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PM3 Semi Empirical Quantum Mechanical Calculations on a Novel *Dichlorobis (N-{4-[(2-pyrimidinyl-kN-amino)sulfonyl}acetamide]copper(II), Containing a Metabolite N-acetylsulfadiazine*

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ABSTRACT

A novel Dichlorobis(N-{4-[(2-pyrimidinyl-kN-amino)sulfonyl}acetamide)copper(II), containing a metabolite N-acetylsulfadiazinehas been synthesized and characterized. However, PM3 semi empirical quantum mechanical calculations were carried out on the most stable structure of the complex to obtain the geometries, thermodynamic parameters, vibrational frequencies, geometric parameters and band gaps of the novel complex. Comparisons were made on the calculated bond distances, bond angles and dihedralwith experimental data, the result obtained compares perfectly well with the experimental data.

Keywords: Geometric parameters, Cu (III) Complex,Dipole moments, Band gaps, modelling.

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.[1]Molecular modeling is an aspect of computational chemistry and a particular molecular system can be modeled with the hope that it could be synthesized in the laboratory, especially for species that are too difficult, dangerous, impossible or too expensive to carry out experimentally. Molecular modeling is a quite accurate method in accounting for properties like geometric and electronic structures, frequencies, chemical shifts, bond distances, bond angles. It is an aspect of chemistry that is fast spreading and has become a useful tool in studying molecular system prior synthesizing the system in the laboratory. It has also aided in our understanding of biochemical processes such as enzymatic reactions, photosynthesis, it assisted in the design of new drugs and chemical compounds in general with specific properties and led to the discovery of structure-property –reactivity relationships. Semi empirical PM3 calculations have been the best in predicting the geometric properties and vibrational frequencies of transition and organometallic metal complexes [2]. This was further confirmed with this study which also shows that PM3 calculations worked perfectly as it predicts closely the calculated properties with experimental results.Dichlorobis(N-{4-[(2-pyrimidinyl-kN-amino)sulfonyl}acetamide]copper(II) containing a Metabolite N-acetyl sulfadiazine was synthesized and was shown to possess significantly greater *in vitro* growth inhibitory activity against *E. coli*, *S. aureus*and *K. pneumonia* than

previous metabolites[3].The usefulness of the Semi-empirical PM3 calculations in predicting the vibrational modes of metal complexes of sulfanilamide was carried out and it was concluded that simulations of IR spectra are becoming an indispensable tool for a normal coordinate analysis and band assignment [4]. It was also reported that PM3 predicted the IR frequencies of hexa-coordinated silicon complexes better than all other methods and DFT at the basis set of 3-21+G* was used to calculate the Si-NMR shifts and gave very close results with experimental data. PM3 and AM1 was also carried out on the tautomerization and acid base properties of [(1-aza-2-benzimidazol-2-ylprop-1-1enyl) aminomethan-1-thione in the gas phase and aqueous phase to elucidate the structure of the compound, it was discovered that the computed data were in excellent correlation with experimental x-ray results [5]. 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 [6]. AM1, ZINDO and ab Initio DFT B3LYP calculations were carried out on pyrazolo[3,4-b] quinolone derivatives as emitting materials, it was established that it is a possible way to design novel material for OLED[7]. Spectroscopic characterization and quantum chemical calculations on the complexes of aluminum (III) with isoquercitrin and the structural model were validated by the good agreement between theoretical and experimental electronic spectra [8]Also, Semi- empirical calculation were carried out on novel aminopyridino – 1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes, it was observed from the calculations that the complex is thermodynamically stable[9].

Computational Methods

Conformational search was performed on the structure of the complex using molecular mechanics force field calculation in aqueous medium which make use of systematic algorithm to obtain the structure with the lowest energy. The best geometric conformer has energy -993.82Kjmol^{-1}, this is to establish the most stable structure [9]. PM3 calculations were carried out on the most stable structure of Cu(II) complex to obtain the parameters, such as bond length, bond angle and dihedrals.Geometric properties were recorded and compared with experimental resultsas shown in tables 1, 2 and 3 below.

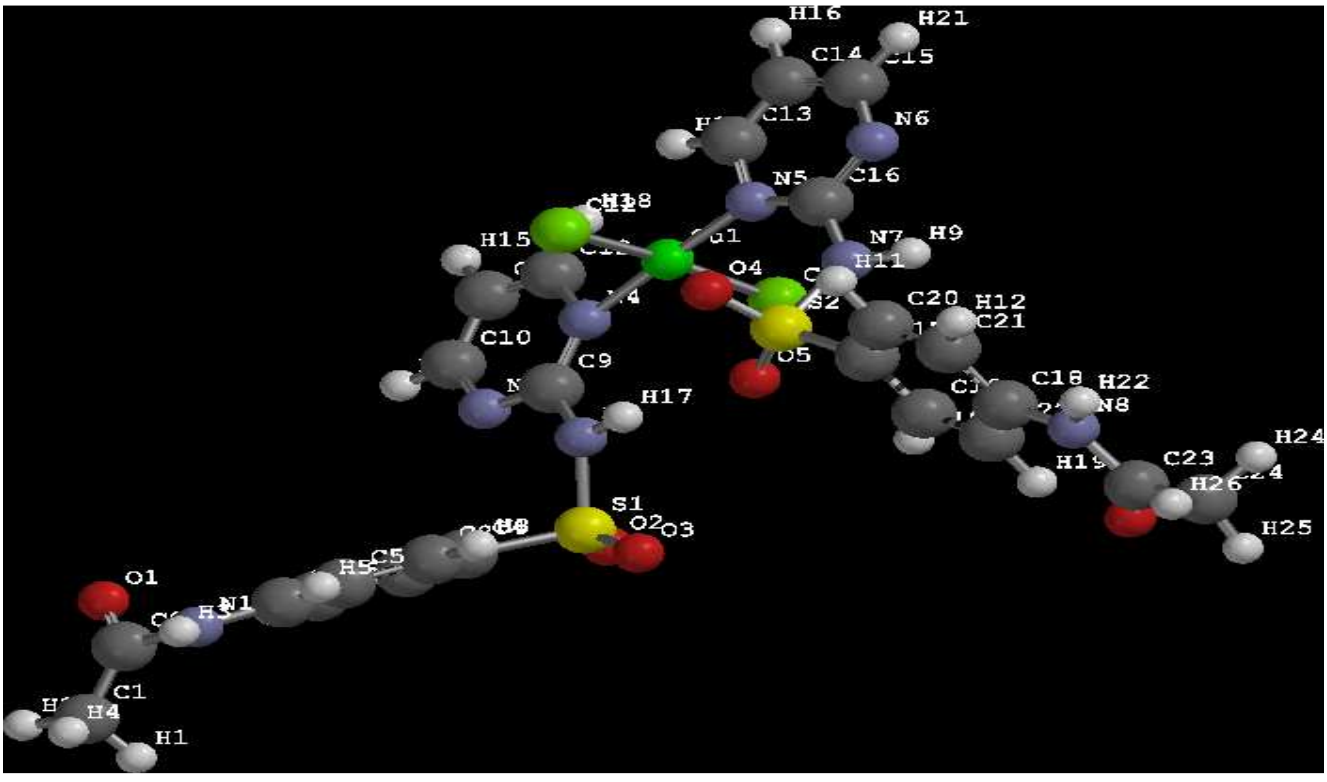
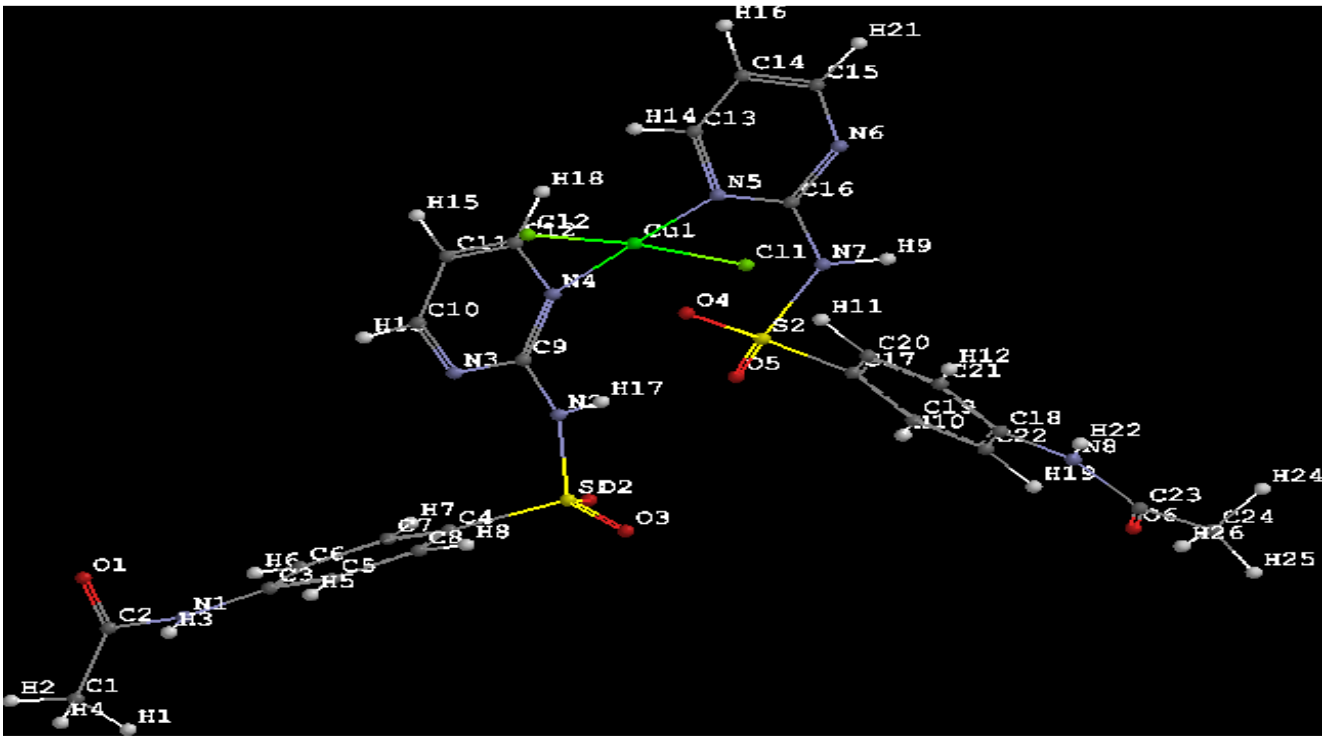


Figure 1a: The structure of the Cu(II) complex after optimization using the PM3 method with the Ball and Spoke Model.

Geometric parameters: The geometric parameters were obtained after optimization of the equilibrium geometries using PM3. The bond distances, bond angles and dihedral angles were measured and recorded and compared with experimental results. PM3 is the best method in predicting the geometric properties of the complex.



Fig, 1b: The structure of the Cu(II) complex after optimization using the PM3 method with the Ball and Wire Model.

Table 1: Selected bond distances

Bond distance	Experimental/Å	PM3/Å
Cu_1-Cl_2	2.25	2.15
Cu_1-N_4	2.07	1.87
S_1-O_2	1.43	1.42
S_1-O_3	1.44	1.43
N_4-C_9	1.35	1.39
N_3-C_9	1.33	1.38
C_{16}-N_7	1.38	1.40
S_1-N_2	1.65	1.79
N_8-C_{18}	1.42	1.41
Cu_1-Cl_1	N/A	2.15
Cu_1-N_2	N/A	1.87
S_2-O_4	N/A	1.44
S_2-O_5	N/A	1.45
N_5-C_{16}	N/A	1.39
N_6-C_{16}	N/A	1.39
C_9-N_2	N/A	1.41
S_2-N_7	N/A	1.81
N_1-C_3	N/A	1.37

Table 2: Selected bond angles

Bond angle	Experimental/°	PM3/°
Cl_2-Cu_1-N_5	90.41	90.74
Cu_1-N_4-C_9	128.80	141.37
Cu_1-N_4-C_{12}	114.5	98.94
C_{16}-N_5-C_{13}	115.8	119.65
C_9-N_3-C_{10}	115.60	120.43
S_1-N_2-C_9	126.80	127.34
N_2-S_1-C_4	106.51	101.89
C_{18}-N_8-C_{23}	123.90	125.87
Cl_1-Cu_1-N_4	N/A	89.66
Cl_1-Cu_1-N_5	N/A	89.49
Cl_2-Cu_1-N_4	N/A	89.94
Cu_1-N_5-C_{16}	N/A	142.72
Cu_1-N_5-C_{13}	N/A	97.39
C_9-N_4-C_{12}	N/A	119.68
C_{16}-N_6-C_{15}	N/A	121.10
S_2-N_7-C_{16}	N/A	132.15
N_7-S_2-C_{17}	N/A	97.02
C_3-N_1-C_2	N/A	126.33

Table 3: Selected Dihedrals

Dihedral	Experimental/°	PM3/°
Cl_1-Cu_1-N_5-C_{16}	-50.10	-74.81
Cu_1-N_5-C_{16}-N_7	-18.50	-4.50
S_2-N_7-C_{16}-N_5	176.2	-43.21
C_4-S_1-N_2-C_9	-59.30	-80.12
N_2-S_1-C_4-C_7	105.70	103.56
C_2-N_1-C_3-C_6	-37.9	-3.26
C_{18}-N_8-C_{23}-O_6	-5.70	-1.27
Cl_1-Cu_1-N_4-C_9	N/A	85.46
Cl_2-Cu_1-N_5-C_{16}	N/A	97.46
Cl_2-Cu_1-N_4-C_9	N/A	-86.81
Cu_1-N_4-C_9-N_2	N/A	-1.10
S_1-N_2-C_9-N_4	N/A	-151.59
C_{17}-S_2-N_7-C_{16}	N/A	-160.00
N_2-S_1-C_4-C_8	N/A	-81.00

Electronic properties: It is important to examine the E HOMO and E LUMO so as to explain the electronic properties of the complex. This was done theoretically using PM3. However, these calculations were examined in the ground state and also in vacuum. It is possible to use them get information by comparing them with similar complexes. The calculated E HOMO and E LUMO, Dipole moment and band gap are recorded in table 4.

Table 4: Electronic Properties

Methods	Dipole moments(Debye)	HOMO energy(eV)	LUMO energy(eV)	Band gaps (Ev)
PM3	22.37	-12.62	-6.81	+5.81

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Thermodynamic properties and stabilities: For complexes to be thermodynamically stable, it is expected that ΔG and ΔH are negative. The more negative they are and the more positive ΔS is the more stable the complex becomes.

Table 5: Thermodynamic Properties

Methods	Heat of formation ($Kjmol^{-1}$)	Free energy($Kjmol^{-1}$)	Enthalpy($Kjmol^{-1}$)	Entropy ($Jmol^{1}K^{-1}$)
PM3	703.16	1785	2021.25	833.87

Vibrational Frequencies: The vibrational frequencies are obtained theoretically. No experimental results to compare with though. The IR absorptions with their corresponding intensities, the IR spectra (fig 2) and the absorption band with their corresponding vibrations in table 7 are shown below:

Table 6: Vibrational frequencies and intensities of Cu (II) complex

Absorptions (cm^{-1})	Intensity
602	4022.08
625	8872.56
657	4626.17
664	2495.97
707	1494.08
721	3011.39
809	3796.57
811	5589.30
833	7340.00
936	3527.05
985	24081.63
1033	3181.90
1100	6733.83
1142	10372.27
1296	7331.79
1499	28632.99
1546	7560.89
1644	10328.85
1696	20788.58
1733	103413.42
2013	92449.51
2882	2769.82
2902	2398.02
2982	1704.09
2996	1163.25
3010	6408.10
3025	3240.52
3058	3869.35
3153	2228.75
3172	29.29
3253	1597.27
3307	321.77
3354	3452.55
3371	42.78

Table 7: Absorption Band with their Corresponding Vibrations (cm^{-1})

Vibrational Frequency (cm^{-1})	Absorptions
3371-3253	N–Hstr
3058	C-Hstr (SP^2)
3172-3153	C-Hstr (SP^3)
3025-2882	C-Hstr (aromatic)
2013	C=Ostr
1696	C=Nstr
1733,1644	C=Cstr
1546-1499	C–Nstr
1296	C-H_{bend}, N-H_{bend}
936	S=Ostr
1142	C-H_{bend}
721	S=Ostr, N-H_{bend}

Fig 2. The IR spectrum of the Cu(II) complex with PM3

RESULTS AND DISCUSSION

The bond length between $Cu_1 – Cl_2$ (2.15), Cu_1- N_4 (1.87), S_1- O_2(1.42), S_1- O_3(1.43), N_3-C_9 (1.38), N_4– C_9(1.39), $C_{16} – N_7$(1.40), $S_1 – N_2$(1.79) and $N_8 – C_{18}$ (1.41) in the calculated data compared with the bond length in the experimental data as we have in $Cu_1 – Cl_2$ (2.25), Cu_1- N_4 (2.07), S_1- O_2(1.43), S_1- O_3(1.44), $N_4 – C_9$(1.35),N_3-C_9 (1.33), $C_{16} – N_7$(1.38), $S_1 – N_2$(1.65) and $N_8 – C_{18}$ (1.42) are in perfect agreement as shown in table 1. The bond angles and dihedrals calculated were also in good agreement with the experimental data except for the calculatedbond length between Cu_1-N_4- C_{12} with bond angle 98.94^0 which has low value compared with the experimental value at 114.50^0.

The HOMO and LUMO energy were calculated so as to be able to account for the electronic properties of the complex. The calculated E- HOMO, E- LUMO transition which result into a $\pi – \pi^*$transitionis -12.62 and -6.81 respectively, this gives a band gap of +5.81 as show in table 4. The calculated thermodynamic properties as show in table 5, with ΔG 0.68, ΔH 0.77 and ΔS 833.87 predict the stability of the novel Cu (II) complex.
The IR absorption with the corresponding intensities are shown in table 6 with absorption band at $1696cm^{-1}$ having the highest intensity of 20788.58 and the absorption band at 3172 cm^{-1} having the lowest intensity of 29.29. The vibrational frequencies and the absorption band were also calculated with $\upsilon(N\text{-}H)_{str}$ at 3371- 3253cm^{-1}, $\upsilon(C\text{-}H)_{str}$of sp^2 at 3058cm^{-1}, $\upsilon(C\text{-}H)_{str}$ of sp^3 between 3172 – 3153 cm^{-1}, $\upsilon(C\text{-}H)_{str}$ of aromatic at 3025 – 2882 cm^{-1}, $\upsilon(C{=}O)_{str}$ at 2013 cm^{-1}, $\upsilon(C\text{-}N)_{str}$at 1546 -1499 cm^{-1}, $\upsilon(C\text{-}H)_{bend}$, $\upsilon(N\text{-}H)_{bend}$ at 1296 cm^{-1}, $\upsilon(S{=}O)_{str}$ at 936 cm^{-1} and $\upsilon(N\text{-}H)_{bend}$ 721 cm^{-1}.

CONCLUSION

In this study, we tried to establish the characterization of the novelcomplex dichlorobis(N-{4-[(2-pyrimidinyl-kN-amino)sulfonyl}acetamide)copper(II), containing a metabolite N-acetylsulfadiazineusing PM3 Semi-empirical quantum mechanical calculations.The optimized geometries, dipole moments, geometric parameters, thermodynamic parameters and vibrational frequencies were calculated and the data obtained from the calculated parameter are shown to be in good agreement with the experimental data. This good agreement is well within the

accuracy of computational results. In conclusion, the modeling and the calculations does not only presented us the opportunity to take a critical look at this novel complex to produce results which were compared with experimental data but has also given us the opportunity to compile fundamental result on properties that cannot be calculated in the laboratory.

REFERENCES

[1] David C Young (**2001**) Computational Chemistry- A practical guide for applying real world problems. Wiley-interscience. ISBN 0-471-33368-9
[2] Warren J Hehre (**2003**) A guide to molecular mechanics and Quantum Chemical calculations in Spartan. Wavefunction, Inc. ISBN 1-890661-18-X.
[3] Joshua A. Obaleye, Mino R. Caira and Adedibu C. Tella **2008**: *Journal, The Japan Society for Analytical Chemistry*- Crystal Structure of Dichlorobis(N-{4-[2-pyrimidinyl-kN-amino)-sulfonyl]phenyl}acetamide)copper(II).
[4] C. Topacli, A. Topacli, 2003: *Journal of Molecular Structure* 654 (**2003**) 131-137.
[5] Jugal K. Puri, Raghubir Singh, Varinder K. Chahal, Raj P. Sharma. **2009**: Novel Hexacoordinated Silicon (IV) complexes of diethylenetriamine Schiff base with SiO_2N_3 Skeleton. *General Papers*. Centre of Advanced Studies and Department of Chemistry, Panjab University, Sec 14, Chandigarh- 160 014, India.
[6] Yusuf Zalaoglu, AsafTolgaUgQualgen, CabirTerzioglu and GureanYildirim (**2010**) *SAü. Fen Bilimleri Dergisi.14. Cilt, 2. Sayi*, s. 66 -76,
[7] Jiunn-Hung Pan, Yu-Ma Chou, Houn-Lin Chiu and Bo-Cheng Wang (**2005**) *Tamkang Journal of Science and Engineering*Vol 8 2 175-183.
[8] Jean Paul Cornard, Jean Claude Merlin (**2002**) *Science Direct Polyhedron* 21, 2801-2810.
[9] Odiaka, T.I., Adejoro, I. A., and Akinyele, O. F. (**2012**) *Am. J. Sci. Indi, Res.* 3(1): 1-13
[10] Warren Hehre and Sean Ohlinger (**2010**) Spartan '10 Tutorial and user's guide. Wavefunction Inc. ISBN978-1-890661-41-4