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## Stability investigations on Cu (II) and Mn (II) compounds of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid using Quantum Chemical Methods.

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### ABSTRACT

A Density functional theory and semi empirical calculations have been carried out on Cu(II) and Mn(II) complexes of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid for stability and molecular properties study. The semi-empirical calculations were performed at PM3 and PM6 levels, while the hybrid B3LYP method with 6-31G\*\* basis set was used for DFT calculations. The predicted geometries using DFT method supported distorted octahedral structures of the complexes. The calculated energy gap, chemical hardness and softness showed that mono Cu(II) and bimetallic Mn(II) complexes would be hard, thermodynamically stable and less polarizable. The stabilization energies calculated at DFT showed the preference for synthesis of mono Cu(II) and bimetallic (or polymeric) Mn(II) complexes as observed experimentally.

**Keywords:** Copper (II), Manganese (II), 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid, molecular properties, Stabilization energy, Quantum Chemical Methods

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## INTRODUCTION

Several 1,2,4-triazine moiety containing compounds are well known in natural materials with some interesting biological and antiviral properties [1-3]. For instance, 4-Amino-5-oxo-3-phenylamino-1,2,4-triazine has been found to have an inhibitory effect on the cell wall lignification. Also, 3,5,6-trisubstituted-1,2,4-triazine derivatives are active as blood platelet aggregation inhibitors, exhibit antiviral inhibitory activity, and anti-HIV activity [4]. Moreover, the triazine moiety, as evidenced by its relatively accessible one-electron reduction potential [5], possesses electron-acceptor properties, which can be tuned by the substituents [6,7]. In most cases, some derivatives possess luminescence properties [8,9]. Many derivatives of 1,2,4-triazine compounds form coloured complexes with different metal ions; these metal complexes have unique properties and novel reactivities which make them useful as analytical reagents. Usually the nature of ligands affect the electronic properties, geometric properties and molecular orbitals of metal ions and thus affect their analytical applications [10-15]. Therefore, turning the optical properties of transition metal complexes by ligands generate very efficient triplet energy and electron transfer reactions, long-lived excited states, charge separated species, and singlet oxygen producers [16].

Nowadays, a wide variety of computational methods is engaged in the computational chemistry community; however, the use of density functional theory (DFT) continues to grow, although semi empirical methods can also give quantitative reasonable information [17-24]. However, among the DFT methods, the hybrid functional B3LYP is the most popular and widely used for studies of organometallic molecules and reactions due to relative accuracy in reproducing the experimental values such as molecular geometry, vibrational frequencies, atomic charges, dipole moment and thermodynamic parameters [25-27]. Therefore, the aim of this present work is to: (i) use quantum chemical calculations (via DFT and semi-empirical methods) to predict the geometries, thermodynamic stabilities and electronic properties of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid (H<sub>2</sub>pdttd) complexes of Cu(II) and Mn(II); (ii) to evaluate the performance of PM6 in calculations molecular parameters for metal complexes in relation to PM3 results; and (iii) to possibly explain the polymeric nature of Mn(II) complex as reported in the literature [28]. The calculated parameters are compared to the available experimental data [28].

## COMPUTATIONAL METHODS

The Cu(II) and Mn(II) compounds of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid (H<sub>2</sub>pdttd) were modeled based on X-ray diffraction data [16]; and optimization was carried out at both semi-empirical and Density Functional Theories (DFT) methods on the most stable conformation from the preliminary conformational search with MMFF method with Monte Carlo search algorithm [29]. The optimization and frequency calculations of the metal complexes Mn(II) and Cu(II) were done using B3LYP/6-31G\*\* and semi empirical (PM3 and PM6) methods. The charge density and reactivity descriptors for the metal complexes were computed at both DFT and semi-empirical levels. The bimetallic form of Cu(II) and Mn(II) complexes of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid (H<sub>2</sub>pdttd) were modelled and optimized at the same levels of theory for the calculations of stabilization energies. The HOMO and LUMO levels were also calculated for easy access to the calculations of frontier molecular orbital energies. All other calculations were performed by the Spartan 14 program [30] implemented on an Intel Core(TM) i3-2350 M CPU, 2.3-GHz computer.

## RESULTS AND DISCUSSION

### *Geometry parameters of the complexes*

Quantum chemical methods (semi-empirical and DFT) were employed for optimization and molecular parameters calculations of the modeled mono Cu(II) and Mn(II) complexes as shown in Figure 1. The geometrical and molecular parameters calculated at both semi-empirical (PM3 and PM6) and DFT/B3LYP/6-31G(d,p) methods are listed in Tables 1 and 2 for Cu(II) and Mn(II) complexes respectively. The calculated geometrical parameters are compared and discussed with X-ray crystallographic data available in literature [28].

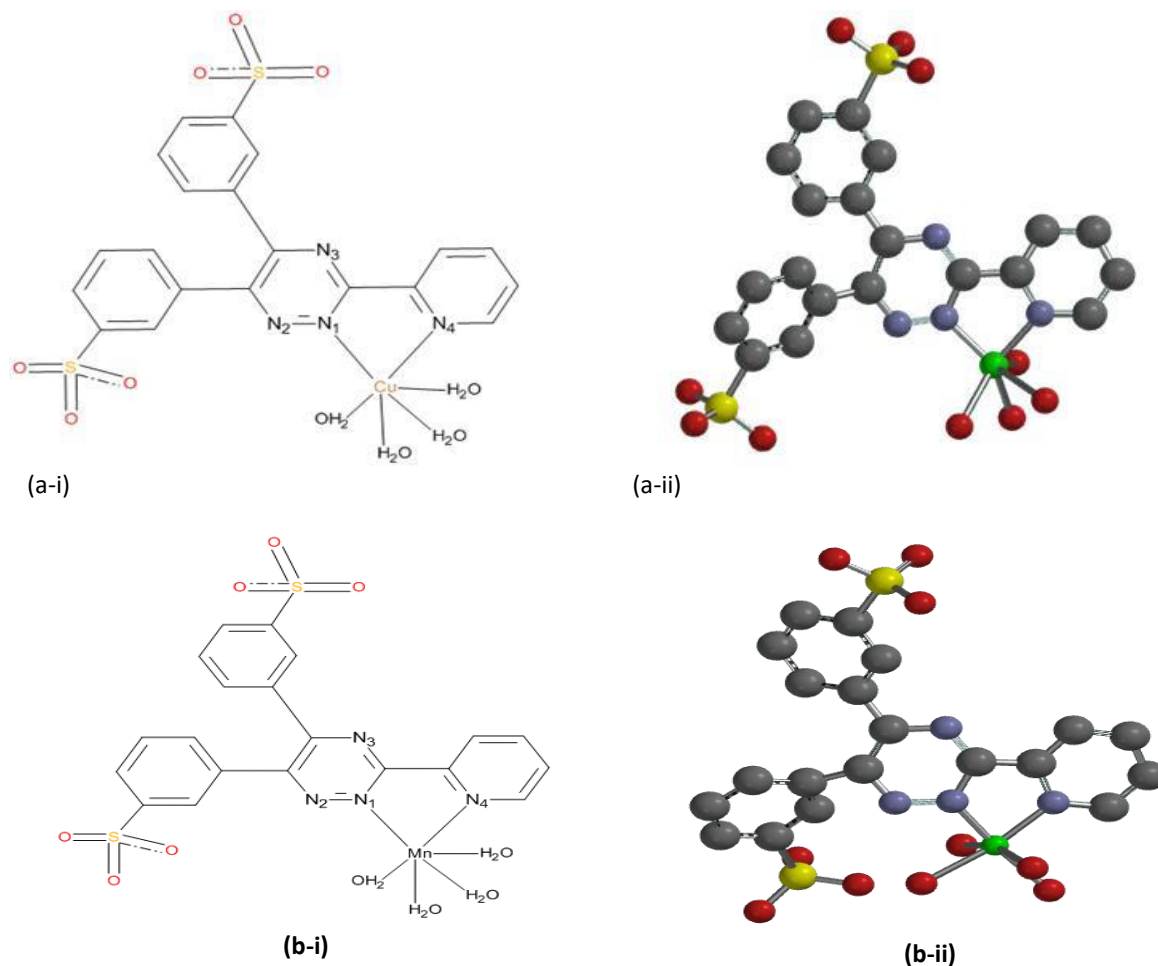


Figure 1: Schematic and optimized structures of the Cu(II) and Mn(II) complexes at DFT method

Table 1: Selected geometrical parameters for Cu (II) complex at semi-empirical (PM3 and PM6) and DFT (B3LYP/6-31G(d,p) methods.

Parameters	Expt. [28]	PM3	PM6	DFT
<b>BOND LENGTH (Å)</b>				
Cu1- O7	2.328	1.840 (0.488)	1.773 (0.555)	2.197 (0.131)
Cu1- O8	2.375	2.007 (0.368)	2.105 (0.270)	2.265 (0.110)
Cu1- O9	1.994	2.005 (-0.011)	2.131 (-0.137)	1.921 (0.073)
Cu1- O10	1.995	1.927 (0.068)	1.771 (0.224)	1.957 (0.038)
Cu1- N1	2.007	1.877 (0.130)	1.874 (0.133)	1.922 (0.085)
Cu1- N4	2.042	1.898 (0.106)	1.868 (0.136)	1.998 (0.044)
<b>BOND ANGLE (°)</b>				
O9-Cu1-O10	91.62	86.23 (5.39)	83.17 (8.45)	94.67 (-3.05)
O10-Cu1-O7	90.63	89.76 (0.87)	85.26 (5.37)	87.80 (2.83)

O7-Cu1-O8	175.05	159.95 (15.10)	147.63 (70.71)	166.32 (8.73)
O8-Cu1-N4	95.40	109.08 (-13.68)	104.34 (-8.94)	97.50 (-2.10)
N4-Cu1-N1	80.27	86.75 (-6.48)	86.34 (-6.07)	84.12 (-3.85)
N1-Cu1-O9	173.87	169.61 (-74.34)	172.32 (1.55)	171.79 (2.08)
O9-Cu1-O7	85.27	78.35 (6.92)	101.79 (-16.52)	88.82 (-3.55)
O8-Cu1-O10	90.24	80.49 (9.75)	79.52 (10.72)	86.54 (3.70)
O8-Cu1-N1	89.51	100.38 (-10.87)	99.71 (-10.20)	94.06 (-4.55)
O10-Cu1-N4	172.23	176.28 (-4.05)	172.00 (0.23)	173.18 (0.95)
O10-Cu1-N1	94.47	95.24 (-0.77)	100.01 (-5.54)	97.30 (-2.83)
O7-Cu1-N4	84.21	88.78 (-4.57)	88.91 (-4.70)	85.23 (-1.02)
O7-Cu1-N1	95.27	105.40 (-10.13)	102.32 (-7.05)	95.62 (-0.35)
O9-Cu1-N4	93.73	106.29 (12.56)	102.78 (-9.05)	98.47 (-4.74)
O8-Cu1-O9	89.84	98.33 (-8.49)	104.34 (-14.50)	85.23 (4.61)

\*Calculated values in parenthesis ( ) is the deviation value of PM3 ( $\Delta_{PM3}$ ), PM6 ( $\Delta_{PM6}$ ) and DFT ( $\Delta_{DFT}$ ) methods from experimental values.

The calculated bond distances using PM6, PM3 and DFT methods for Cu1-O10 (Cu-O7) are 1.771Å (1.773Å), 1.927Å (1.840Å) and 1.957Å (2.197Å) respectively. The experimental corresponding values these bond distances were 1.995 and 2.328Å for Cu1-O10 and Cu1-O7?? respectively. This showed that calculated Cu1-O10 (Cu1-O7) bond distance deviated from experimental values by 0.068(0.488Å), 0.224(0.555Å) and 0.028(0.131Å) for PM3, PM6 and DFT calculations respectively. For Cu1-O9 (Cu1-O8) and Cu1-N4 (Cu1-N1) bond distances, the calculated values at PM3, PM6 and DFT methods are 2.005 (2.007Å) and 1.898 (1.877Å), 2.131 (2.105Å) and 1.868 (1.874Å), and 1.921 (2.265Å) and 1.998 (1.922Å) respectively.

Similarly, the calculated Mn-O10 (Mn-O7) bond distance at PM3, PM6 and DFT methods are 2.224(1.955Å), 1.833(2.375Å) and 2.148Å (2.001Å) respectively. The experimental corresponding values these bond distances were 2.152 and 2.193Å for Mn1-O10 and Mn1-O7 respectively. This showed that calculated Mn1-O10 (Mn1-O7) bond distance deviated from experimental values by 0.072(0.238Å), 0.319 (0.182Å) and 0.003(0.192Å) for PM3, PM6 and DFT calculations respectively. Also, Mn1-O9 (Mn1-O8) bond distances are 2.183 (1.916Å), 1.829 (2.388Å) and 2.113 (2.117Å) as revealed by PM3, PM6 and DFT calculations respectively; and experimentally reported at 2.143 (2.161Å). The Mn1-N4 (Mn1-N2) are calculated at PM3, PM6 and DFT methods to be 1.867 (1.861Å), 1.806 (1.795Å) and 1.960 (1.831Å) respectively (Table 2). These are observed experimentally at 2.274 and 2.276 Å for Mn1-N4 and Mn1-N2 respectively. Generally, bond lengths predicted at DFT are closer to the experimental values than the semi-empirical methods; and also, the bond lengths calculated using PM3 method are more accurate than that of PM6; thus PM3 is expected to give better predictions.

Furthermore, the bond angles/bite angles O7-Cu1-O8 (O7-Cu1-O9) for Cu(II) complex are 159.95° (78.35°), 147.63° (101.79°) and 166.32° (88.82°) for PM3, PM6 and DFT calculations respectively; and experimentally observed at 173.03° (85.27°). Also, O7-Cu1-N1 (N1-Cu1-N4) bond angles are 169.61°(86.75°), 172.32° (86.34°) and 171.79° (84.12°) for PM3, PM6 and DFT calculations respectively (Table 1). The calculated bond angles using all the three computational methods showed Jahn- Teller distortion around N-Cu-N bond angle as observed experimentally in the complex displaying [28, 31].

**Table 2: Selected geometrical parameters for Mn (II)?? complex at semi-empirical (PM3 and PM6) and DFT (B3LYP/6-31G(d,p) methods**

BOND LENGTH (Å)				
PARAMETERS	EXPT [28]	PM3	PM6	DFT
Mn1-O10	2.152	2.224(-0.072)	1.833(0.319)	2.148(0.003)
Mn2-O7	2.193	1.955(0.238)	2.375(-0.182)	2.001(0.192)
Mn2-O9	2.143	2.183(-0.040)	1.829(0.314)	2.113(0.030)
Mn2-N4	2.274	1.867(0.407)	1.806(0.468)	1.960(0.314)
Mn2-N2	2.276	1.861(0.415)	1.795(0.481)	1.831(0.445)
Mn2-O8	2.161	1.916(0.245)	2.388(-0.227)	2.117(0.044)
BOND ANGLE (°)				
	EXPERIMENTAL	PM3	PM6	DFT
O1-Mn2-O10	85.6	90.37 (-4.77)	81.64 (3.96)	80.56 (5.04)
O6-Mn2-O9	91.9	112.55(-20.65)	118.07(-26.17)	93.29(-1.39)
O10-Mn2-O9	95.2	65.02(30.18)	66.47(28.73)	91.68(3.52)
O10-Mn2-N4	174.6	164.38(10.22)	177.45(-2.85)	169.12(5.48)
O10-Mn2-N3	102.0	121.20 (-19.20)	123.94(-21.94)	102.70 (-0.70)
O6-Mn2-N4	87.8	86.52(1.28)	91.20(-3.40)	88.77 (-0.97)
O6-Mn2-N3	91.1	97.17 (-6.07)	112.64(-21.54)	90.38(0.72)
O11-Mn2-O6	177.6	160.07(17.53)	166.64(10.96)	169.15(8.45)
O8-Mn2-N2	162.4	160.88 (1.52)	161.99 (0.41)	161.20 (1.20)
O1-Mn2-N3	87.6	94.32 (-6.72)	97.37 (-9.77)	93.64 (-6.04)
O1-Mn2-N4	93.7	92.98 (0.72)	97.35(-3.65)	93.67 (0.03)
N4-Mn2-N3	72.6	84.31 (-11.71)	86.20(-13.60)	79.70 (-7.10)

\*Calculated values in parenthesis ( ) is the deviation value of PM3 ( $\Delta_{PM3}$ ), PM6 ( $\Delta_{PM6}$ ) and DFT ( $\Delta_{DFT}$ ) methods from experimental values.

The bond angles for Mn(II) complex calculated using PM3, PM6 and DFT for O6-Mn2-O9 (O9-Mn-O10) are 112.55° (65.02°), 118.07° (66.47°) and 93.29° (91.68°) respectively compared to 91.90° (95.20°) as observed experimentally. Thereto, the O10-Mn-N3 (O6-Mn-N4) bond angles are calculated to be 121.20° (86.52°), 123.94° (91.20°) and 102.70° (88.77°) at PM3, PM6 and DFT respectively; these angles are observed experimentally at 102.00° and 87.80° respectively (Table 2). The N4-Mn2-N2 bond angle was calculated at PM3, PM6 and DFT to be 84.31°, 86.20° and 79.70° respectively against 72.60° as reported experimentally. The bite angles showed that the complexes are distorted octahedral structures. Therefore bite angles predicted at DFT and PM3 are closer to the experimental values than PM6, although DFT calculations shows superior results (i.e. reproduced the experimental results).

#### Frontier molecular orbitals

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular (LUMO) are known as frontier molecular orbitals (FMO). The FMOs plays an important role in the optical and electrical properties, as well

as in quantum chemistry [32]. The HOMO represents the ability to donate an electron to electron deficient molecule; this is also related to the ionization potential. The binding ability of the ligand to the metal increases with increasing HOMO energy values. The LUMO as an electron accepting ability (i.e. relating to electron affinity; ability to accept electron from electron-rich molecule), this is also given information on electron affinity ability of a compound. The FMO plots show that the HOMO and LUMO of mono Cu(II), bimetallic Cu(II) and bimetallic Mn(II) complexes are mainly on sulfonic acid and pyridyl-triazine-metal respectively; however both the HOMO and the LUMO of mono Mn(II) complex are on pyridyl-triazine-metal as shown in Figure 2. The  $\Delta_{\text{HOMO-LUMO}}$  which is energy separation between the HOMO and the LUMO is very essential to evaluate the energetic behaviour of the complex [33,34]. Therefore, the FMO energies ( $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $E_{\text{HOMO-LUMO}}$ ) calculated for the Cu(II) using semi-empirical and DFT methods are -8.77, -3.85 and 4.92eV; -8.08, -3.23 and 5.45; -0.75, 1.42 and 2.17eV for PM3, PM6 and DFT respectively. For Mn(II) complex, the FMO are -8.95, -3.85 and 5.10eV; -8.55, -2.78 and 5.77eV; -0.59, -2.54 and 1.95eV for PM3, PM6 and DFT respectively (Figure 2). Also for bimetallic Cu(II) complex, the FMO energies are -8.52,-4.47 and 4.05 eV; -8.10, -4.00 and 4.10 eV; and -0.95, 1.61 and 2.56 eV as calculated at PM3, PM6 and DFT respectively. For bimetallic Mn(II) complex, they are -9.36, -2.79 and 6.57eV; -9.98, -3.30 and 6.68 eV; and -0.79, 1.98 and 2.77 eV for PM3, PM6 and DFT calculations respectively (Figure 3). The energy gap calculated at DFT revealed that mono Cu(II) complex is hard and more thermodynamically stable than mono Mn(II) complex; but on the other hand bimetallic Mn(II) complex is more thermodynamically stable than the corresponding Cu(II) complex, these are in line with the experimental observations [28].

The dipole moment ( $D$ ) is a parameter of the electronic distribution in a molecule which can be related to the dipole-dipole interactions of the ligands and metal surface [35]. Ligand with larger dipole moment forms more stable complex [37-38]. The D.M values calculated at DFT, PM3 and PM6 are 15.78/18.09, 24.90/38.24 and 24.22/47.43 Debye respectively for mono Cu(II)/bimetallic Cu(II) complex; this is calculated at DFT, PM3 and PM6 to be 13.77/17.18, 21.71/22.54 and 33.25/38.92 Debye respectively for mono Mn(II)/bimetallic Mn(II) complex as shown in Table 3.

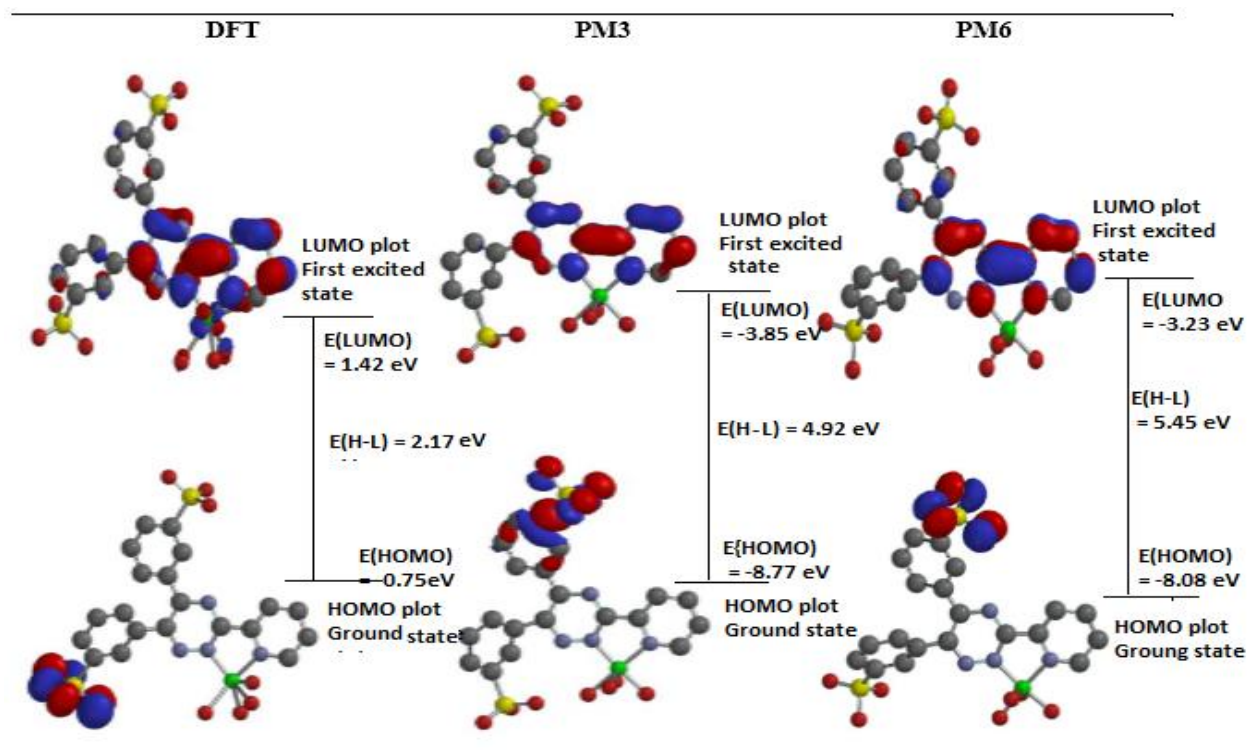


Fig 2a: Frontier Molecular Orbitals for mono Cu(II) complex

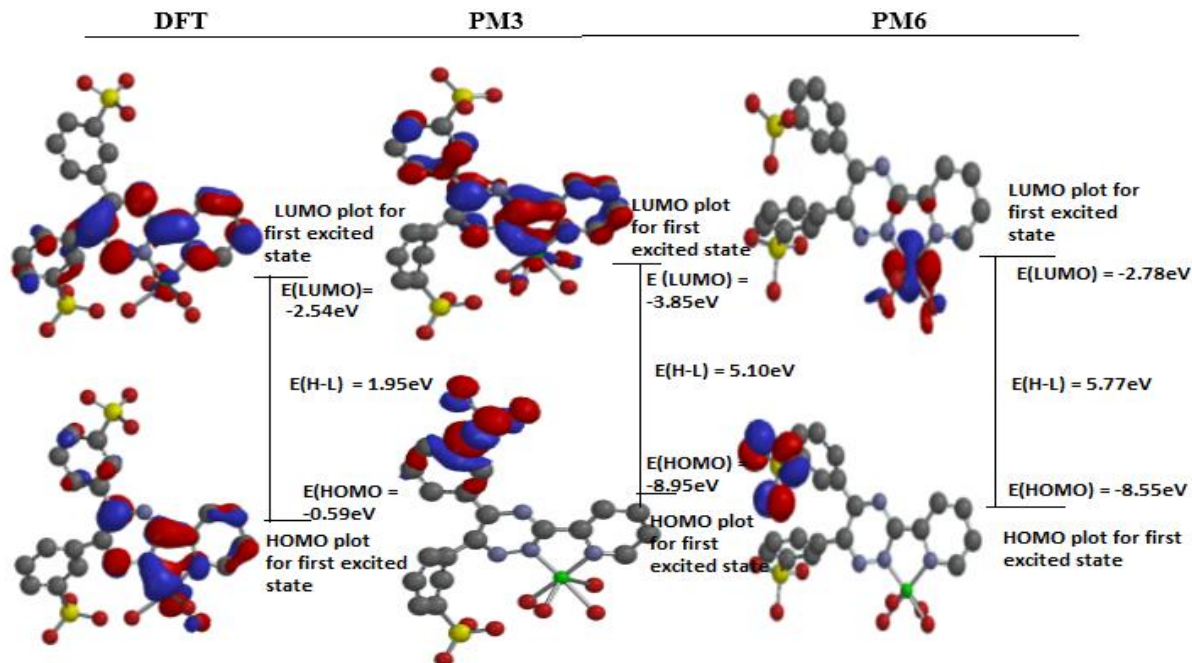


Fig 2b: Frontier Molecular Orbitals for mono Mn(II) complex

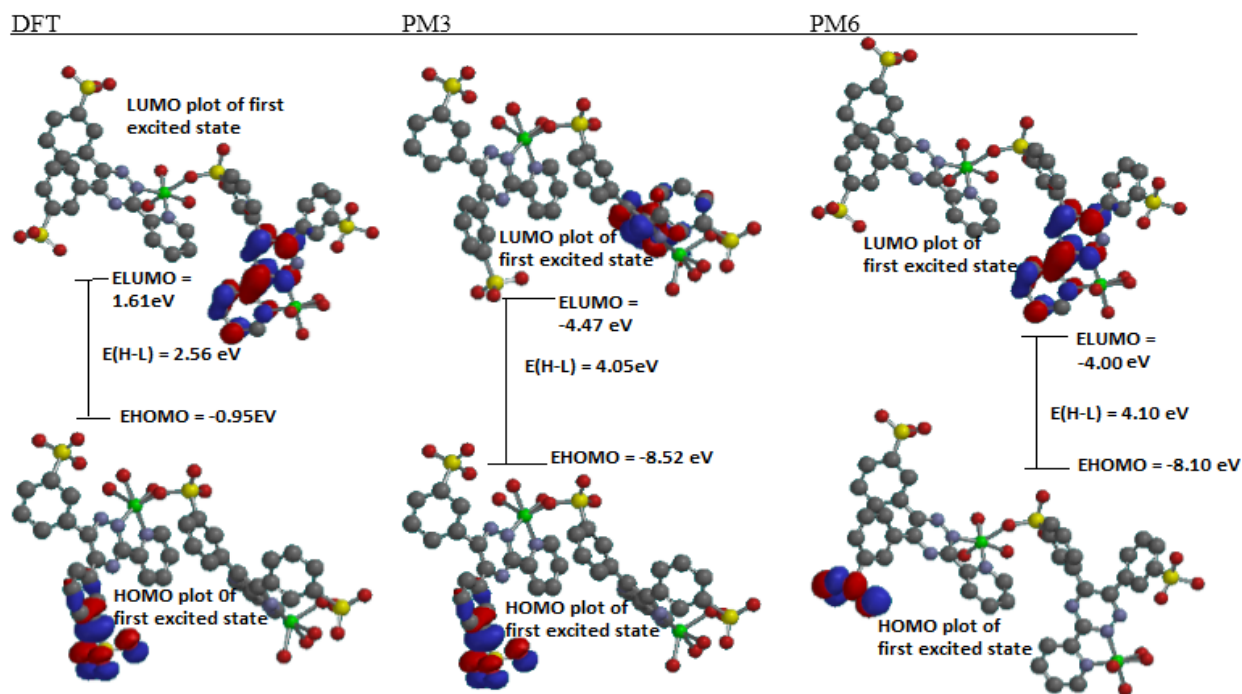
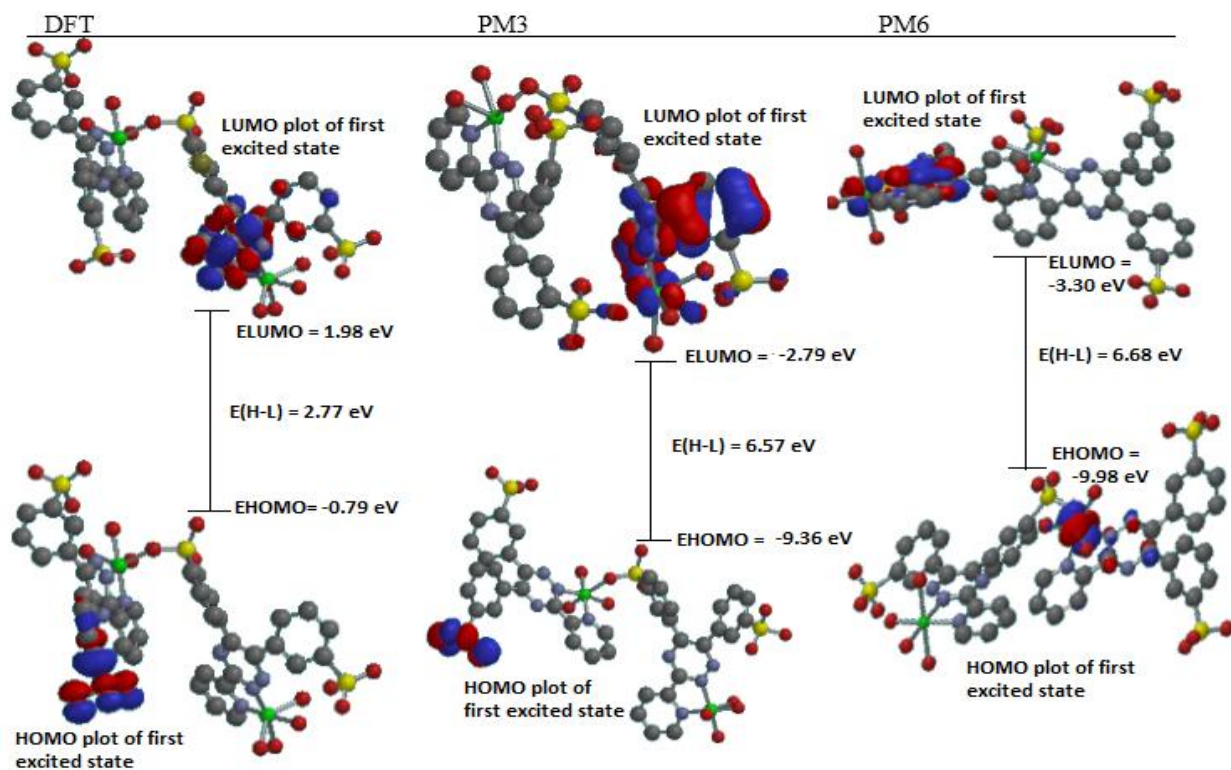


Fig 2c: Frontier Molecular Orbitals for bimetallic Cu(II) complex



**Fig 2d: Frontier Molecular Orbitals for bimetallic Mn(II) complex**

Conceptual DFT based molecular descriptors have helped in many ways to understand the structure of molecules and their reactivity by calculating the global electrophilicity/nucleophilicity ( $\omega$ ), chemical potential ( $\mu$ ) and chemical hardness ( $\eta$ ). Parr et al. [39] proposed the global electrophilicity power of a ligand as  $\omega = \mu^2/2\eta$ . These indices measure the stabilization in energy when the system acquires an additional electronic charge from the environment. Electrophilicity encompasses both the ability of an electrophile to acquire additional electronic charge and the resistance of the system to exchange electronic charge with the environment. However, studies have revealed that the electrophilicity/nucleophilicity index is a very useful structural descriptor of the analysis of the chemical reactivity of molecules [40]; Using the FMO energies, the chemical potential and chemical hardness can be expressed as:  $\mu = 1/2 (E_{\text{HOMO}} + E_{\text{LUMO}})$  and  $\eta = 1/2 (-E_{\text{HOMO}} + E_{\text{LUMO}})$  [41, 42]. The calculated chemical potential values using DFT, PM3 and PM6 methods are -0.335/-0.330, -6.31/-6.495 and -5.655/-6.050 eV for mono Cu(II)/bimetallic Cu(II) complex respectively; and -1.565/-0.595, -6.400/-6.075 and -5.665/-6.640 for mono Mn(II)/bimetallic Mn(II) complex respectively. It has been suggested that a good electrophile is characterized by a high value of chemical potential ( $\mu$ ), it has the ability to acquire additional electronic charge is a better descriptor of global chemical reactivity [32].

Chemical hardness ( $\eta$ ) is another important parameter used as a criterion of chemical reactivity and stability. The hardness signifies the resistance towards the deformation of electron cloud of chemical systems under small perturbation encountered during chemical process. Soft systems are large and highly polarizable, while hard systems are relatively small and much less polarizable. The calculated  $\eta$  of the values using DFT, PM3 and PM6 methods are 1.087/1.280, 2.460/2.025 and 2.425/2.050 eV for mono Cu(II)/bimetallic Cu(II) complex respectively. This was calculated for mono Mn(II)/bimetallic Mn(II) complex to be 0.975/1.385, 2.550/3.285 and 2.885/3.340 eV at DFT, PM3 and PM6 respectively. This implies that mono Cu(II) and bimetallic Mn(II) complexes are harder, more thermodynamic stable and less polarizable; thus they are not easily undergo changes in electron density and are less polarizable [32,43].



A good and/or more reactive nucleophile is characterized by a high value of  $\omega$  and in opposite a good electrophile is characterized by a lower value of  $\omega$ . The calculated  $\omega$  values using DFT, PM3 and PM6 are 0.0517/0.043, 8.093/10.416 and 6.594/8.927 eV for mono Cu(II)/bimetallic Cu(II) complex respectively; and 1.256/0.128, 8.030/5.617 and 5.560/6.600 eV for mono Mn(II)/bimetallic Mn(II) complex respectively.

**Table 3: Calculated dipole moment (*D.M*), global electrophilicity ( $\omega$ ), chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ) and total energy.**

	D.M (Debye)	$\omega$	$\mu$ (eV)	$\eta$ (eV)	$\sigma$ (eV)	Energy(a.u.)	S.E (kcal/mol)
Cu(II) complex							
DFT	15.78 (18.09)	0.052 (0.043)	-0.335 (-0.330)	1.085 (1.28)	0.461 (0.781)	-4181.5457 (-8235.094)	-2.62x10 <sup>2</sup> (+7.96x10 <sup>4</sup> )
PM3	24.90 (38.24)	8.093 (10.416)	-6.310 (-6.495)	2.460 (2.025)	0.203 (0.494)	-305.72 (-563.15)*	-1.56x10 <sup>3</sup> (-1.79x10 <sup>3</sup> )
PM6	24.22 (47.43)	6.594 (8.927)	-5.655 (-6.05)	2.425 (2.05)	0.183 (0.488)	-226.64 (-379.76)*	-5.72x10 <sup>2</sup> (-1.07x10 <sup>3</sup> )
Mn(II) complex							
DFT	13.77 (17.18)	1.256 (0.128)	-1.565 (-0.595)	0.975 (1.385)	0.513 (0.722)	-3692.132 (-7755.174)	+1.51x10 <sup>3</sup> (-5.78x10 <sup>4</sup> )
PM3	21.71 (22.54)	8.030 (5.617)	-6.400 (-6.075)	2.550 (3.285)	0.196 (0.304)	-284.19 (-614.24)*	-9.23x10 <sup>2</sup> (-2.36x10 <sup>3</sup> )
PM6	33.25 (38.92)	5.560 (6.600)	-5.665 (-6.640)	2.885 (3.34)	0.173 (0.299)	-229.99 (-665.67)*	-4.44x10 <sup>2</sup> (-1.09x10 <sup>3</sup> )

\*Semi-empirical energies represent heat of formation (kcal/mol) and parameters for bimetallic (II) complexes are in values parentheses.

**Table 4: Mulliken charges on the selected atoms of Cu(II) and Mn(II) Complexes calculated by B3LYP/6-311G(d,p) Method.**

Atom	Ligand	Cu(II) complex	Mn(II) complex
N1	-0.314	-0.312	-0.315
N2	-0.294	-0.277	-0.333
Metal ion	-	0.469	1.012
Double Metal complex			
N1	-	-0.310	-0.302
N2	-	-0.365	-0.360
N3	-	-0.280	-0.288
N4	-	-0.382	0.307
M1(M2)	-	0.446 (0.498)	1.002 (1.023)

The stabilization energy of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid (ligand) involved in coordination with Cu (II) and Mn (II) ions are calculated at both semi-empirical and DFT methods as presented in equation 1 [21-24].

$$\text{Stabilization energy (S.E)} = E[M(\text{II})L] - [E(M^{2+}) + 4E(\text{H}_2\text{O}) + E(L)] \quad \text{----- (1)}$$

where M = Cu or Mn, L = -(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid and E = energy of each specie,  ${}^{\circ}\text{H}_f$  = standard heat of formation calculated using semi-empirical (PM3 and PM6) methods for each specie.

The total energies calculated at DFT for the two complexes [CuL] and [MnL] are -4181.546 and -3692.132 au respectively; and -8235.094 and -7755.174 au for bimetal complexes of Cu(II) and Mn(II) ions respectively (Table 3). The heat of formation ( $\Delta H_f$ ) calculated at PM3 (PM6) are -305.72 (-226.64) and -563.15 (-379.76) kcal/mol for mono Cu(II) and bimetallic Cu(II) complexes respectively. For Mn(II) complex ion, the  $\Delta H_f$  calculated at PM3 and PM6 are -284.19 and -229.99 kcal/mol for mono Mn(II) complex ion; and -614.24 and -665.67 kcal/mol for bimetallic Mn(II) complex ion respectively. The calculated S.E (kcal/mol) for mono Cu(II) and Mn(II) complexes are  $-1.56 \times 10^3$  and  $-9.23 \times 10^2$  at PM3; and  $-4.44 \times 10^2$  and  $-5.72 \times 10^2$  at PM6 showing that formation of mono Cu(II) complex ion is favoured over the counterpart Mn(II) complex. However, the formation of bimetallic Mn(II) complex is favoured thermodynamically in line with experimental results [28] as shown in Table 3. The S.E calculated at DFT for mono Cu(II) and bimetallic (Cu(II) complexes are  $-2.62 \times 10^2$  and  $+7.96 \times 10^4$  kcal/mol respectively, whereas these are calculated to be  $+1.51 \times 10^3$  and  $-5.78 \times 10^4$  kcal/mol for mono and bimetallic Mn(II) complexes respectively. The S.E calculated at DFT showed that formation of mono Mn(II) complex and bimetal Cu(II) complex are not feasible thermodynamically. Therefore, this might account for inability to synthesize mono Mn(II) and bimetallic Cu(II) complexes as observed experimentally [28].

### CONCLUSION

In this paper, quantum chemical calculations were carried out on Cu(II) and Mn(II) compound of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid (H<sub>2</sub>pdt). The geometric and electronic properties have been keenly studied using semi-empirical (PM3 and PM6) and DFT/B3LYP/6-31G(d,p) methods. The computational results revealed that geometries and molecular parameters calculated at DFT agreed with/closer to the experimental data than semi-empirical methods; and the results from PM3 calculations are superior to PM6. The calculated reactivity indices showed that mono Cu(II) and bimetal Mn(II) complexes are harder, more thermodynamic stable and less polarizable. The stabilization energies calculated especially using DFT method showed that that formation of mono Mn(II) complex and bimetal Cu(II) complex are not feasible but rather mono Cu(II) and bimetallic Mn(II) complexes are thermodynamically favoured. This might account for the synthesis mono Cu(II) and polymeric nature Mn(II) complexes.

### REFERENCES

- [1] Heilman PW., Geilman RD., Scozzie AJ., Wayner RJ., Gullo MJ., and Aryan SZ. J. Pharm. Sci. 1980; 69: 282.
- [2] Schilt AA., and Dunbar WE. Talanta 1969; 16: 519.
- [3] Tang D., Wang J., Wu P., Guo X., Li J-H., Ysng S., Chen B., RSC Advances 2016; 6: 12514-12518.
- [4] Bereau V., Rey J., Deydier E., Marrot J. Inorg Chim Acta, 2003; 351: 389.
- [5] Behl M. and Zentel R., Macromol. Chem. Phys. 2004; 205: 1633.
- [6] (a) Del Sesto RE., Botoshansky M., Kaftory M., Arif AM. and Miller JS. Cryst Eng Comm, 2002; 4: 117.
- [7] Shichibu Y., Negishi Y., Tsukuda T., Teranishi T., J. Am. Chem. Soc. 2005; 127: 13464-13465.
- [8] (a) Pang J., Tao Y., Freiberg S., Yang XP., D'Iorio M. and Wang S. J. Mater. Chem., 2002; 12: 206.
- [9] Murase T. and Fujita M. J. Org. Chem., 2005; 70: 9269.
- [10] Kirschner S., Wei YK., Francis D., and Bergman JG. J. Med. Chem., 1966; 9: 369.
- [11] Abdel-Rahman RM., Makki MST., Ali TE., Ibrahim MA. European Journal of chemistry, 2010; 1(3): 236-245.
- [12] Ramadan AAT., El-Beahry MA., Ismail AL., and Mahmoud M. Monatsh. Chem., 1994; 125: 1171.
- [13] Ramadan AAT., Abdel-Rahman RM., and Seda MH. Asian J. Chem., 1992; 4(3): 569-578.
- [14] Ramadan AAT., Abdel-Rahman RM., El-Beahry MA., Ismail AL., and Mahmoud M. Thermochim. Acta, 1993; 222: 291-303.
- [15] Taha A., El-Shetary B., and Linert W. Monatsh. Chem., 1993; 124: 135-147.
- [16] Juris A., Balzani V., Barigelletti F., Campagna S., Belser P., Zelewsky AV. Coord. Chem. Rev., 1988; 84: 85-277.
- [17] Frison G., Ohanessian G., Journal of Computational Chemistry 2008; 29: 416 – 433.
- [18] Adeoye IO., Odunola OA., Oladipo MA. and Semire B. J. Chem. 2010; 7: 517 – 525.
- [19] Seguel GV., Rivas BI. and Paredes C. J. Chil. Chem. Soc. 2010; 55: 355-358.
- [20] Adekunle FAO., Semire B. and Odunola OA. Asian Journal of Chemistry 2013; 25(13): 7371 – 7376.
- [21] Adekunle FAO., Semire B. and Odunola OA. Elixir Comp. Chem. 2013; 61: 17019 – 17023.

- [22] Adekunle FAO., Semire B. and Odunola OA. *Synth. React. Inorg. Met.- Org. Chem.* 2015; 45(8): 1102 -1107.
- [23] Adekunle OF., Obi-Egbedi N., Semire B. and Odunola OA. *Elixir Comp. Chem.* 2016; 95: 40727-40731.
- [24] Adekunle OF., Obi-Egbedi N., Semire B. and Odunola OA. *Elixir Appl Chem.* 2016; 95: 40583-40588.
- [25] Vladimirova KG., Freidzon AY., Kotova OV., Vaschenko AA., Lepnev LS., Bagatur'yants AA., Vitukhnovskiy AG., Stepanov NF., Alfimov MV. *Inorg Chem.* 2009; 48: 11123–11130.
- [26] Das C., Adak P., Mondal S., Sekiya R., Kuroda R., Gorelsky SI., Chattopadhyay SK., *Inorg. Chem.* 2014; 53: 11426–11437.
- [27] BingolAlpaslan Y., Alpaslan G., Alaman Agar A., Ocaklskeleli N., Oztekin E. *J. Mol. Struct.* 2011; 995: 58–65.
- [28] Ibrahim AO., Zhou Y., Jiang F., Chen L., Li X., Xu W., Onawumi OOE., Odunola OA., and Hong M. *Eur. J. Inorg. Chem.* 2011; 5000–5005.
- [29] Spartan user's guide, Wave function, Inc, Irvine, CA, 92612 USA
- [30] Spartan 14, Wavefunction, INC, Irvine CA 92612, USA.
- [31] Tynan E., Jensen P., Kruger PE., Mees AC, Nieuwen-hyyzen M. *Dalton Trans.*, 2003; 1223.
- [32] Fleming L. *Frontier Orbitals and Organic Chemical reactions*, John Wiley & Sons, London, (1976).
- [33] Zhou Z., Parr RG. *J. Am. Chem. Soc.* 1990; 112: 5720-5724.
- [34] Pearson RG. *J. Am. Chem. Soc.* 1988; 110: 2092-2097.
- [35] Yüce AO, Mert BD, Kardaş G., Yazıcı B., *Corrosion Science* 2014; 83: 310-316.
- [36] Saha GB., Springer, 2010; 6.
- [37] McMurry F. *Chemistry* fourth edition. Pearson Education. New Jersey, 2002.
- [38] Targema M., Obi-Egbedi NO. and Adeoye MD. *Computational and Theoretical Chemistry*, 2013; 1012: 47-53.
- [39] Parr RG., Szentpály LV., Liu S. *J. Am. Chem Soc.* 1999; 121: 1922- 1924.
- [40] Semire B., Odunola OA. *Int. J Chem. Mod.* 2013; 4: 87-96.
- [41] Koopmans TA. *Physica* 1993; 1: 104-113.
- [42] Sinhaa L., Prasada O., Narayana V., Shuklab S.R. *J. Mol. Simul.* 2011; 37: 153-163.
- [43] El-t. Ashoor S., Shawish HB. *Phys. Mater. Chem.* 2015; 3(1): 7-11.