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Semi-Empirical and DFT Studies of Mixed-Ligand Complexes of Cu(II) Dimethylglyoxime.

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ABSTRACT

Abstract: The non-electrolyte mixed-ligand complexes of the general formula [M(Hdmg)B], M=Cu(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 obtained the geometric properties such as bond length, bond angle and dihedrals. Thermodynamic parameters, vibrational and electronic properties, dipole moments and HOMO-LUMO band gaps of the complex with different substituents were also calculated. These properties were obtained using the PM3 and DFT with B3LYP at 6-31G* level. Comparisons were made and it was observed that the calculated data are in good agreement with experimental data.

KEYWORDS: Geometric parameters, Semi-Empirical, Dipole moments, Band gaps modelling.

RESUMO

Os complexos metal-ligante mistos que são não-eletrólitos e tem a formula geral [M(Hdmg)B], M=Cu(II), Hmg=anion dimetilglioximato, B=2-aminofenol (2-aph), dietilamina(dea) ou acído malonico (MOH) foram sintetizados e caracterizados. Foram efetuados cálculos teóricos para obter propriedades geométricas tais como comprimentos de ligação, ângulos e diedros.Propriedades termodinâmicas, vibracionais e eletrônicas, momentos dipolares e intervalos de bandas HOMO-LUMO também foram calculadas para o complexo com susbtituintes diferentes. Os cálculos foram efetuados com métodos PM3 e DFT com B3LYP no nível 6-31G. Os valores calculados estão de acordo com dados experimentais.

PALAVRAS CHAVE

Parâmetros Geométricos, Métodos Semi-Empíricos, Modelos de Intervalos entre Bandas

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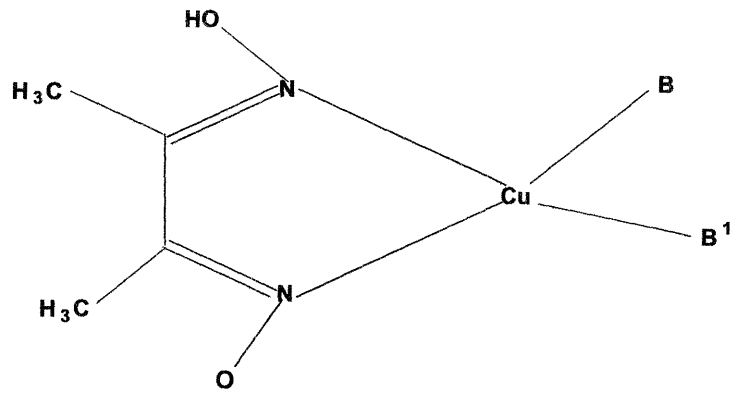
INTRODUCTION

The term computational chemistry is generally used when a mathematical method is sufficiently well developed that it can be used automatically on a computer. Quantum mechanics gives a mathematical description of the behavior of electrons that has never been found to be wrong. However, the quantum mechanical equations have never been solved exactly for any chemical system other than the hydrogen atom. Thus, the entire field of computational chemistry is built around approximate solutions. Some of these solutions are very crude but are still more accurate than any experiment that has yet been conducted (David, 2001) It also helps chemists to make predictions before running the actual experiment so that they can be better prepared for making observations (Shodor, 1999-2000). Chelation chemistry 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). Metal complexes, especially mixed-ligands are reported to exhibit different activities (Kudirat *et al.*, 1994; Yeamin *et al.*, 2003; Oguniran *et al.*,2007). Molecular modeling is an aspect of computational chemistry that gives accurate results compared with experimental results. It is used to account for properties such as bond length, bond angle, dihedrals vibrational frequencies atomic charge distributions etc. (Conradie, 2010). PM3 semi empirical quantum mechanical calculations were carried out on a Novel Dichlorobis (N-{4-[(2-pyrimidinyl-kNamino)sulfonyl}acetamide]copper(II), Containing a Metabolite N acetylsulfadiazine and the result obtained compares perfectly well with the experimental data. (Adejoro, *et al*, 2012). Quantum mechanical calculations were carried out on mixed-ligand complex of Co (II) dimethylglyoximes. It was observed that the calculated data agreed well with experimental data. (Adejoro *et al.*, 2013). 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). Theoretical calculations on novel aminopyridino – 1-4-□-cyclohexa-1, 3-diene iron

tricarbonyl complexes reveals that the complex is thermodynamically stable (Odiaka et al, 2010). Theoretical investigations were carried out on the characterization of 6-methyl 1,2,3,4 – tetrahydroquinoline using quantum mechanical calculation methods and it was observed that the calculated bond length and bond angles were in good agreement with experimental data (Yusuf, 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.



Scheme 1: Structure of the complex B= 2-aminophenol(2-aph) B^1 = Hydrogen
B= diethylamine (dea) B^1 = diethylamine(dea)
B= malonic acid (MOH) B^1 = Hydrogen

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, 2003). 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.

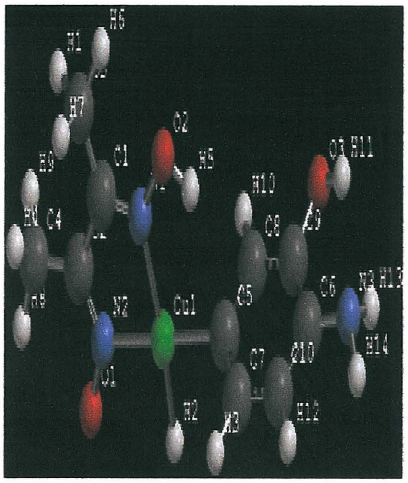


Fig1a: CuHdmg(2-aph)

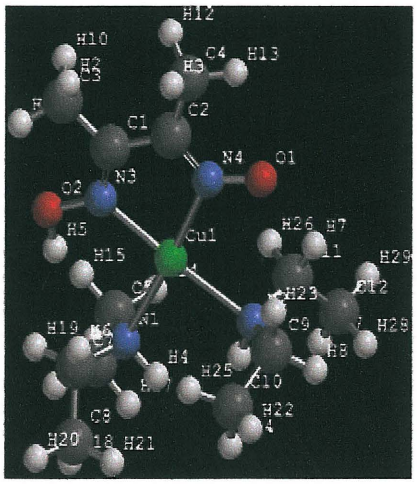


Fig 1b:CuHdmg(dea)$_2$

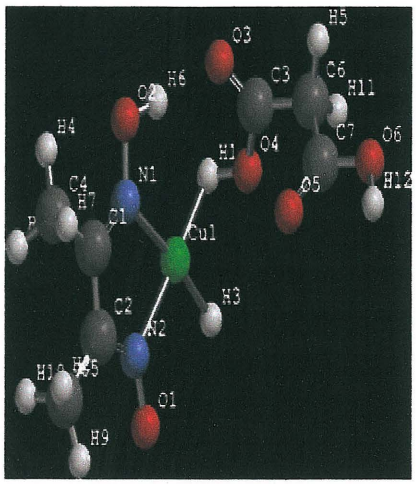


Fig 1c: CuHdmg(MO)

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

RESULTS AND DISCUSSION

Geometric parameters: Calculations were carried out on the structure with the lowest values; this was obtained using confomer distribution calculation with MMFF$_{aq.}$ Geometric parameters were obtained after optimization using Semi-Empirical PM3 and DFT/B3LYP/(6-31G*). The bond distances, bond angles, and dihedrals are calculated as shown in tables 1a, 1b and 1c below.

Table 1a: Selected bond distances, bond angle and dihedral of 2 aminophenol dimethylglyoxime Copper(II)

Bond length	PM3	DFT/ B3LYP	Bond Angle	PM3	B3LYP	Dihedral	PM3	B3LYP
Cu_1-H_2	1.5728	1.4433	Cu_1-N_3-C_5	107.186	114.061	Cu_1-N_4-C_6-C_5	4.343	0.169
Cu_1-N_3	1.9038	1.9204	Cu_1-N_3-O_8	136.372	129.476	Cu_1-N_3-C_5-C_6	-10.005	-4.625
Cu_1-N_4	1.8535	1.9578	Cu_1-N_4-C_6	106.311	112.378	Cu_1-N_3-O_8-H_9	1.702	16.131
Cu_1-C_{18}	1.9402	1.8752	Cu_1-N_4-O_7	128.955	125.627	Cu_1-N_3-C_5-C_{10}	171.615	175.127
N_3-C_5	1.3373	1.3088	Cu_1-C_{18}-C_{20}	153.233	123.328	Cu_1-N_4-C_6-C_{14}	-177.473	179.848
N_3-O_8	1.4859	1.3945	Cu_1-C_{18}-C_{21}	83.976	116.132	Cu_1-C_{18}-C_{21}-C_{22}	178.532	169.405
N_4-C_6	1.3769	1.3440	H_2-Cu_1-N_3	157.252	172.573	Cu_1-C_{18}-C_{20}-C_{23}	-177.473	-168.251
N_4-O_7	1.2188	1.2605	H_2-Cu_1-N_4	90.358	102.999	Cu_1-C_{18}-C_{20}-H_{24}	3.319	13.132
C_5-C_6	1.4368	1.4447	H_2-Cu_1-C_{18}	82.432	73.040	H_2-Cu_1-N_4-C_6	-2.824	-11.871
C_5-C_{10}	1.4888	1.4998	N_3-Cu_1-H_3	157.252	172.573	H_2-Cu_1-N_3-C_5	-82.824	149.237

Table 1b: Selected bond distances, bond angle and dihedral of Diethylamine Dimethylglyoxime Copper(II)

Bond Length	PM3	B3LYP	Bond Angle	PM3	B3LYP	Dihedral	PM3	B3LYP
Cu_1-N_2	1.9320	3.9201	Cu_1-N_2-H_3	103.163	54.936	Cu_1-N_7-C_9-C_8	0.517	-18.437
Cu_1-N_4	1.9324	1.9373	Cu_1-N_2-C_{21}	102.451	111.455	Cu_1-N_6-C_8-C_9	5.822	-13.070
Cu_1-N_6	1.9196	1.8853	Cu_1-N_2-C_{28}	126.021	130.234	Cu_1-N_6-O_{11}-H_{12}	-17.112	51.323
Cu_1-N_7	1.8809	2.0193	Cu_1-N_4-H_5	103.289	115.754	Cu_1-N_6-C_8-C_{13}	-175.270	166.573
N_2-H_3	1.0021	1.0195	Cu_1-N_4-C_{35}	126.696	108.552	Cu_1-N_7-C_9-C_{17}	-179.387	161.818
N_2-C_{21}	1.5169	1.4697	Cu_1-N_4-C_{42}	105.525	104.270	Cu_1-N_2-C_{21}-H_{22}	-2.115	-1.793
N_4-C_{28}	1.5335	1.4754	Cu_1-N_6-C_8	106.950	112.908	Cu_1-N_2-C_{21}-H_{23}	-116.219	-115.141
N_4-H_5	1.0026	1.0214	Cu_1-N_6-O_{11}	139.133	127.637	Cu_1-N_2-C_{21}-C_{24}	118.936	120.945
N_4-C_{35}	1.5403	1.4917	Cu_1-N_7-C_9	105.580	108.702	Cu_1-N_2-C_{28}-H_{29}	-48.472	25.561
N_4-C_{42}	1.5151	1.4979	Cu_1-N_7-O_{10}	132.786	125.496	Cu_1-N_2-C_{28}-H_{30}	65.983	139.453

Table 1c: Selected bond distances, bond angle and dihedral of Malonic acid Dimethylglyoxime Copper(II)

Bond Length	PM3	B3LYP	Bond Angle	PM3	B3LYP	Dihedral	PM3	B3LYP
Cu_1-H_2	1.5743	1.4627	Cu_1-N_3-C_5	92.444	114.020	Cu_1-N_4-C_6-C_5	-25.760	2.302
Cu_1-N_3	1.9010	1.9207	Cu_1-N_3-O_8	131.792	128.240	Cu_1-N_3-C_5-C_6	42.890	0.236
Cu_1-N_4	1.8636	1.9181	Cu_1-N_4-C_6	95.966	111.452	Cu_1-N_3-O_8-H_9	-110.392	-36.557
Cu_1-H_{10}	2.2507	3.1134	Cu_1-N_4-O_7	135.264	124.791	Cu_1-H_{10}-O_{13}-C_{11}	-134.354	167.536
N_3-C_5	1.3791	1.3042	Cu_1-H_{10}-O_{13}	55.591	36.586	Cu_1-N_3-C_5-C_{14}	-144.524	-178.713
N_3-O_8	1.4769	1.3842	H_2-Cu_1-N_3	173.479	160.211	Cu_1-N_4-C_6-C_{18}	160.508	-179.451
N_4-C_6	1.3935	1.3368	H_2-Cu_1-N_4	83.955	87.183	H_2-Cu_1-N_3-C_5	-47.190	-63.844
N_4-O_7	1.2043	1.2328	H_2-Cu_1-H_{10}	93.867	105.784	H_2-Cu_1-N_4-C_6	-137.441	160.465
C_5-C_6	1.4267	1.4507	N_3-Cu_1-H_2	173.479	160.211	H_2-Cu_1-N_4-O_7	33.666	-24.602
C_5-C_{14}	1.4819	1.4955	N_3-Cu_1-N_4	89.526	84.197	H_2-Cu_1-N_3-O_8	-177.240	124.947

Electronic properties: It is important to examine the HOMO-LUMO so as to explain the electronic properties of complexes. The electronic structure of the metal complex is described by its band structure (David, 2001). This is obtained from HOMO-LUMO energy calculation. The calculated HOMO-LUMO band gap using PM3 method is greater than that of the DFT/B3LYP/6-31G* that is for CuHdmg(2-aph) is +8.07, CuHdmg(dea)$_2$ is +8.25 and CuHdmg(MO) is +7.59 while with DFT/B3LYP/6-31G* it is +3.46, +3.13 and +2.52eV for the three complexes respectively as shown in table 2. This result shows that PM3 method have a better predictive ability of the stability of the metal complexes than DFT/B3LYP/6-31G* method.

Table 2: Dipole moments E HOMO, E LUMO, Band gaps of the Cu(II) complex.

COMPLEXES	Dipole moment/debye		EHOMO/ eV		ELUMO/eV		Bandgap/Ev	
	PM3	DFT	PM3	DFT	PM3	DFT	PM3	DFT
CuHdmg(2-aph)	4.71	5.47	-8.82	-5.24	-0.75	-1.78	+8.07	+3.46
CuHdmg $(dea)_2$	7.77	6.79	-7.20	-3.69	1.05	-0.56	+8.25	+3.13
CuHdmg(MO)	4.80	4.54	-12.96	-9.80	-5.37	-7.28	+7.59	+2.52

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 3 with PM3 ΔG (-0.040, -0.172 and -0.037), ΔH (-0.097, -0.239 and -0.094) and ΔS (504.21, 589.76 and 500.44), with DFT/B3LYP/6-31G* ΔG (-2419.395, -2484.051 and -2474.570), ΔH (-2419.336, -2483.982 and -2474.570) and ΔS (515.16, 611.10 and 509.21) for CuHdmg(2-aph), CuHdmg$(dea)_2$ and CuHdmg(MO) respectively. The values as obtained from DFT at B3LYP level with 6-31G* basis set, predicts the stability of the Dimethylglyoxime Cu(II) complexes better than PM3.

Table 3: Thermodynamic properties

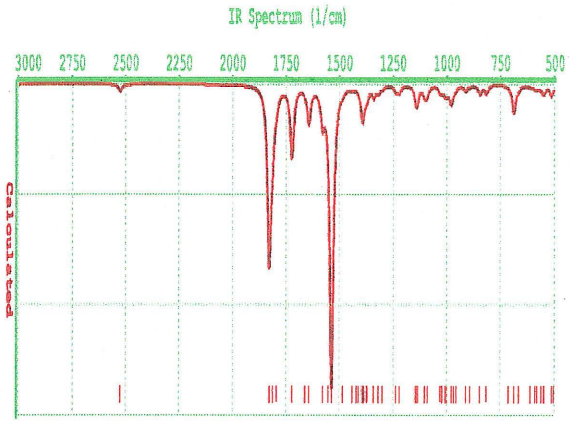
COMPLEXES	Methods	Heat of formation $kJmol^{-1}$	SCF Total energy/au	Free energy/ au	Enthalpy/ au	Entropy $Jmol^{-1}K^{-1}$
CuHdmg(2aph)	PM3	-427.365	-	-0.040	-0.097	504.21
	DFT/6-31G*	-	-2419.589	-2419.395	-2419.336	515.16
CuHdmg$(dea)_2$	PM3	-534.401	-	-0.172	-0.239	589.76
	DFT/6-31G*	-	-2484.427	-2484.051	-2483.982	611.10
CuHdmg(MO)	PM3	-344.490	-	-0.037	-0.094	500.44
	DFT/6-31G*	-	-2474.792	-2474.628	-2474.570	509.21

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 complexes are shown tables 4 with their corresponding IR spectra in figures 1a, b and c. The □(O-H) obtained with DFT(3624 - 3510 cm^{-1}), (3154 cm^{-1}) and (3701–3647 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 □(N-H) (3896-3870 cm^{-1}) and (3479-3449 cm^{-1}), □(N-O) (1487 cm^{-1}), (1458cm^{-1}) and (1458cm^{-1}) are also closer to experimental values while there is a large variation between the theoretical band obtained for

□(Cu-N) (2114, 1648, 987 cm^{-1}) compared with experimental data (520 cm^{-1}) for 2-aph, $(dea)_2$ and MO respectively.

Table 4: Absorption bands with their corresponding vibrations of the Cu(II) complexes.

Complexes	Vibrations	Experimental	PM3	DFT
CuHdmg (2aph)	O–H stretching	3451	3896-3870	3624 - 3510
	N-H stretching	3253	3524-3393	3553 – 3470
	C-N stretching	1461	1721	1658
	N-O stretching	1298	1827	1487
	C–H unsaturation	N/A	3087-3041	3205 – 3189
	Cu-N stretching	N/A	3144	2114
	C=C aromatic	N/A	1812-1793	1650 – 1610
	C-H saturation	N/A	3076-3165	3065 – 3038
	C–C stretching	N/A	1579-1536	1528 – 1030
CuHdmg $(dea)_2$	O – Hstretching	3399	3940	3154
	Cu – Nstretching	520	744	765
	N – Ostretching	1197	1691	1458
	C = N stretching	1462	1718 -1501	1648
	N – H stretching	N/A	3348	3479-3449
	C – H stetching	N/A	3180 -3177	3161-3142
	C – H bending	N/A	1454	1556
	C – C stretching	N/A	1565	1548
	O – H bending	N/A	1323	895
CuHdmg (MO)	O-H stretching	3424	3888	3701 – 3647
	Cu–N stretching	510	1128	987
	C=N stretching	1461	1400	1658– 1395
	O-H bending	N/A	829	
	C=O stretching	N/A	2118-1960	1906 – 1704
	N–O Stretching	N/A	1887	1208
	C–C stretching	N/A	1606-1438	1575 – 1433
	Cu-H stretching	N/A	3664-3129	3653-2009
	C-H saturation	N/A	3161-3152	3306-1521



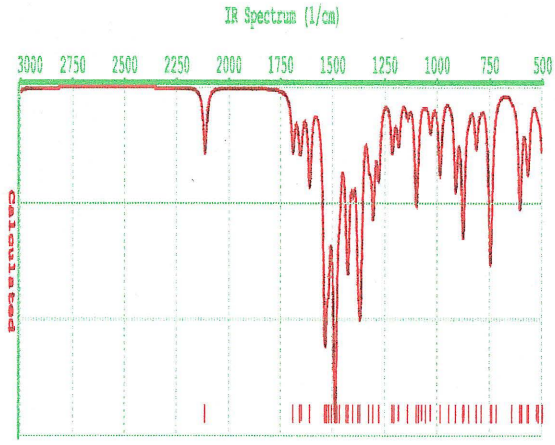
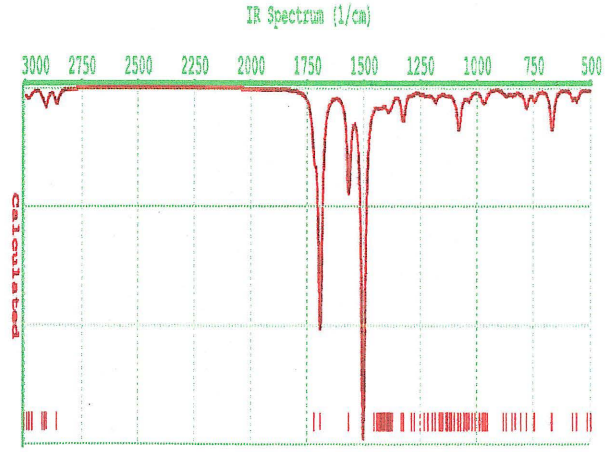


Fig 1a: 2 aminophenol dimethylglyoxime Copper(II) with PM3 with DFT/B3LYP/6-31G*



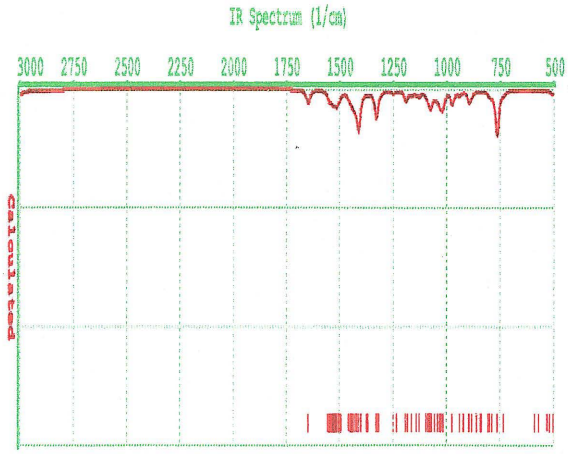
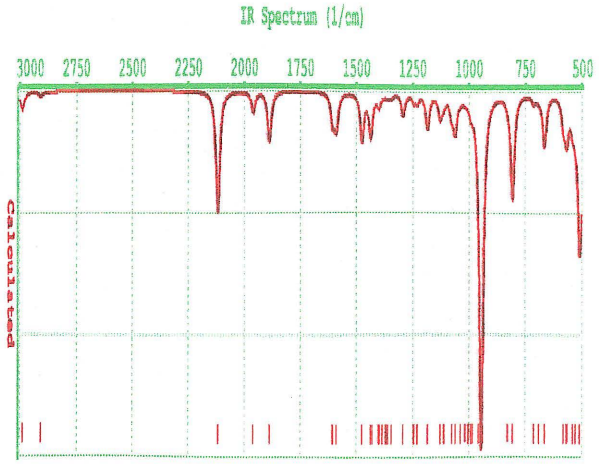


Fig1b: Diethylamine dimethylglyoxime Copper(II) with PM3 with DFT/B3LYP/6-31G*



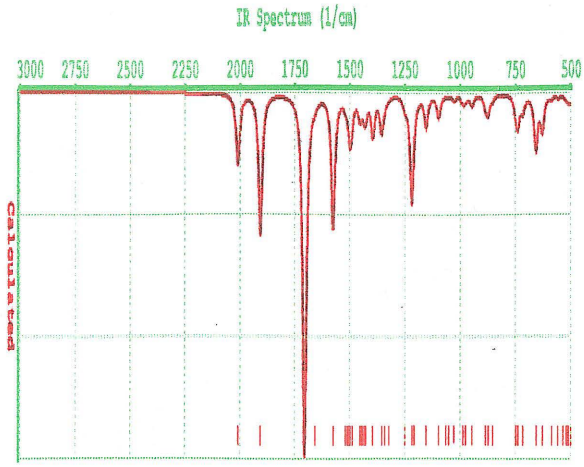


Fig 1c:Malonic acid dimethylglyoxime Copper(II) with PM3 with DFT/B3LYP/6-31G*

Electronic Spectra: In the electronic spectra of the complexes, the absorption bands observed in the UV/Visible region (table 5) 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 for [Cu(Hdmg)(MO)] showed a broad asymmetric ligand field band as reported experimentally which correspond to $^2Eg \rightarrow {}^2T_{2g}$ in a nearly octahedral arrangement(Osunlaja, et al 2009). The UV/Visible spectrum of CuHdmg(2-aph) showed (fig 2a) well resolved absorption bands at 303nm, 318nm, these transitions are attributed to metal-ligand charge transfer transitions while the band at 443nm may account for d-d transition with d-orbital of the metal ion. The UV/Visible spectrum of CuHdmg(dea) (fig 2b) presents two distinct bands at 323nm and 364nm attributed to metal-ligand charge transition while the unresolved band at 621nm may account for d-d transition with d-orbital of the metal ion. Likewise the bands in the UV/Visible spectrum of CuHdmg(MO) (fig 2c) at 333nm, 372nm and 423nm are due to metal-ligand charge transfer transitions while the band at 928nm is attributed to the d-d transition within the d-orbitals of the metal ion.

Table 5: Ultra-Violet /Visible Copper(II) complexes with DFT/B3LYP/6-31G*

CuHdmg (2-aph)		**CuHdmg $(dea)_2$**		**CuHdmg (MO)**	
Wavelength (nm)	Intensity	Wavelength(nm)	Intensity	Wavelength(nm)	Intensity
303.11	0.175889	323.20	0.0007745	333.18	0.0138492
318.80	0.0224263	328.25	0.0062329	346.59	0.0029771
337.88	0.0522114	343.16	0.0120341	354.95	0.0039590
375.52	0.0920143	364.22	0.0569927	372.64	0.0013333
443.93	0.0038168	369.55	0.0361022	423.84	0.0661973
501.93	0.0031115	621.96	0.0103669	928.64	0.0002647

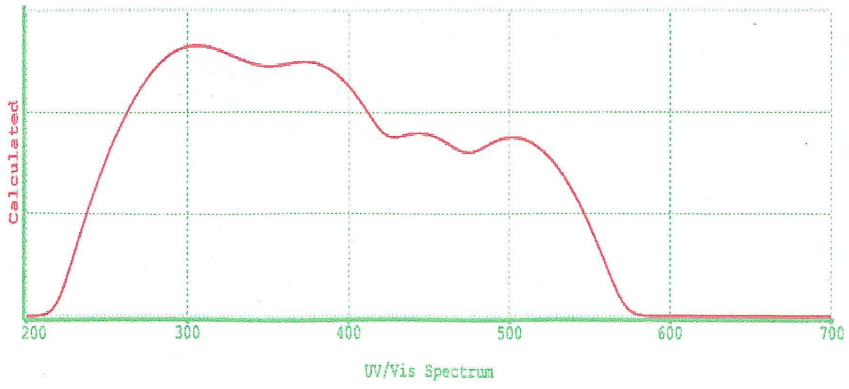


Fig 2a: Ultra violet/Visible spectra of 2 aminophenolglyoxime Copper(II)

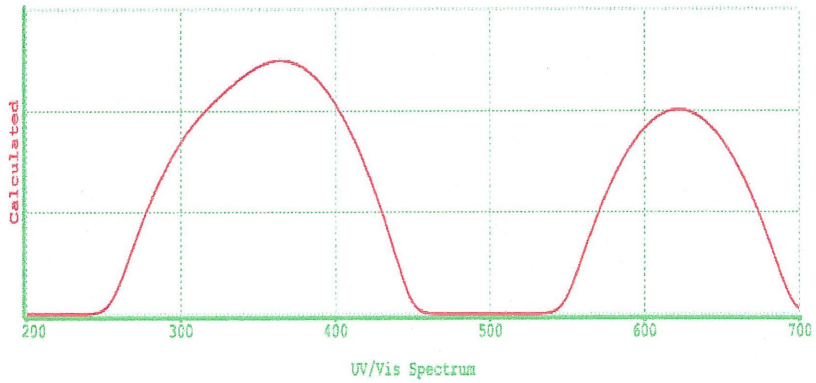


Fig 2b: Ultra-violet/Visible spectra of Diethylamine Dimethylglyoxime Copper(II)

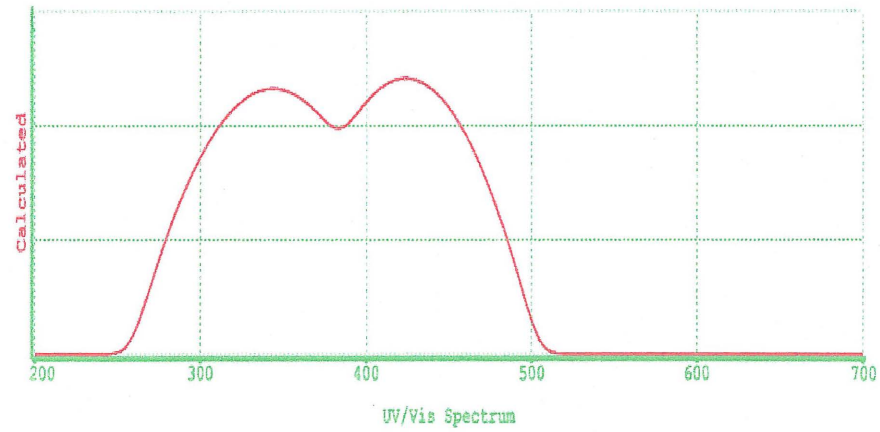


Fig 2c: Ultra-violet/Visible spectra of Malonic acid Dimethylglyoxime Copper(II)

CONCLUSION

The properties of Cu(II) mixed-ligand complexes of dimethylglyoxime were calculated using PM3 in Semi-empirical and DFT/B3LYP/6-31G* methods. The optimized geometries, dipole moments, geometric parameters, thermodynamics parameters and vibrational frequencies were investigated. Computational method has presented 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 and vibrational frequencies of these compounds, the PM3 semi-empirical calculation is the best though could not account for the chemical shifts which was accounted for by the DFT/B3LYP/6-31G*. It can then

be concluded that both methods (Semi-empirical PM3 and DFT/B3LYP) should be used to predict the properties of transition metal complexes.

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