



Electronic Structure of Suggested Nickel Metal Complexes: DFT Calculations

Alaa S. Hussein^{1*}, Zainab G. Abdulkareem², Hamid I. Abbood³

Abstract

SDD bases were used to maintain relaxation of the proposed nickel-metal complexes. The DFT method was used in the Gaussian software package. The results showed that the energy of the ground state of the complexes decreases with increasing number of electrons in the complex. The energy gap for the complexes varied depending on the coordination of the complexes and the subgroups in each complex. The N2 complex is a softer complex compared to the other two. The N1 complex with two amine groups as ligands in the complex appeared as an absorption in the infrared range. The results gave us the idea to propose new nickel-metal complexes with chelating ligands with mixed donors for the catalytic treatment.

Key Words: Nickel Metal Complex, DOS, HOMO, LUMO and Electronic Softness.

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Introduction

Monohydroxamic acid forms typical octahedral complexes with transition metals by coordinating via oxygen atoms and forming oxygen bonds from reasonably ionic metals [1]. Because hydroxamic acids are closely related to iron transport phenomena, the selectivity of this mechanism is important because other metal ions, which may be essential or have a toxic effect on the body, are present in the environment [two]. They are known to act as antibiotics, antibiotic antagonists, tumor inhibitors and many of them are used as medicines [3]. It has been shown that hydroxamic acids have different biological activities, many of which are due to their complex properties towards transition metal ions [4]. Brown and Roche, 1982 [5] first observed the N-bond model (which indicates the deprotonation of nitrogen of the hydroxam group) in nickel (II) complexes with glycoam hydroxamic

acids, and few examples have been used since then. 33
Aminohydroxamic acid, coordinated by N, has also been prepared in multinuclear complexes with a hydroxam bridge function [6]. Other examples are the complexes of Ni (II) and Cu (II) with (hydroximino) propanohydroxamic acid, which have an N-bond mode, which provides a new example of the function of the neighboring donor, which facilitates this mode of attachment [6]. The interaction of hydroxamic acids with nickel (II) is important because they act as strong and specific inhibitors of the nickel urease enzyme. [7].

Theory

This work manages the electronic structure of rhenium metal buildings using the three parameters B3LYP (exchange of three Becke parameters with the connecting practice Lee, Yang

Corresponding author: Alaa S. Hussein

Address: ^{1*}Al-Mustaqbal University College, Pharmacy Department, Iraq; ²Al-Mustaqbal University College, Pharmacy Department, Iraq; ³Al-Zahraa University for Women, Karbala, Iraq.

^{1*}alaa.allabban@gmail.com

²zainabghaleb@gmail.com

³hamedaltamimi95@yahoo.com

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and Parr) (DFT) and SDD (ECP Triple Zeta from Stuttgart) Dresden (potentially effective kernel) established [8,9]. The electronic properties were determined according to the Koopmans theorem [10,11]. The excitation energies and the vibration progress are completed using the theory of using the thickness TD as a function of time [12-14].

Results and Discussion

Figure 1: shows the relaxing structures of the three nickel-metal complexes, which are designated N1, N2 and N3, respectively. In N1, Table 1 shows the optimization parameters (links in angstroms and angles in degrees) for the complexes examined. The results in Table 1 are in good agreement with theoretical studies [15, 16]. Table 2 shows the energies of the nickel complexes, since their relaxation comprised the total energy of the soil AND in a. u, EHOMO with a busy orbital energy with high molecular weight, ELUMO with a busy orbital energy with low molecular weight and an energy gap, for example in eV. As shown in Table 2, TE decreased with increasing number of electrons in the complex [15]. For example, it was in the range of 2,039 eV for the N1 complex to 0.186 eV for the N2 complex, the N3 complex has 1,237 eV. The change observed in the energy gap is due to the change in the ligands in the complex. The presence of CN in the N2 complex instead of NH2 in the N1 complex leads to a reduction in the energy gap of the nickel-metal complex. The previous result is found in frontier molecular orbitals, in which they are constructed from the linear combination of atomic orbitals for all atoms in each complex. Figure 2 shows the behavior of the energy gap for the investigated nickel complexes.

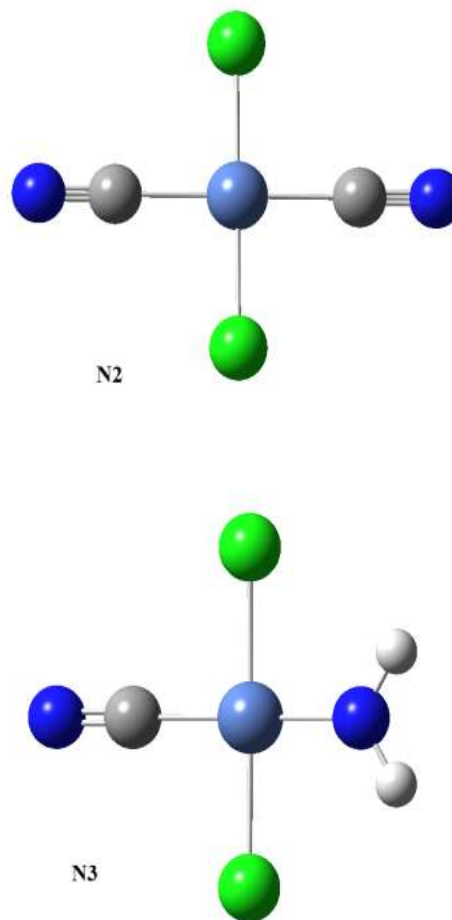
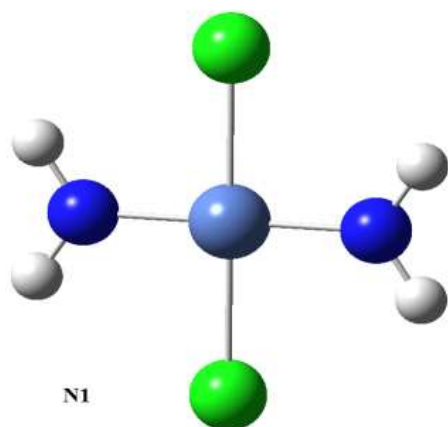


Figure 1. The relaxing structures of nickel-metal complexes
 Table 1. The optimize parameters of Nickel metal complexes

Structure	Bonds		Angles	
1	Ni - Cl (1,2)	2.2527	Cl - Ni - N (2,1,4)	90°
	Ni - N (1,4)	1.7367	Ni - N - H (1,4,6)	122.0461°
	N - H (4,6)	1.023	H - N - H (6,4,7)	115.9079°
2	Ni - Cl (1,2)	2.1432	Cl - Ni - C (2,1,4)	90°
	Ni - C (1,4)	1.9004		
	C ≡ N (4,6)	1.1866		
3	Ni - Cl (1,2)	2.2262	Cl - Ni - N (2,1,4)	90.3493°
	Ni - N (1,4)	1.7381	Cl - Ni - C (2,1,7)	89.6507°
	Ni - C (1,7)	1.8439	Ni - N - H (1,4,5)	122.498°
	N - H (4,5)	1.0297	H - N - H (5,4,6)	115.0041°
	C ≡ N (7,8)	1.1957		



Table 2. E_T , E_{HOMO} , E_{LUMO} and E_g of Nickel metal complexes

Structure	E_T ((a. u))	E_{HOMO} ((eV))	E_{LUMO} ((eV))	E_g (eV)
1	-1203.25785	-7.699	-5.6598	2.039112
2	-1276.85302	-9.36847	-9.18153	0.18694
3	-1240.06311	-8.60166	-7.36411	1.23755

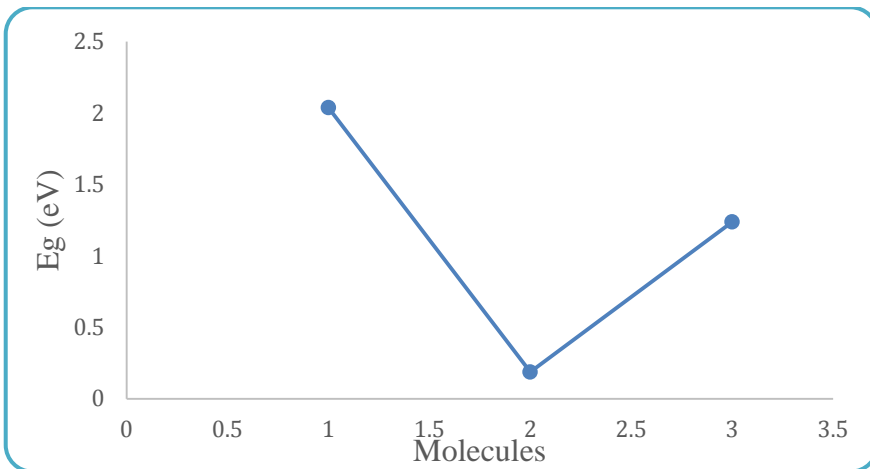


Figure 2. The energy gap of Nickel metal complexes

Table 3 shows the results of certain energies eV for the investigated nickel-metal integrated buildings: ionization energy IE, electronic affinity EA, electrochemical hardness H, electronic softness S and electrophilic index W. The energies mentioned were calculated according to Koopmans' theorem.

Table 3. Some energies of Nickel metal complexes

Structure	I_E (eV)	E_A (eV)	H(eV)	S (1/eV)	W(eV)
1	7.699	5.6598	1.0196	0.49038	21.878
2	9.3684	9.18153	0.09343	5.35331	460.178
3	8.6016	7.36411	0.618745	0.80814	51.494

Table 3 showed the Nickel metal complexes have higher values of IE but N1 complex has the lowest

in which refers to that these complexes need to high energy to donating an electron to become cation. On the other hand, the three Nickel complexes have high EA but N2 complex has the highest with high ability to accepting an electron to becomes anion. These results are due to coordination of the complexes. Figure 3 shows the IE and EA of the complexes examined.

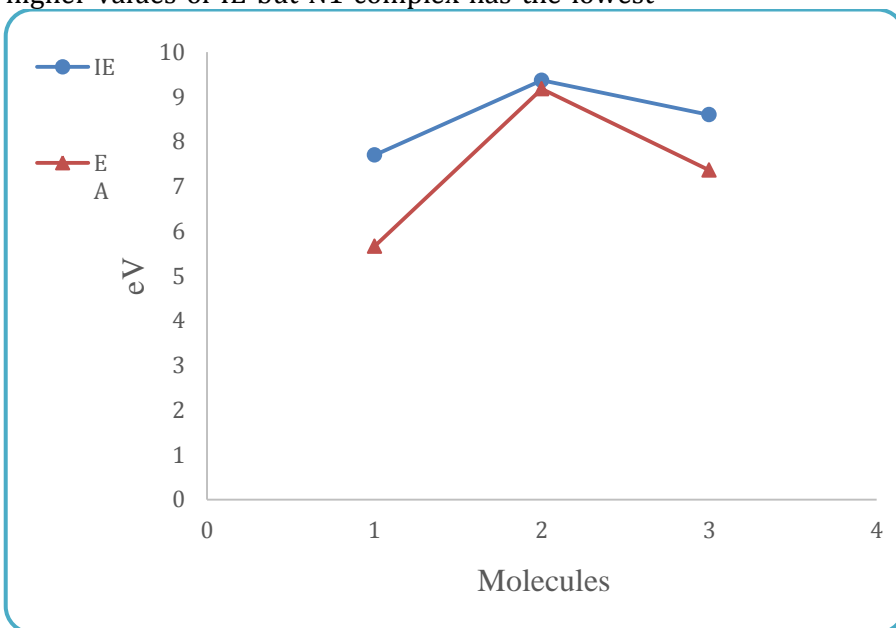


Figure 3. IE and EA of nickel-metal complexes

Figure 4 showed the global quantum parameters electrochemical hardness H and electronic softness



S. The Nickel complexes under study have low values of H with relatively high values of S, complex N2 has the highest value of electronic softness in comparison with the others. Soft complex needs small excitation energies to appear charge

transfer. Above result is due to contribution of the electrons in the complex and the high contribution of electron density is from the d-orbital for Nickel atom.

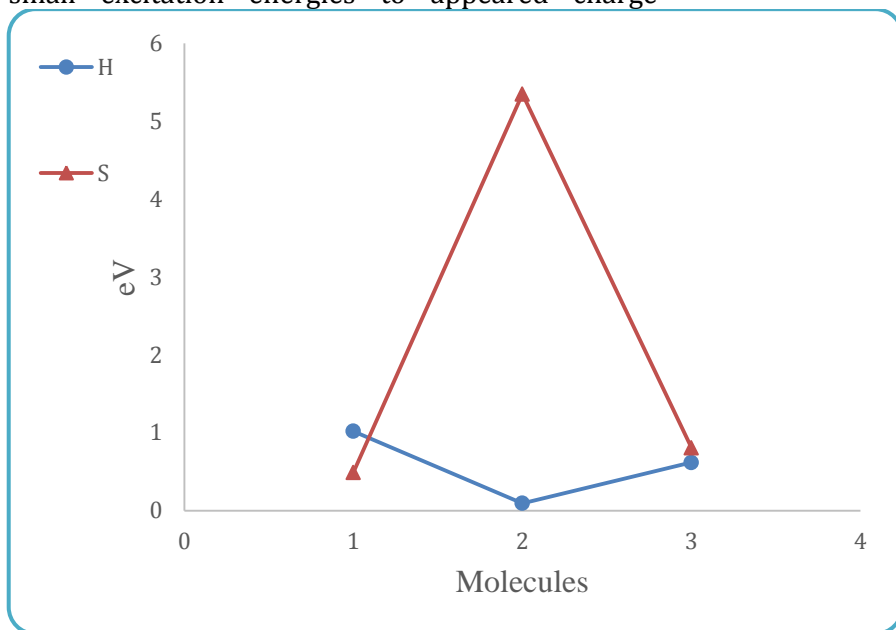


Figure 4. H and S of Nickel metal complexes

Figure 5 showed the Nickel metal complexes have low values of electrophilic index W, the ranking of W is in the order:

$$N1 > N3 > N2$$

The N1 complex has a high ability to interact with other species or molecules in the vicinity of the complex compared to others. 36

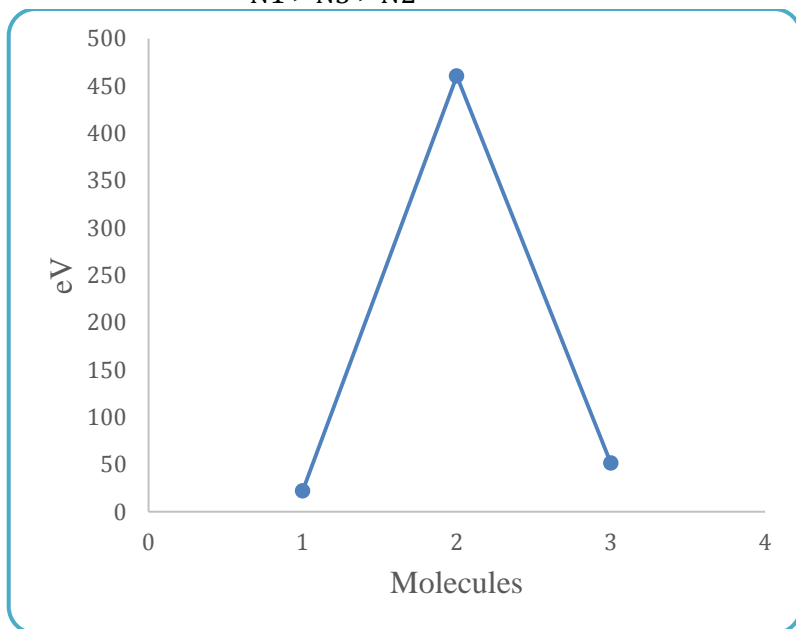


Figure 5. The W of Nickel metal complexes

Figure 6 illustrates the Density of States (DOS) for the studied Nickel metal complexes. As seen, few degeneracy of states was observed for the three complexes and the number of degenerate states in

the HOMOs are greater than the states in LUMOs, in which refers to low charge transition can be obtained in the studied complexes. Above results help us to suggest new Nickel complexes containing



chelating ligands with mixed donors.

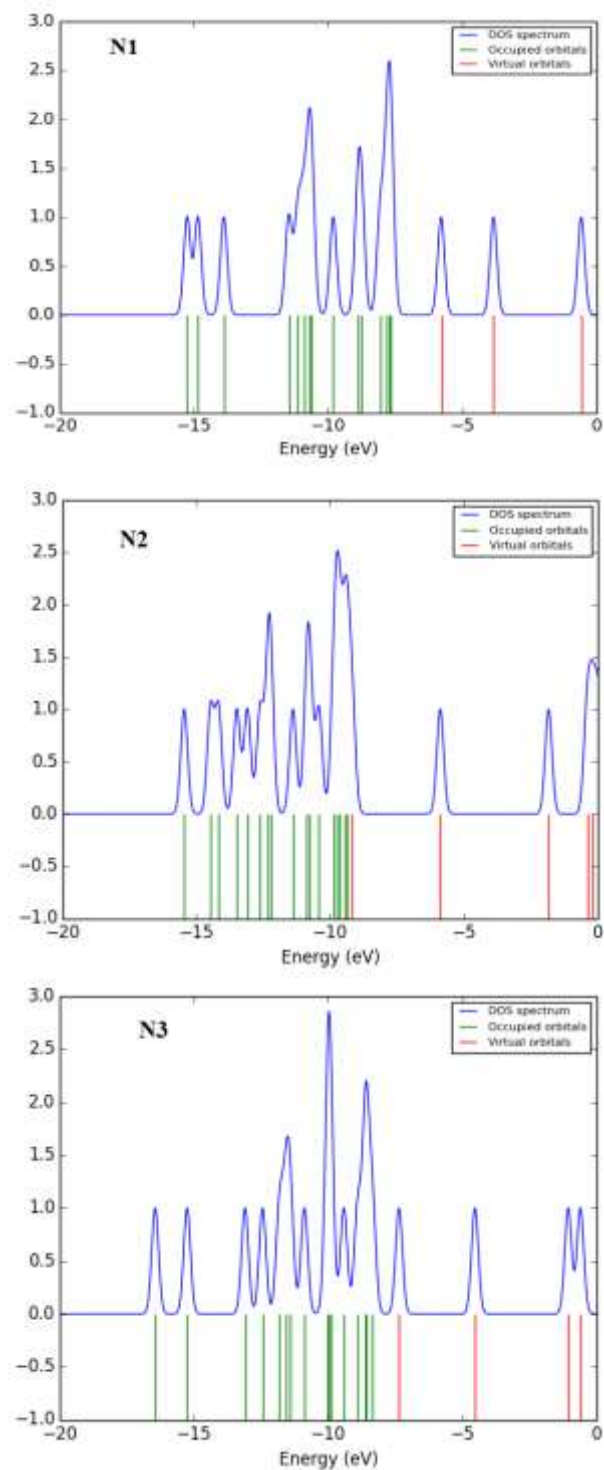
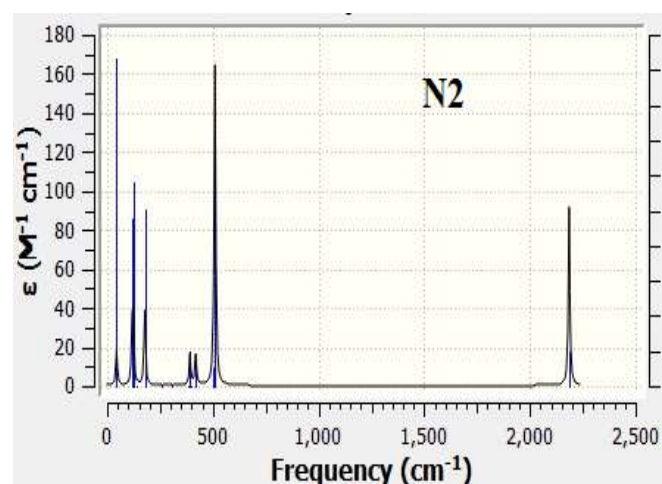
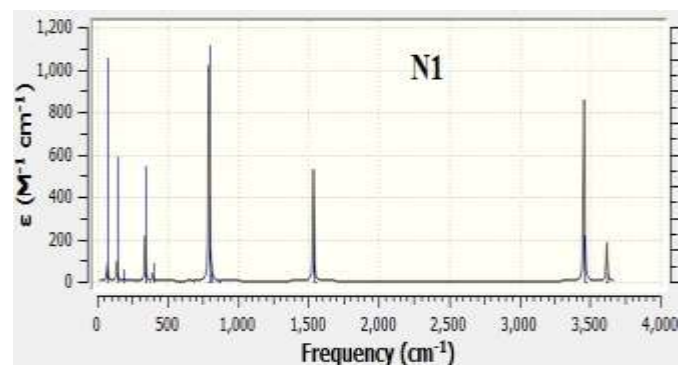


Figure 6. The DOS of Nickel metal complexes

Figure 7 shows the infrared-IR spectra of the studied Nickel complexes. For complex N1, the stretching N-H bonds were observed at (3460.17-3621.85) cm^{-1} , with maximum intensity 248.329 $\text{M}\cdot\text{cm}^{-1}$ corresponding to 3460.17 cm^{-1} where the bending N-H bonds were observed at (852.95-1552.98) cm^{-1} . The stretching Ni-amine were

observed at 811.27 cm^{-1} . The stretching Ni-Cl bonds were observed at low frequency equals 280.79 cm^{-1} and the bending Ni-Cl bonds at 194.49 cm^{-1} .

For complex N2, the stretching C-N bonds were observed at (2185.78-2189.54) cm^{-1} . The stretching Ni-cyanide were observed at 395.29 cm^{-1} and the bending Ni-cyanide were observed at 118.23 cm^{-1} , the stretching Ni-Cl bonds at 307.24 cm^{-1} . For complex N3, the stretching N-H bonds were observed at (3393.81-3545.83) cm^{-1} with intensity 132.503 $\text{M}\cdot\text{cm}^{-1}$, the bending N-H bonds were observed at 1535.79 cm^{-1} . The stretching c-N bond was observed at 2080.35 cm^{-1} corresponding to intensity 287.998 $\text{M}\cdot\text{cm}^{-1}$. The stretching Ni-amine was appeared at 743.67 cm^{-1} and the stretching Ni-cyanide was appeared at 478.97 cm^{-1} . The stretching Ni-Cl bonds were observed at 293.72 cm^{-1} .



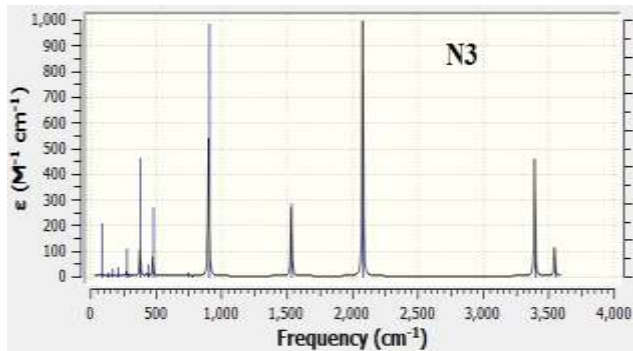


Figure 7. The IR-spectra of Nickel metal complexes

Figure 8 illustrates the spectra of the UV-Vis of the studied complexes. Only complex N1 was appeared absorption in infrared region at maximum wavelength 1122.08 nm corresponds to excitation energy 1.104 eV with oscillation strength 0.0031. Two transition states was recorded, the first is from HOMO-5 to LUMO with probability 13%, and the second is the most probable from HOMO to LUMO with probability 90%.

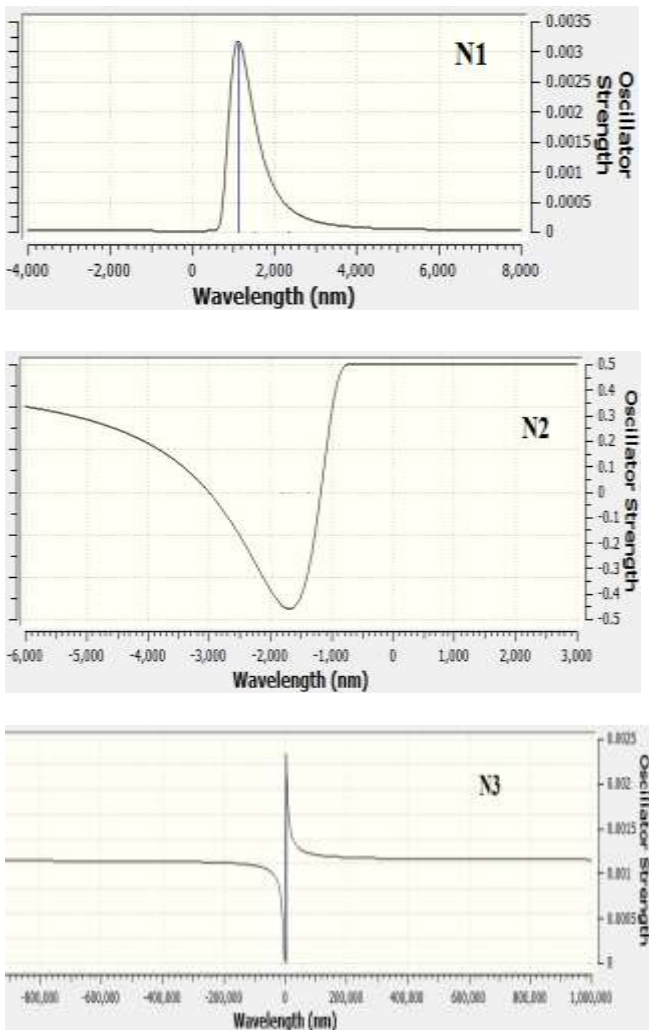


Figure 8. The UV-Vis spectra of Nickel metal complexes

Conclusions

Good relax for the studied Nickel metal complexes was obtained by employing the DFT method with SDD basis set. The energy gap for the complexes was varied depending on the coordination of the complexes and the subgroups in each complex. Complex N2 is more soft compared with the two others. Complex N1 with two amine groups as ligands in the complex was appeared absorption in the infrared region.

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