Theoretical Study of Mixed-Ligand Complexes of Ni (II) Dimethylglyoxime: A Theoretical approach (Semi-empirical and DFT methods)

I.A. Adejoro, B. Akintoye, O.O. Adeboye and O. F. Akinyele
Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

ABSTRACT

The synthesis of non-electrolyte mixed-ligand complexes of the general formula [M(Hdmg)B], Ni(II), Hdmg=dimethylgloximato monoanion, B=2-aminophenol(2-aph), diethylamine (dea) or malonic acid (MOH) has been synthesized and characterized. However theoretical calculations were carried out to obtain the geometric and thermodynamic parameters, vibrational and electronic parameters, dipole moments and HOMO-LUMO band gaps of the complex with different substituents. These properties were obtained using the PM3 and DFT with B3LYP at 6-31G* level. Comparisons were made on the calculated bond length, bond angle, dihedrals and vibrational frequencies and it was observed that the calculated data are in good agreement with experimental data.

Introduction

Computational chemistry is a method that is used to investigate materials that are too expensive to buy. It also helps chemists to make predictions before running the actual experiment so that they can be better prepared for making observations (Shador, 1999-2000). Metal complexes has been gaining recognition in recent times because of its great importance in medicine and related areas of life sciences. It is also important in the design of respiratory, slow and controlled release drugs. It has also been established that the efficacies of some therapeutic agents increase upon coordination (Ajibola, 1990; Obaleye et al, 1997). Molecular modeling is an aspect of computational chemistry that gives accurate results compared with experimental results. PM3 semi empirical quantum mechanical calculations were carried out on a Novel Dichlorobis (N-{4-[(2-pyrimidinyl-kN-amino)sulfonyl}acetamide]copper(II), Containing a Metabolite N-acetylsulfadiazine and the result obtained compares perfectly well with the experimental data. (Adejoro, et al, 2012). Calculations on novel polymeric Zn (II) complex containing the anti-malarial Quinine as ligands gives values that agrees perfectly well with experimental data (Adejoro, et al, 2013). It is used to account for properties such as bond length, bond angle, dihedrals vibrational frequencies atomic charge distributions etc (Conradie, 2010). Theoretical calculations on novel aminopyridino – 1-4-η-cyclohexa-1, 3-diene iron tricarbonyl complexes reveals that the complex is thermodynamically stable (Odiaka et al, 2010). This work used theoretical approach using semi-empirical PM3 and Density Functional Theory (DFT) methods of calculation in Spartan to validate the experimental result obtained by Osunkoya et al, 2011.

Computational Methodology

Conformational search was performed on the molecule to locate the structure with the lowest energy. The conformational search was carried out using molecular mechanics force field (MMFF) which is quite successful in assigning low energy conformers and in providing quantitative estimates of conformational energy differences (Warren, J. Hehre, 2003).
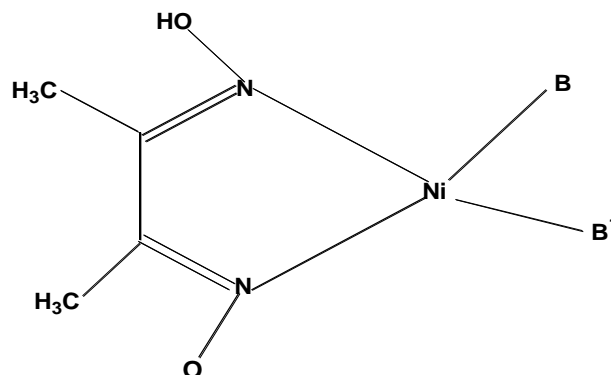
Scheme 1: Structure of the complex B= 2-aminophenol(2-aph) B¹ = Hydrogen B= diethylamine (dea) B¹ = diethylamine(dea) B= malonic acid (MOH) B¹ = Hydrogen

Semi-empirical PM3 and Density functional methods was used to carry out molecular calculations on the complexes. The structures were fully optimized and geometric calculations were done to obtain the bond length, bond angle, and bond dihedrals of the complexes. Thermodynamic calculations, vibrational and electronic properties, heat of formation, dipole moment, E-HOMO, E-LUMO, band gaps.
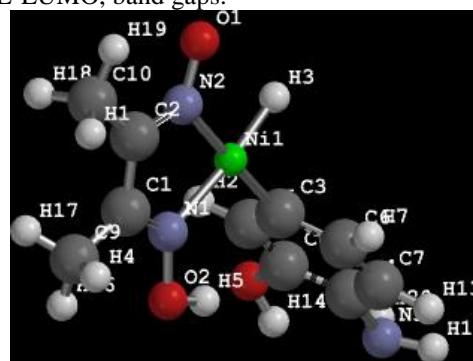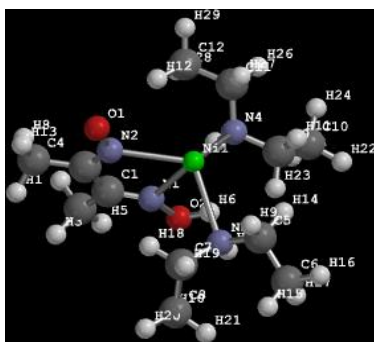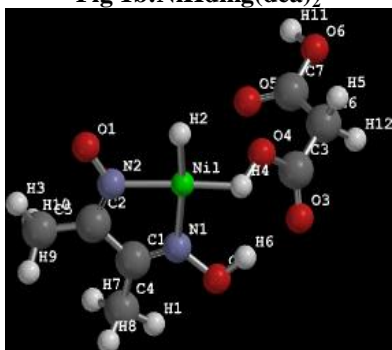

Fig 1a: CoHdmg(2-aph)

Tele:
E-mail addresses: ia.adejoro@mail.ui.edu.ng

Fig 1b:NiHdmg(dea)₂

Fig 1c: CoHdmg(MO)

The structures of mixed-ligand of Ni (II) complex.

Results and Discussion

Geometric parameters: Calculations were carried out on the structure with the lowest values; this was obtained using conformer distribution calculation with MMFF$_{aq.}$ Geometric parameters were obtained after optimization using PM3, DFT (6-31G*). The bond distances, bond angles, and dihedrals were shown below.

Electronic properties: The electronic structure of the metal complex is described by its band structure (David, 2001). This is obtained from HOMO-LUMO calculation. The calculated HOMO-LUMO band gap using PM3 method is greated than that of the DFT/B3LYP/6-31G* that is for NiHdmg(2-aph) is +6.64, NiHdmg(dea)₂ is +8.06 and Nidmg(MO) is +8.06 while with DFT/B3LYP/6-31G* it is +3.01, 7.13 and 3.55 eV for the three complexes repectively.as shown in table 4. This result shows that PM3 method have a better predictive ability the stability of the metal complexes compare with DFT/B3LYP/6-31G* method.

Thermodynamic properties and stabilities: The stability of a complex depends greatly on the thermodynamic parameters. Complexes are thermodynamically stable if ΔG and ΔH are negative. The more negative ΔG and ΔH, the more positive ΔS and the more stable the complex becomes. As shown in table 5 with PM3 ΔG (-0.218, -0.226 and -0.778), ΔH (-0.161, -0.161 and -0.722) and ΔS (499.03, 491.75 and 491.73), with DFT/B3LYP/6-31G* ΔG (-2287.091, -2351.755 and -2342.723), ΔH (-2287.034, -2351.686 and -2342.666) and ΔS (505.82, 504.68 and 504.68) for NiHdmg(2-aph), NiHdmg(dea)₂ and NiHdmg(MO) respectively. The values as obtained from DFT at B3LYP level with 6-31G* basis set, predicts the stability of the Dimethylglyoxime Ni(II) complexes better compared with PM3.

Vibrational Frequencies: The vibrational frequencies obtained theoretically were in perfect agreement with experimental result and experimental spectral results suggest the binding of Hdmg, 2-amino phenol or malonic acid through the N atom and O atoms respectively to the metal ion. It was discovered that DFT with basis set 6-31G* has values closer to experimental values. The absorption bands and their corresponding vibrations for the three complxes are shown tables 6,7 and 8 with their corresponding IR spectra in figures 2a, b and c. The υ(O-H) obtained with DFT(3717–3547 cm⁻¹), (3658 cm⁻¹) and (3682–3687 cm⁻¹) for 2-aph, (dea)₂ and MO respectively compared well with experimental value which was attributed to the O---H-O hydrogen bridges between the dimethylglyoximato ions(Nakamoto, 1986). The band υ(N-H) (3578–3489 cm⁻¹) and (3456-3392 cm⁻¹), υ(N-O) (1378 cm⁻¹), (1521-1509 cm⁻¹) and (1519cm⁻¹) are also closer to experimental values while there is a large variation between the theoretical band obtained for υ(Ni-N) (3120 – 3066, 866 and 1037 cm⁻¹) compared with experimental data (520 cm⁻¹) for 2-aph, (dea)₂ and MO respectively.
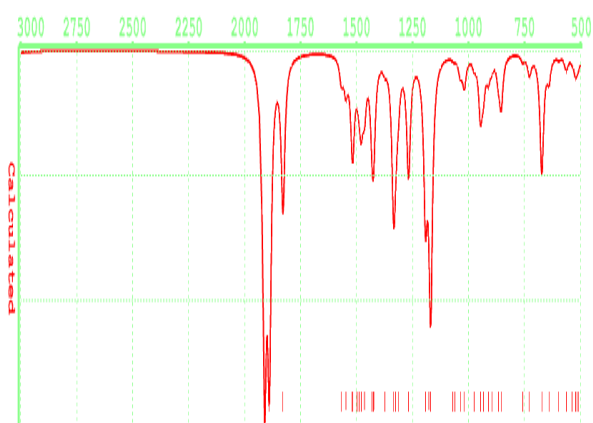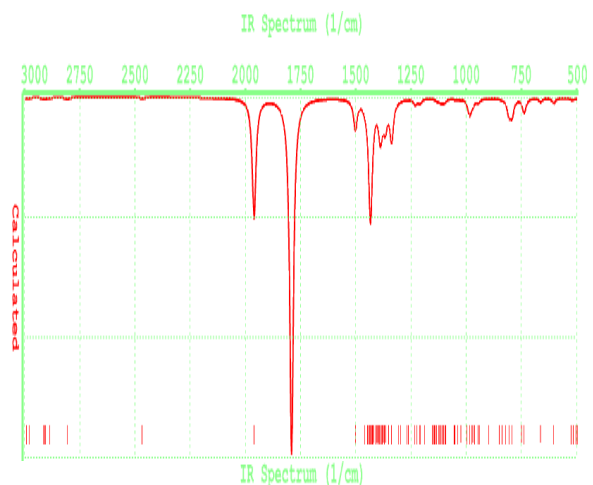

Fig 2a NiHdmg(2-aph) with PM3 with DFT/B3LYP/6-31G*

while the unresolved band at 452nm may account for d-d transition with d-orbital of the meatal ion. Likewise the bands in the UV/Visible spectrum of NiHdgm(MO) (fig3c) at 425nm, 440nm and 476nm are due to metal-ligand charge transfer transitions while the band at 511nm is attributed to the d-d transition within the d-orbitals of the metal ion.

Fig 2b: NiHdmg(dea)$_2$ with PM3 with DFT/B3LYP/6-31G*

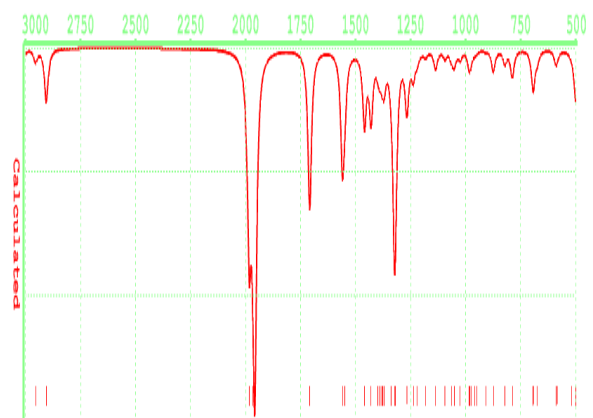**Fig 3a Ultra-Violet/Visible spectra of aminophenol Dimethylglyoxime Nickel(II)**

Fig 2c:NiHdmg(MO) with PM3 with DFT/B3LYP/6-31G*

Electronic Spectra: In the electronic spectra of the complexes, the absorption bands observed in the UV/Visible region (table7) are presumed to be either due to charge transfer or intra-ligand transitions from the ligands or d-d transitions from the metal ions. The UV/Visible spectra data except for [Ni(Hdmg)(MO)] showed two major absorption bands as reported experimentally and the two d-d transition are assigned to 3T1g(F)3→ 3A2g and 3T2g(F)3→ 3A2g respectively (Osunlaja, et al 2011). The UV/Visible spectrum of NiHdmg(2-aph) showed (fig3a) well resolved absorption bands at 398nm, 343nm, these transitions are attributed to metal-ligand charge transfer transitions while the band at 456nm may account for d-d transition with d-orbital of the metal ion. The UV/Visible spectrum of NiHdmg(dea) (fig3b) presents two distinct bands at 383nm and 427nm attributed to metal-ligand charge transition
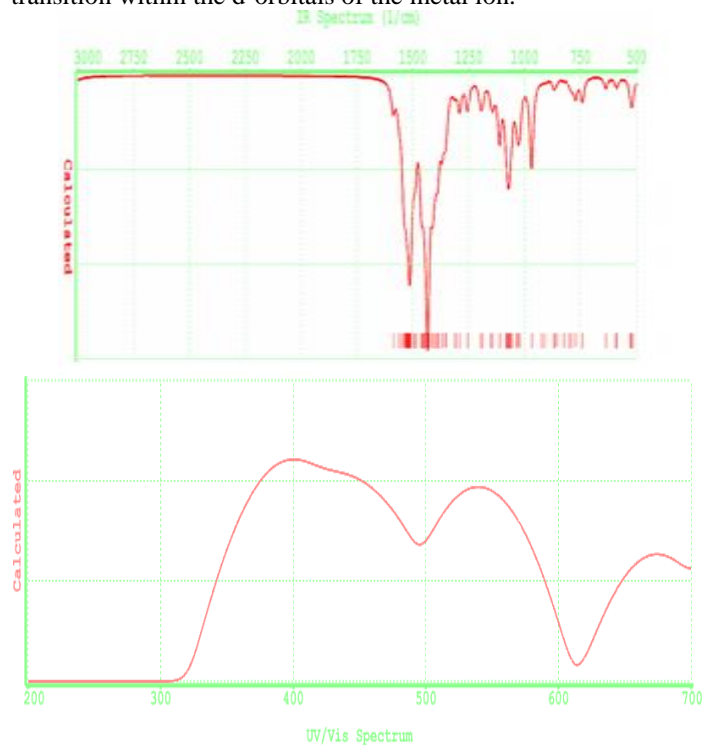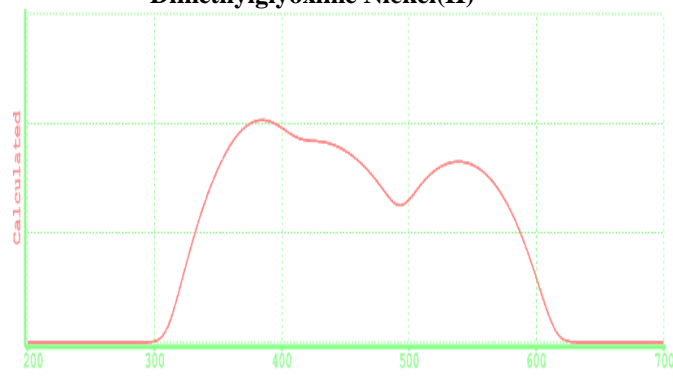
Fig 3b: Ultra-Violet/Visible spectra of Diethylamine dimethylglyoxime Nickel(II)
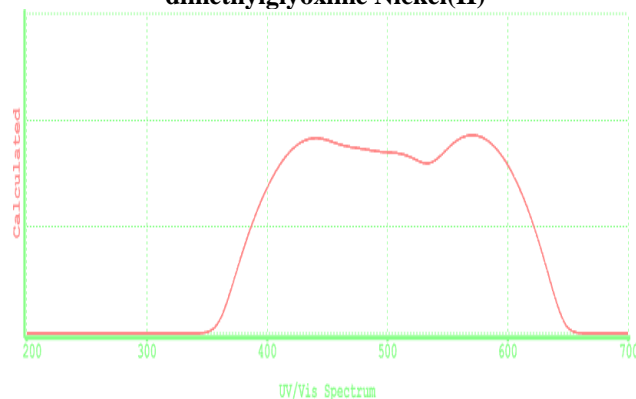

Fig 3c: Ultra-Violet/Visible spectra of Malonic acid dimethylglyoxime Nickel(II)

Table 1: Selected bond distances, bond angles, and dihedrals of 2- aminophenol dimethylglyoxime Nickel(II) (Å)

Bond length	PM3	DFT/ B3LYP 6-31G	Bond angles	PM3	DFT/ B3LYP 6-31G	Dihedrals	PM3	DFT/B3LYP 6-31G*
Ni_1-H_2	1.7794	2.8825	Ni_1-N_3-C_5	106.294	115.257	Ni_1-N_4-C_6-C_5	-0.220	1.632
Ni_1-N_3	1.8217	1.8635	Ni_1-N_3-O_8	79.774	125.071	Ni_1-N_3-C_5-C_6	18.538	6.756
Ni_1-N_4	1.7881	1.8517	Ni_1-N_4-C_6	109.706	115.328	Ni_1-C_{10}-C_{12}-C_{15}	-160.345	-55.201
Ni_1-C_{10}	2.1865	2.1516	Ni_1-N_4-O_7	119.615	120.319	Ni_1-C_{10}-C_{13}-C_{14}	120.022	56.072
N_3-C_5	1.4358	1.3140	Ni_1-C_{10}-C_{12}	69.587	75.286	Ni_1-N_3-O_{18}-H_9	-161.599	-48.693
N_3-O_8	1.4847	1.3893	Ni_1-C_{10}-C_{13}	161.834	72.350	Ni_1-C_{10}-C_{12}-H_{16}	32.318	122.086
N_4-C_6	1.4243	1.3359	H_2-Ni_1-N_3	173.553	165.006	Ni_1-N_4-C_6-C_{23}	177.360	-178.023
N_4-O_7	1.1832	1.2467	H_2-Ni_1-N_4	90.477	81.632	H_2-Ni_1-N_3-C_5	92.568	-5.402
C_5-C_6	1.3734	1.4396	H_2-Ni_1-C_{10}	33.826	18.490	H_2-Ni_1-N_4-C_6	-164.705	-178.649
C_5-C_{19}	1.4695	1.4952	N_3-Ni_1-H_2	173.553	165.006	H_2-Ni_1-N_4-O_7	12.078	1.521

Table 2: Selected bond distances, bond angles, and dihedrals of Diethylamine dimethylglyoxime Nickel(II) (Å)

Bond length	PM3	DFT/ B3LYP 6-31G	bond angles	PM3	DFT/ B3LYP 6-31G	Dihedrals	PM3	DFT/ B3LYP 6-31G
Ni_1-N_2	1.8470	1.8802	Ni_1-N_2-C_8	108.362	116.230	Ni_1-N_3-C_9-C_8	-6.073	1.682
Ni_1-N_3	1.7981	1.8963	Ni_1-N_2-O_{11}	81.974	124.684	Ni_1-N_2-C_8-C_9	-11.874	-9.834
Ni_1-N_4	1.9228	1.9535	Ni_1-N_3-C_9	111.574	115.492	Ni_1-N_2-O_{11}-H_2	171.558	110.618
Ni_1-N_6	1.9391	1.9751	Ni_1-N_3-O_{10}	121.267	124.829	Ni_1-N_2-C_8-C_{13}	170.499	171.770
N_2-C_8	1.4308	1.3211	Ni_1-N_4-H_5	108.151	106.965	Ni_1-N_3-C_9-C_{17}	176.404	-178.870
N_2-O_{11}	1.5042	1.4160	Ni_1-N_4-C_{21}	96.817	111.681	Ni_1-N_4-C_{21}-H_{22}	111.919	62.220
N_3-C_9	1.4280	1.3421	Ni_1-N_4-C_{28}	131.790	111.706	Ni_1-N_4-C_{21}-H_{23}	-4.204	-52.642
N_3-O_{10}	1.1908	1.2576	Ni_1-N_6-H_7	110.477	100.387	Ni_1-N_4-C_{21}-C_{24}	-125.898	-174.299
N_4-H_5	1.0018	1.0210	Ni_1-N_6-C_{35}	89.824	112.829	Ni_1-N_4-C_{28}-H_{29}	-52.992	13.290

Table 3: Selected bond Distance, Bond Angle and Dihedrals for the Malonic acid diethylglyoxime Nickel(II) (Å)

bBond Length	PM3	DFT/ B3LYP 6-31G	bond angles	PM3	DFT/ B3LYP 6-31G	Dihedrals	PM3	DFT/ B3LYP 6-31G
Ni_1-H_2	1.6055	1.4804	Ni_1-N_3-C_5	97.966	111.805	Ni_1-N_4-C_6-C_5	-9.563	-4.873
Ni_1-N_3	1.8741	1.9014	Ni_1-N_3-O_8	91.614	121.745	Ni_1-N_3-C_5-C_6	40.765	20.966
Ni_1-N_4	1.7816	1.8270	Ni_1-N_4-C_6	105.348	113.670	Ni_1-N_3-O_8-H_9	-157.951	-110.168
Ni_1-H_{10}	2.4220	2.4282	Ni_1-N_4-O_7	127.557	127.436	Ni_1-H_{10}-O_{13}-C_{11}	-123.165	-154.043
N_3-C_5	1.4017	1.3273	Ni_1-H_{10}-O_{13}	47.481	50.031	Ni_1-N_3-C_5-C_{14}	-142.129	-162.018
N_3-O_8	1.4541	1.4413	H_2-Ni_1-N_3	175.752	170.807	Ni_1-N_4-C_6-C_{18}	167.788	179.026
N_4-C_6	1.4192	1.3640	H_2-Ni_1-N_4	88.805	92.573	H_2-Ni_1-N_3-C_5	40.366	48.250
N_4-O_7	1.1930	1.2493	H_2-Ni_1-H_{10}	103.141	117.377	H_2-Ni_1-N_4-C_6	-148.000	-158.575
C_5-C_6	1.3966	1.4198	N_3-Ni_1-H_2	175.752	170.807	H_2-Ni_1-N_4-C_7	32.769	21.822
C_5-C_{14}	1.4773	1.4413	N_3-Ni_1-N_4	90.339	83.843	H_2-Ni_1-N_3-O_8	-74.306	-95.583

Table 4: Electronic Properties of the Ni (II) complexes

COMPLEXES	Dipole moment/debye		EHOMO/ eV		ELUMO/eV		Bandgap/eV	
	PM3	DFT	PM3	DFT	PM3	DFT	PM3	DFT
NiHdmg(2-aph)	1.54	5.69	-12.08	-9.23	-5.44	-6.64	+6.64	+3.01
NiHdmg (dea)$_2$	1.55	4.46	-8.94	-8.87	-0.88	-1.74	+8.06	+7.13
NiHdmg(MO)	3.75	3.59	-8.94	5.29	-0.88	-1.74	+8.06	+3.55

Table 5: Thermodynamic properties of the Nickel(II) complexes

COMPLEXES	Methods	Heat of formation kJmol^{-1}	SCF Total energy/au	Free energy/ au	Enthalpy/ au	Entropy Jmol^{-1}K^{-1}
NiHdmg(2aph)	PM3	-1104.503	-	-0.218	-0.161	499.03
	DFT/6-31G*	-	-2287.293	-2287.091	-2287.034	505.82
NiHdmg(dea)$_2$	PM3	-1583.084	-	-0.226	-0.161	491.75
	DFT/6-31G*	-	-2352.134	-2351.755	-2351.686	504.68
NiHdmg(MO)	PM3	-2495.829	-	-0.778	-0.722	491.73
	DFT/6-31G*	-	-2342.723	-2342.723	-2342.66	504.68

Table 6: Absorption Bands with their corresponding Vibration. Ni (II) complexes (cm⁻¹)

Complexes	Vibrations	Experimental	PM3	DFT
NiHdmg (2aph)	O–H stretching	3415	3862 – 3827	3717 – 3547
	N-H stretching	3253	3528 – 3411	3578 – 3489
	Ni-N stretching	520	1161	3120 – 3066
	N-O stretching	1240	2006	1378
	Ni–H stretching	N/A	2288	3259
	C–C stretching	N/A	1769	1529
	C–N stretching	N/A	1492	1636 – 1558
	C=C stretching	N/A	1082	1623
	C-H saturation	N/A	3157-3144	1558
	C-H aromatic	N/A	3065 – 3025	3247 – 3220
NiHdmg (dea)₂	O – Hstretching	3446	3819	3658
	C = Nstretching	1462	1502	1588
	Ni – Nstretching	520	792	866
	N – Ostretching	1239	1960	1521-1509
	N – Hstretching	N/A	3339-3317	3456-3392
	C – Hstretching	N/A	3182-3178	3185
	C – Cstretching	N/A	1791	1541
	C – Hbending	N/A	1447	1072
Ni Hdmg (MO)	O–H stretching	3443	3872-3623	3682 – 3687
	C-O stretching	1377	1983	1889-1828
	N-O saturation	1239	1966 – 1958	1519
	Ni-N stretching	520	1136	1037
	C-N stretching	1461	1559 -1370	1567 – 1334
	Cu-H stretching	N/A	3664 – 3129	3653 – 2009
	C–C stretching	N/A	1708 – 1319	1547
	C–H stretching	N/A	3012 – 2954	3148 – 3094
	Ni–H stretching	N/A	1183	1911
	C-H saturation	N/A	3161-3129	3653

Table 7: Wavelength and intensity of Nickel(II) complexes (nm)

NiHdmg (2-aph)		NiHdmg (dea)₂		NiHdmg (MO)	
Wavelength	Intensity	Wavelength	Intensity	Wavelength	Intensity
398.48	0.0252079	383.96	0.0112627	425.21	0.00103689
343.65	0.0107276	427.19	0.00376201	440.97	0.00366562
456.93	0.00341757	452.32	0.00155451	476.55	0.00230483
539.63	0.00751611	473.91	0.000143928	511.68	0.00202609
674.35	0.000340581	527.78	0.001181173	564.12	0.00280195
742.59	0.00161888	549.05	0.00123535	577.02	0.00282956

Conclusion

The properties of the Ni(II) mixed-ligand complexes of dimethylglyoxime were calculated using Semi-empirical and DFT methods. The optimized geometries, dipole moments, geometric, thermodynamics, vibrational and electronic parameters were investigated. Computational method has presented us the opportunity to take a critical look at this mixed-ligand complexes of dimethylglyoxime to produce results which compared favourably well with experimental data. It has also given us the opportunity to compute results on the properties that cannot be obtained in laboratory experiments. In studying and predicting the geometric parameters, vibrational and electronic properties of these compounds, the PM3 semi-empirical method accounted well for the geometri parameters whle the DFT/B3LYP/6-31G* for the vibrational and electronic frequencies . It can then be concluded that both methods (Semi-empirical PM3 and DFT/B3LYP) could be used for predicting the properties of transition metal complexes.

References

1. A.A. Osunlaja, N. P. Ndahi and J. A. Ameh(2009) Synthesis, physico-chemical and Antimicrobial properties of Co(II), Ni(II) and Cu(II) mixed-ligand complexes of dimethylglyoxime - Part I

2. Nakamoto,K, 1986. Infrared and Raman Spectra ofInorganic and Coordination Compounds. 3rd Edn.,John Wiley and Sons New York, pp:194-197,205-233.

1. Obaleye, J.A., J.B. Nde-aga and E.A. Balogun, 1997. Some antimalaria drug metal complexes: Synthesis, characterization and their in vivo evaluation against malaria parasite. Afr. J. Sci., 1: 10-12

2. Oguniran, K.O., A.C. Tella, M. Alensela and M.T. Yakubu, 2007. Synthesis, physical properties, antimicrobial potentials of some antibiotics complexes with transition metals and their effects on alkaline phosphatase activities of selected rat tissues. Afr. J. Bio., 6(10): 1202-1208.

3. Osunlaja, A.A., N.P. Ndahi and J.A. Ameh, and A.Adetoro 2010. Synthesis, physico-chemical and antimicrobial properties of Co (II), Ni (II) and Cu (II) mixed-ligand complexes of dimethylglyoxime

4. Peter J. Sadler and Zijian Guo(1998) Metal complexes in medicine: Design and mechanism of action.

5. Robert, A.B.,1994.Chelating agents and the regulation of metal ions. Meta-based Drugs,1 (2-3):87-106.

6. Shayma A. Shaker(2009) Synthesis and Characterization of Mixed Ligand Complexes of 8-Hydroxyquinoline and *o*-

hydroxybenzylidene-1-phenyl-2,3-dimethyl-4-amino-3-pyrazolin-5-on with Fe(II), Co(II), Ni(II) and Cu(II) ions

7. Shazia Rafique*, Muhammad Idrees, Anwar Nasim, Haji Akbar and Amin Athar (2010) Transition metal complexes as potential therapeutic agents – Journal of Biotechnology and Molecular Biology Reviews vol.5(2) Pp.38-45. National Centre of Excellence in Molecular Biology, University of punjah, Lahore53700, Pakiatan.

8. Sonja B. Braun-Sand and Olaf Wiest, 2002: Theoretical Studies of Mixed Valence Metal Complexes for Molecular Computing. Journal of Physical Chemistry A (2003) 107, 285-291. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556-5670

9. Taura DW, Okoli AC, Bichi AH (2004). In –vitro antibacterial activities of ethanolic extracts of Annona Cosmosus L. Alliums Sativum L. and Aloe barbadensis L. in Comparison with Ciprofloxacin.

10. Warren Hehre and Sean Ohlinger (2010) Spartan '10 Tutorial and user's guide. Wavefunction Inc. ISBN978-1-890661-41-4

11. Warren J Hehre (2003) A guide to molecular mechanics and Quantum Chemical calculations in Spartan. Wavefunction, Inc. ISBN 1-890661-18-X

12. Yusuf Zalaoglu, Asaf Tolga Ulgen, Cabir Terzioglu and Gurean Yildirm (2010) Theoretical study on the characterization of 6-methyl 1,2,3,4-Tetrahydroquinoline using quantum mechanical calculation methods.