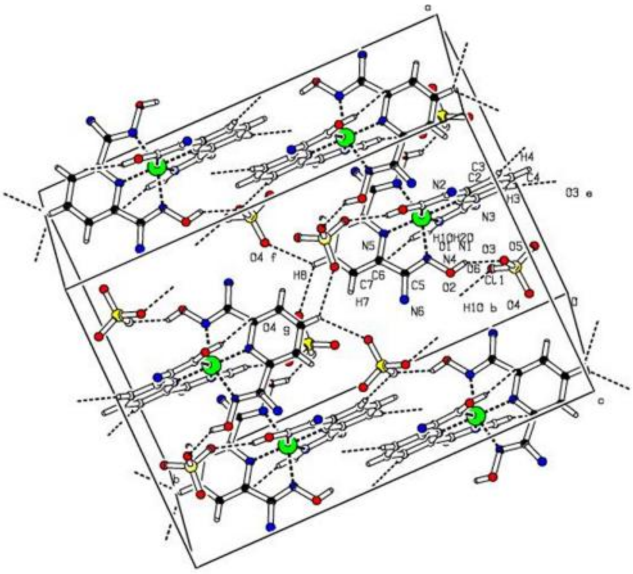

Fig.3. Crystal packing of the complex showing the H-bonding patterns

Table 5. Hydrogen bond lengths (A) and angles (°)

D-H...A	D-H	H...A	D...A	*D-H...A*
N6 -- H1N6 .. O4 ^{i}	0.9400	2.0300	2.882(5)	*150.00*
O1 -- H1O .. O6 ^{ii}	0.8200	2.1200	2.908(4)	*162.00*
N3 -- H1N3 .. O5^{iii}	0.8300	2.4300	3.212(4)	*156.00*
O2 -- H2O .. O3	0.8200	2.0000	2.729(4)	*147.00*
N3 -- H2N3 .. N6^{ii}	1.0600	2.2500	3.241(5)	*155.00*
N6 -- H2N6 .. O2	0.9400	2.1700	2.544(5)	*103.00*
C3 -- H3 .. O3^{iii}	0.9300	2.3700	3.231(5)	*153.00*
C8 -- H8 .. O4^{iv}	0.9300	2.5900	3.280(6)	*132.00*
C8 -- H8 .. O4^{v}	*0.9300*	*2.5900*	*3.280(6)*	*132.00*

i: 1/2-x,1/2-y,1-z, ii : 1/2-x,1/2-y,-z, iii : x,-y,-1/2+z, iv : 1/2+x,1/2+y,z, v : 1/2-x,1/2+y,1/2-z

Only closests perchlorate oxygens atoms to Nickel (O3, O4 and O6); appears to be tucked into the pocket created by the tilting of the ligand rings to ensures the cohesion of the building cristalin by strong O-H ... O and O-H ... N hydrogen bonds in pairs; to gives rise to binary-level graph set motifs [40] consisting of three $R_4^4(n)$ different ring running through the a, b and c axis direction as follows:

In the crystal packing, each [NiL2] $^{2+}$ ion is connected to two adjacent perchlorate ion $(ClO4)^-$ through two strong hydrogen bonds: O1- H1O…O6 of 2.908(4) A° which binds the hydroxide oxime oxygen (O1) with the perchlorate oxygene (O6) ; and N6-H1N6…O4 hydrogen hydrogen bond of 2.882(5) A° who connected the free amine (N6) with the perchlorate oxygen (O4) In such away to give infinite one-dimention $C_2^2(12)$ double ribbons in the c direction. An ample view of the the packing proves that the centro-symmetric $R_4^4(22)$ rings illustrate how the beighboring moieties link to each other throught two O1- H1O…O6 and two N6-H1N6…O4 interactions. These rings are connected together by the metallic center Ni.(Figure.4) .

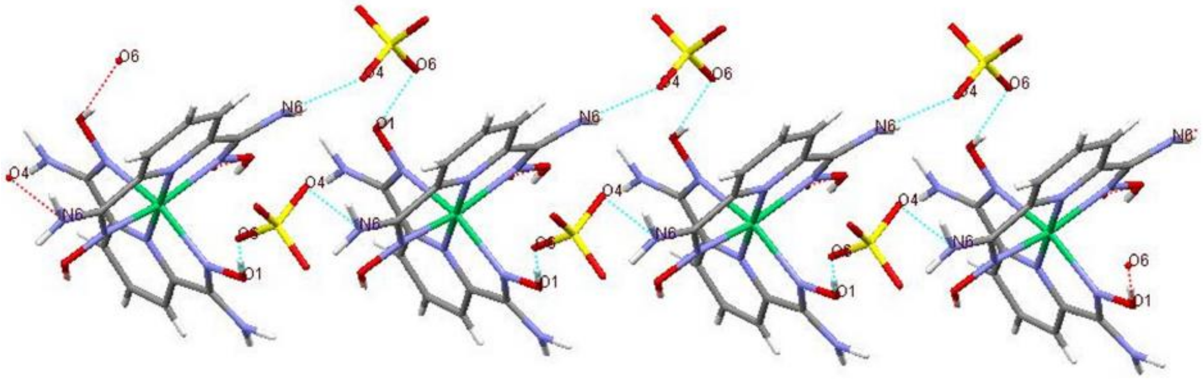

Fig.4. A fragment of the structure showing the first-level graph-set $C_2^2(12)$ and $R_4^4(22)$ descriptors with hydrogen bonds as dashed lines

Also Each [NiL2] $^{2+}$ ion is linked to the two perchlorate ion $(ClO4)^-$ with two strong hydrogen bonds O2-H2O…O3 of 2.729(4).A° and N6-H1N6…O4; in away that the hydroxide oxime oxigen (O2) link the oxygen perchlorate ion (O3) to yilded the primery-level graph set motif $D_2^2(9)$. another primery-level graph set motif $D_2^2(9)$ will be yilded by the hydrogen bond witch link the nitrogen of the free amine (N6) and the perchlorate oxygen (O4). Together; these two primery-level graph gives rise to the formation of binary-level cycles $R_4^4(18)$. Although the latter binds the two (NiL$_2$) $^{2+}$ but it does not reach the two metal ions (Figure.5).

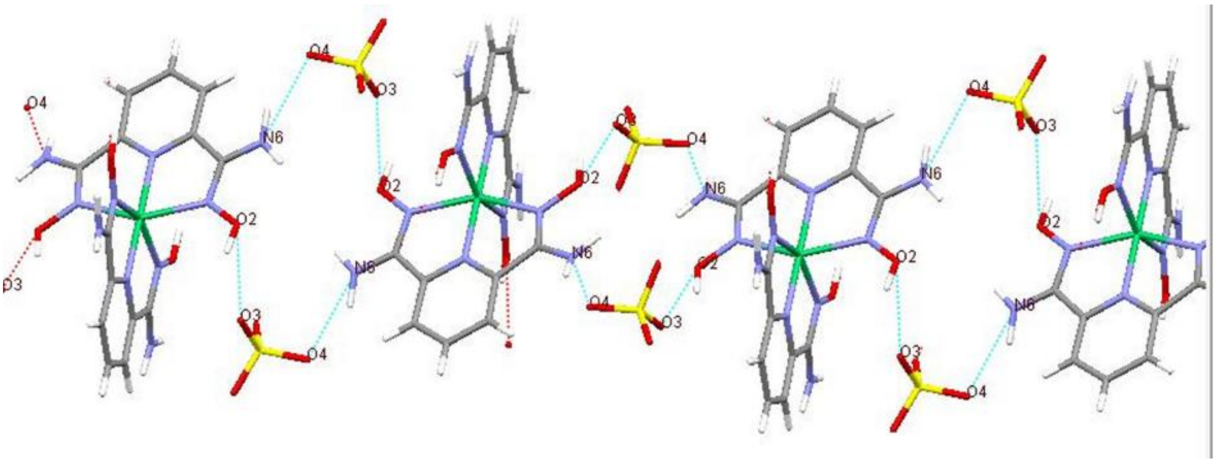

Fig.5. A fragment of the structure showing the first-level graph-set $D_2^2(9)$ and $R_4^4(18)$ descriptors with hydrogen bonds as dashed lines

Furthermore, With a third binery-level graph set $R_4^4(20)$ the [NiL$_2$] 2+ ions has been also connected by a strong O-H…O of 2.908(4) A° and 2.729(4) A° hydrogen bonds between two different oxygen hydroxyd oxime functions (O1 and O2) and two different oxygens perchlorate ion (O6 and O4) respectively, the combination of these two connecting leads to the birth of infinite chain $C_2^2(11)$, the combination of two chains of this type, leaving the appearance of the graph binary $R_4^4(20)$ (Figure 6).

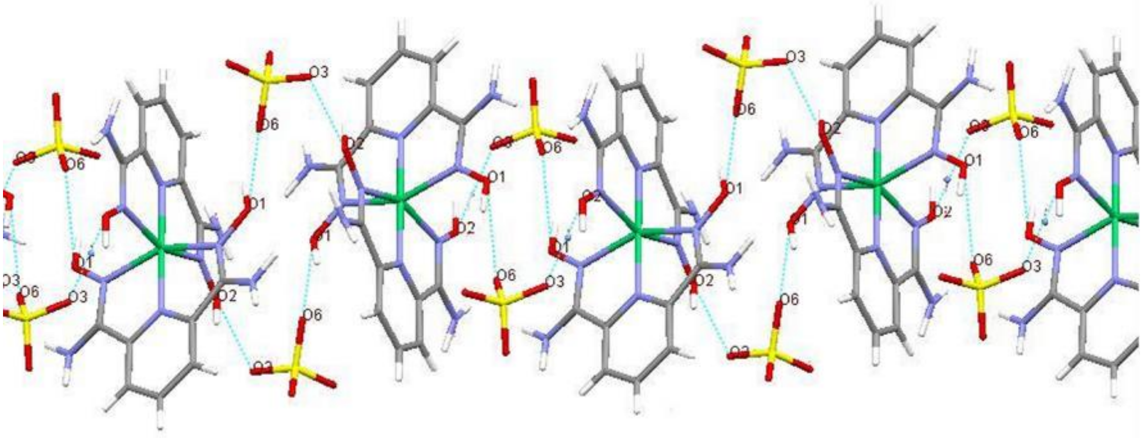

Fig.6. A fragment of the structure showing the first-level graph-set $C_2^2(11)$ and $R_4^4(20)$ descriptors with hydrogen bonds as dashed lines

2.4 Computation

Optimized structure of Ni(II) complex is obtained at same level of theory in vacuo. Optimized structure of nickel complex and its bond lengths and angles are given in Fig. 1.b, Table 3 and Table 4, respectively.

The harmonies between experimental and calculated structural parameters are investigated and these harmonies are represented in Figure.7.

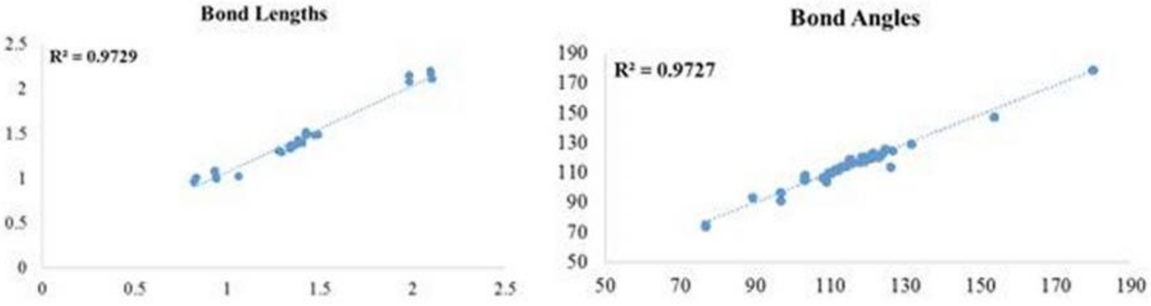

Fig.7. Distribution graphs between experimental and calculated structural parameters

According to Figure 7, regression coefficients (R^2) are calculated as 0.9729 and 0.9727 for bond lengths and angles, respectively. These results show that there is an agreement between experimental and structural parameters.

Vibrational spectrum of Ni(II) complex is calculated at same level of theory and represented in Figure 8.

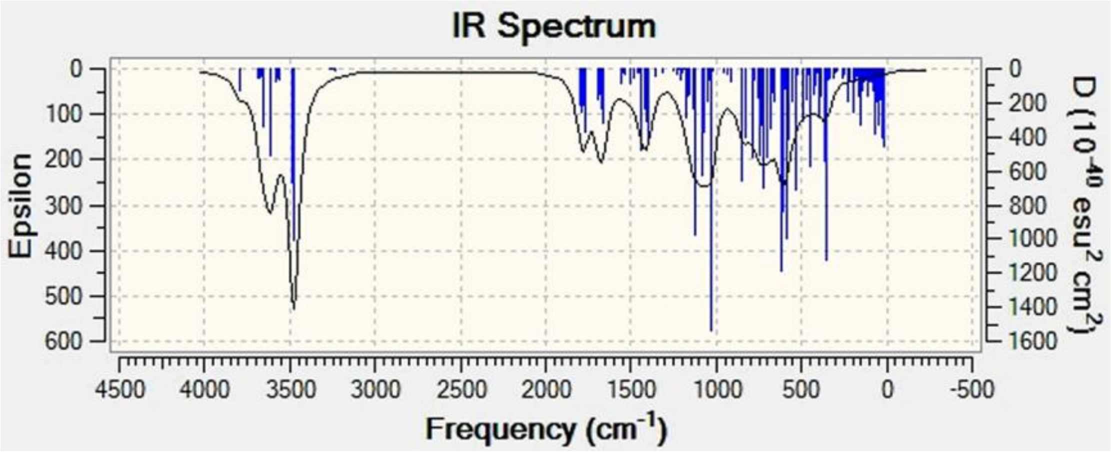

Fig.8. Calculated IR spectrum of Ni(II) complex at M062X/6-31+G(d)(LANL2DZ) level in vacuo

Calculated stretching frequencies are obtained as: ν_{OH} (3789, 3655 and 3471 cm^{-1}), ν_{NH} (3484 cm^{-1}), $\nu_{C=N}$ (1788 cm^{-1}), $\nu_{C\text{-}N}$ (1437 cm^{-1}), $\nu_{Cl\text{-}O}$ (1067cm^{-1}). These frequencies are not scaled and these are harmonic frequencies.

Frontier molecular orbitals is playing important role in determination of chemical reactivity. Multiplicity of investigated compound is two. Thus, there is single occupied molecular orbital (SOMO) in mentioned Ni complex. The energy levels of lowest unoccupied molecular orbital (LUMO), SOMO and highest occupied molecular orbital (HOMO) are calculated at same level of theory. The contour diagrams of these molecular orbitals are represented in Figure 9.

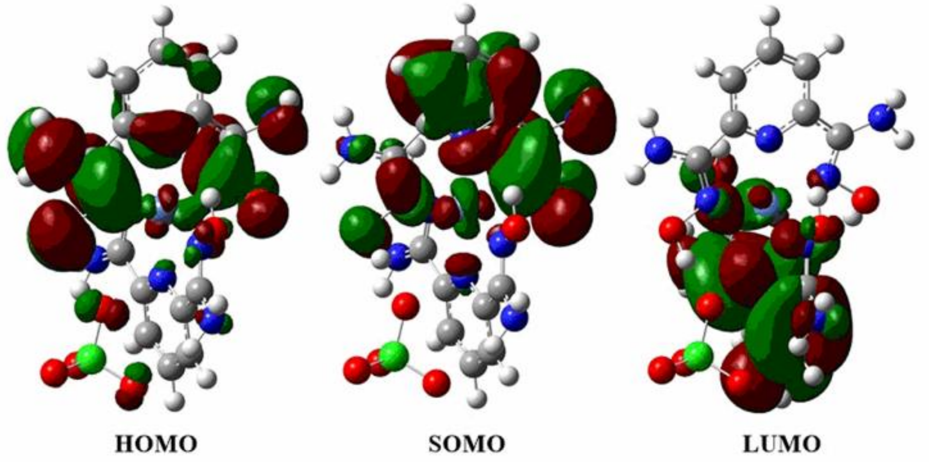

Fig.9. Contour diagrams of HOMO, SOMO and LUMO of mentioned Ni(II) complex at B3LYP/6-31++G(d,p)(LANL2DZ) level in gas phase

According to the Figure 9, electrons of HOMO are mainly located on nitrogen and oxygen atoms and electron of SOMO is mainly localized on benzene ring. As for the LUMO, if Ni(II) complex accepts electrons from appropriate molecule, electrons will mainly localized on ligands.

The nuclear magnetic resonance (NMR) spectra have become a classy and powerful nondestructive analytical technology that has found a variety of applications in many different research fields. Chemical shifts (in ppm) are recognized as an important part of the information contained in NMR spectra. They are important for structural interpretation due to their sensitivity to conformational variations. Tetramethylsilane (TMS) is selected as reference substance and this molecule optimized at B3LYP/6-31++G(d,p) level. Chemical shifts of hydrogen and carbon atoms are given in Table 6.

Table 6. Calculated chemical shifts (ppm) of carbon and hydrogen atoms at B3LYP/6-31++G(d,p)(LANL2DZ) level in vacuo

^{13}C-NMR		^{1}H-NMR	
Atoms	Chemical Shift (ppm)	Atoms	Chemical Shift (ppm)
C1	151.624	C3*H*	8.3985
C1a	146.481	C3a*H*	8.8228
C2	146.358	C4*H*	9.7885
C2a	139.411	C7*H*	6.5502
C3	140.946	C7a*H*	8.0142
C3a	128.689	C8*H*	6.7756
C4	154.207	*N3H*	1.3100, 1.3379
C5	167.288	N3a*H*	2.7796, 1.0690
C5a	162.678	N6*H*	6.2296, 8.1692
C6	171.076	N6a*H*	4.2351, 7.4493
C6a	148.268	O1*H*	13.1946
C7	106.161	O1a*H*	16.6286
C7a	141.759	O2*H*	16.6467
C8	142.312	O2a*H*	14.695

As theoretically, Chemical shift values of hydrogen and carbon atoms are a good agreement with theoretical expectation.

3. EXPERIMENTAL

3.1 Synthesis

2,6-Dicyanopyridine was synthesized from pyridine-2,6- dicarboxylic acid (Aldrich Chemical Co.) according to the procedure of Banks and Brookes [41].

3.1.1 *Preparation of pyridine-2,6-diamidoxime, $C_7H_9N_5O_2$ (L)*

An aqueous solution (100 cm^3) containing hydroxylamine hydrochloride (2.43 g, 35 mmol) neutralized with sodium hydroxide (1.4 g, 35 mmol) was added to ethanol (100 cm^3) containing 2,6-dicyanopyridine (1.95 g, 15 mmol). The reaction mixture was heated at 70°C with stirring for 1 h, and upon cooling to 10°C yielded (L) (5.21 g, 89%), m.p. 213 °C . υ_{max}/Cm^{-1} (KBr disc): 3482 (asym) and 3414 (sym) (NH); and 3352 (sym) (OH); 1653 (sym) (C=N); 958 (sym) (NO). NMR [$(CD_3)_2SO$; dH(250 MHz) 9.86 (s, 2 H, NO-H), 7.85 (m, AB_2, 3 H, pyridinering), 6.29 (s, 4 H, NH_2).

3.1.2 Preparation of bis(pyridine-2,6-diamidoxime)nickel(II) Perchlorate, $[Ni(C_7H_9N_5O_2)]^{2+}$, $2[ClO_4]^-$

Solid (L) (1.45 g, 10 mmol) was added to a heated aqueous solution (100 cm^3) containing nickel (II) Perchlorate (1.31g, 5 mmol). The resulting green solution was stirred at 80–90 °C for 1 h and allowed to stand overnight at room temperature.

The resulting green crystals of (1) were filtered off and washed with absolute ethanol and diethyl ether (5.30 g, 83.5%).

3.2 Instrumentation

A green block crystal of the complex, with dimensions of 0.01 × 0.02 × 0.04 mm was selected and mounted on an Oxford Diffraction Xcalibur, Atlas, Gemini ultra diffractometer with Mo Kα radiation ($\lambda = 0.71073$ A°), equipped with the required cooling using φ and ψ scans at 293 K in the range of $3.0<\theta<29.3°$.The unit cell determination and data reduction were performed using the CrysAlis program [42]. A total of 5825 reflections were collected, of which 2770 were independent and 1874 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using the program SIR2004 [43] and was refined by full-matrix least squares technique on F2 including all reflections with SHELXL- 1997 program [44]. Both softwares were included within the WingX crystallographic software package [45].

All non-hydrogen atoms were anisotropically refined. All of the hydrogen atoms were located from the difference Fourier map and were fixed in calculated positions with distances constraints of C-H = 0.93 A and

N-H = 0.86 A, and refined in riding mode with Uiso(H) = 1.2 Ueq(C,N). The refinements converged at conventional R factor of 0.0747 and wR of 13.17%. Maximum and minimum peaks in the final difference Fourier syntheses were 0.670 and -0.592 e A-3. Structural representations of the complex were drawn using ORTEP-3 [46] and MERCURY [47]. Analyses were carried out by the program PLATON [48], as incorporated in the WinGX [49] suite.

The FT-IR has been carried out to analyse the chemical bonding and molecular structure of the compound. The FTIR spectrums of the ligand was recorded in frequency region between 4000-400 cm^{-1} with a FTIR NEXUS NICOLET Spectrometer in KBr pellets.

The ^1H NMR was recorded on a Bruker 300 MHZ instrument at 23°C to confirm the molecular structure of the ligand.

3.3 Computational details

Numerical calculations were done with GaussView 5.0.8 [49] and Gaussian 09 AM64L-G09RevD.01 package program [50]. B3LYP was selected as computational method for studied complex. As for the basis set, LANL2DZ and 6-31++G(d,p) were selected for metal atom and the rest atoms in molecule, respectively. NMR spectrum is calculated at B3LYP/6-31++G(d,p)(LANL2DZ) with GIAO method [51–54] in vacuo.

4. CONCLUSION

The experimental and theoretical structural investigations of an octahedral Ni(II) complex with oxime ligands were successfully performed by single-crystal XRD and quantum chemical computations. Any differences observed between the experimental and computed values may be due to the fact that the computations were performed for a single molecule in the gas phase, whereas the experimental values in the solid phase were recorded in the presence of intermolecular interactions. To summarize, the following conclusions can be drawn:

1. The complex crystallizes in the monoclinic system, space group C2/c with a centro-symmetric molecule in the asymmetric unit.
2. Crystals of the complexe (1) suitable for X-ray study were grown from alcohol solution. Shows the expected 6-coordinate metal complex with two (L) ligands coordinated to the metal centre, with a degree of distortion from an octahedral geometry. The equatorial plane is formed by four N atoms of imine ligands. The axial positions where occupied by two N atoms of pyridine ligands. Whereas two symmetry- perchlorate counter-ions are illustrated in the structure for the retained charge of the complex.
3. The crystal structure of [L] shows the oxime nitrogens are not available for tridentate co-ordination in conjunction with the pyridine nitrogen. Upon addition of nickel(II), free rotation about the C(2)-C(1) bonds results in proper positioning of the oxime nitrogens .
4. The structure is held together through N-H…O and O-H…O hydrogen bonds occurring between the coordinated oxime molecules and the perchlorate counter-ions and resulting in infinite chains obtained by $R_4^4(22)$, $R_4^4(18)$ and $R_4^4(20)$ rings .
5. The coordination sphere of Nickel atoms of complex displays deformation due to difference coordinate nitrogen hybridation and the Jahn–Teller effect.
6. Computational investigations of the complex are done by using B3LYP method with 6-31++G(d,p)(LANL2DZ) basis set in vacuo; are in good agreement with experimental results.

5. SUPPLEMENTARY MATERIALS

CCDC 1401464 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: 00441223 336033.

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