Asian Journal of Chemistry; Vol. 33, No. 6 (2021), 1222-1228

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23150

Synthesis, DFT and Bio-Potential Activities of Mn(II) and Hg(II) Complexes with Bidentate (*E*)-*N′*[(*E*)-3-Phenylallylidene]benzene-1,2-diamine

R. SELVARANI[1,*], S. BALASUBRAMANIYAN[1], K. RAJASEKAR[1], M. THAIRIYARAJA[2] and R. MEENAKSHI[3]

[1]Department of Chemistry, Government Arts College (Affiliated to Bharathidasan University, Tiruchirappalli), Ariyalur-621713, India
[2]Department of Physics, Government Arts College (Affiliated to Bharathidasan University, Tiruchirappalli), Ariyalur-621713, India
[3]Department of Physics, Cauvery College for Women (Autonomous) (Affiliated to Bharathidasan University, Tiruchirappalli), Tiruchirappalli-620002, India

*Corresponding author: E-mail: selvasekar2008yoki@gmail.com

Received: 1 February 2021; *Accepted*: 17 March 2021; *Published online*: 5 June 2021; AJC-20347

A new bidentate Schiff base (*E*)-*N′*[(*E*)-3-phenylallylidene]benzene-1,2-diamine derived from the condensation of *o*-phenylenediamine and cinnamaldehyde and its Mn(II) and Hg(II) complexes were synthesized and characterized by elemental analysis, molar conductance, magnetic moment, electronic spectra, IR, far-IR and NMR (^{1}H & ^{13}C) spectral studies. The elemental analysis and these metal proposed the metal:ligand stoichiometry and molecular formulae of the metal complexes. The molar conductance and electrochemical property indicates monomeric, neutral nature and redox properties of the metal complexes. The UV-visible spectral study supports the octahedral geometry for Mn(II) complex and square planar geometry for Hg(II) complex and further confirmed by magnetic moment. IR spectral data examined the coordination mode but far-IR is useful to identify the metal-ligand vibrations. The geometry, magnetic property and unsymmetrical nature of these metal complexes corroborated by NMR (^{1}H & ^{13}C) spectra. The DFT of Mn(II) complex studied and the structure optimized by B3LYP/Lan L2DZ using Gaussian 09W. Quantum chemical calculations were done by Mullikan population analysis, HOMO-LUMO and molecular electrostatic potential. The *in vitro* biological screening effects of the investigated complexes were tested against some bacteria and fungus by agar-well diffusion method. The results indicated that Mn(II) and Hg(II) complexes exhibit potentially active than the Schiff base which was further confirmed by pharmacokinetics study. The antioxidant activity of Schiff base and its Mn(II) complex was examined by radical scavenging DPPH method.

Keywords: *o*-Phenylenediamine, Cinnamaldehyde, Quantum chemical, Biological screening, Antioxidant, Pharmacokinetics.

INTRODUCTION

Schiff base is an important class of ligand in the development of coordination chemistry. These ligands are considered as "privileged ligand" because they are easily prepared by the condensation of aldehyde and amine [1,2]. Metal complexes of Schiff base have been presented as building block in supramolecular assembly [3,4]. Schiff base derivative shows special centre of attraction in many fields like medicines, biological, clinical, analytical, pharmacological studies, *etc.* [5,6]. Cinnamaldehyde is the main components of cinnamon from bark extract. It is used in aroma compounds in natural perfume, sweet and fruity scents [7] by the smell of cinnamon in almond, apricot and butterscotch [8,9]. It is a potential anti-obesity drug due to its low toxicity, eco-friendly, food flavouring, medical herb and renowned strong adsorption properties [10]. *o*-Phenylenediamine (OPD) is used as an antioxidant in rubber product and also in photoluminescence, catalytic activity and pharmaceutical with various diketone [11].

Due to the high-spin, octahedral Mn(II) often present in the active centers of enzymes [12], among the d^{10} group of transition metals, mercury complexes have attracted a great deal of attention due to its flexible coordination from linear (two-coordinate) to pentagonal bipyramid (seven-coordinate) and several distorted forms [13]. Thus present study aims to synthesis of Mn(II) and Hg(II) metal complexes with Schiff base derived from cinnamaldehyde and *o*-phenylenediamine and characterized by various physico-chemical, spectral, DFT and explored its biopotential studies.

EXPERIMENTAL

All the chemicals *viz. o*-phenylenediamine, cinnamaldehyde, potassium thiocyanate, manganese nitrate and mercury chloride, solvents and reagents were of AnalaR grade (99% pure) used as such without further purification. The synthesized Schiff base and its complexes were stable under norma conditions. Elemental analysis was carried out using elemental Vario make EL-III model instrument at 950-1200 ºC temperature. Molar conductance of the Schiff base metal complexes where predicted in acetonitrile solution at 10^{-3} M concentration at room temperature by using Systronic conductivity bridge with dip-type conductivity cell made by platinum black. The magnetic moments of metal(II) complexes were measured using a Lake Shore 7410 vibrating sample magnetometer (VSM) at room temperature. Electronic spectra were recorded in solid state spectral method (DRS method) on JASCO-V650 model spectrometer in the range of 200-800 nm. Using Shimadzu, FT-IR-4100 type-A model IR spectrometer, IR spectral data of Schiff base and its metal(II) complexes were recorded in the range of 4000 to 400 cm^{-1} using KBr pellet technique. The Far IR spectra of the metal(II) complexes were recorded in a Bruker, Germany, 3000 Hyperion Microscope with Vertex 80 FTIR system model instruments. The ^1H & ^{13}C NMR spectra of Schiff base and its diamagnetic Hg(II) complex were carried out by Bruker instrument in DMSO-d_6. The DFT calculations of the synthesized Mn(II) complex were carried out using Gaussian09W.

Synthesis of Schiff base: One-pot multi-component condensation reaction of 0.624 g (4.70 mmol) of cinnamaldehyde (in 10 mL diethyl ether) and 0.486 g (4.40 mmol) of *o*-phenylenediamine (in 10 mL ethanol) and using water as a green solvent and stirred continuously for about 10-15 min at room temperature, shiny powdered yellow colour precipitate was formed [14]. The product was purified by simple filtration followed by washing with water and dried in the desiccators.

Synthesis of Mn(II) complex: A Schiff base (1.77 g, 7.96 mmol) in 35 mL ethanol was mixed with $Mn(NO_3)_2$ (1 g, 3.98 mmol in 10 mL of methanol) and anionic ligand *viz.,* potassium thiocyanate (0.770 g, 7.96 mmol in 10 mL of water) was mixed and stirred continuously for 10-15 min at room temperature. A pale yellow colour precipitate was obtained and purified by simple filtration followed by several washings with distilled water and finally dried in desiccator (yield: 82.05%).

Synthesis of Hg(II) complex: A Schiff base (0.818 g, 3.68 mmol) in 35 mL ethanol solution was mixed with mercury(II) chloride (1 g, 3.68 mmol in 10 mL of methanol) and added anionic ligand *viz.,* potassium thiocyanate (0.716 g, 7.36 mmol in 10 mL of water). The solution was stirred continuously for 10-15 min at room temperature resulted in the formation of the pale yellow precipitate. The product was filtered followed by several washings with distilled water and finally dried in desiccator (yield: 80.55%).

RESULTS AND DISCUSSION

The newly synthesized Schiff base and its metal(II) complexes are quite stable under normal conditions in the solid state. Based on the elemental analysis and metal estimation, it is suggested that the metal complexes are conformable with the ratio 1:1 for metal to ligand.

Molar conductance: Molar conductance of 10^{-3} M acetonitrile solutions of the metal complexes was determined. The molar conductance values are presented in Table-1. The values indicated that the synthesized complexes are non-electrolytes, consequently no anions or cations are present outside the coordination sphere. The molar conductance values are too low to account for an ionic complex and therefore, these complexes are considered to be neutral [15].

ESI mass spectra: ESI mass spectrum of Schiff base recorded at room temperature. It is revealed that the empirical formula of the Schiff base also support its stability. The *m/z* value of 222 confirmed by the molecular ion peak of Schiff base ($C_{15}H_{14}N_2$) but the fragments at 105 and 117 corresponds to the substituent $C_6H_6N_2^-$ and $C_9H_8^+$, respectively observed without the cleavage of ring [16] (Fig. 1).

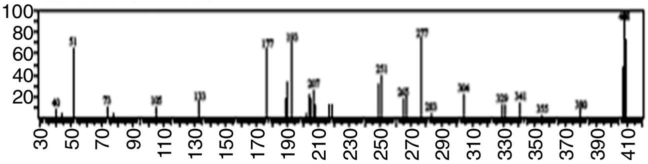

Fig. 1. Mass spectrum of Schiff base

UV-visible spectra: The Schiff base shows the absorption band at 391 nm, which is assigned to π-π* transition of C=N chromospheres. Mn(II) complex show three bands at 907, 788 and 299 nm assignable to $^4T_1g \rightarrow {}^6A_{1g}$ (G), $^4T_{2g} \rightarrow {}^6A_{1g}$ (4G) and $^4A_{1g}$ (4G)$\rightarrow {}^6A_{1g}$ transitions, which lie in the same range as reported for octahedral Mn(II) ion [17] (Fig. 2). The effective magnetic moment 5.80 BM is an additional evidence for an octahedral structure.

In Hg(II) complexation, the Schiff base band shifted to the wave length region at 327 nm and 394 nm because the coordination of azomethine nitrogen with Hg(II) ion. The Hg(II)

TABLE-1
ANALYTICAL DATA OF THE SYNTHESIZED SCHIFF BASE AND ITS Mn(II) AND Hg(II) COMPLEXES

Schiff base/ Complex	m.w. (g/mol)	m.p. (°C)	Colour	Elemental analysis (%): Found (calcd.)					Molar conductance (Ohm^{-1} cm^2 mol^{-1}
				C	H	N	S	M	
Schiff base	222.30	117	Shiny yellow	80.97 (80.19)	6.29 (6.30)	12.59 (12.52)	–	–	–
$[Mn(SB)_2(SCN)_2]$	615.72	155	Pale yellow	6236 (62.30)	4.54 (4.90)	13.64 (13.10)	10.39 (10.98)	8.92 (8.10)	12.50
$[Hg(SB)(SCN)_2]$	539.07	120	Pale Yellow	37.84 (37.29)	2.59 (2.90)	10.38 (10.10)	11.87 (11.10)	37.21 (37.90)	16.60

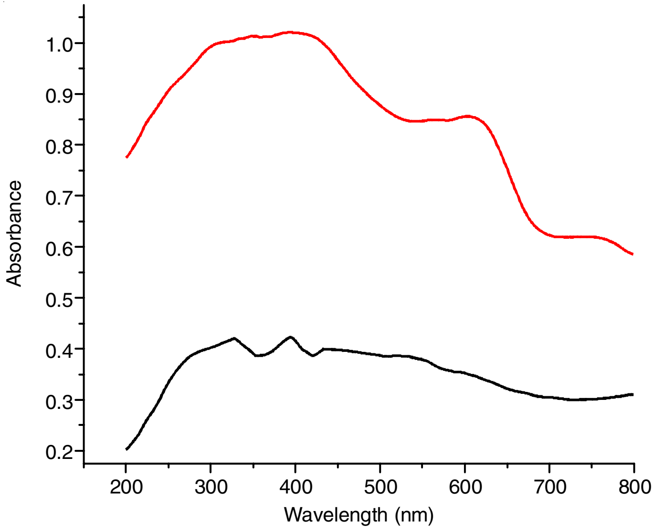

Fig. 2. UV-visible spectra of Mn(II) and Hg(II) complex

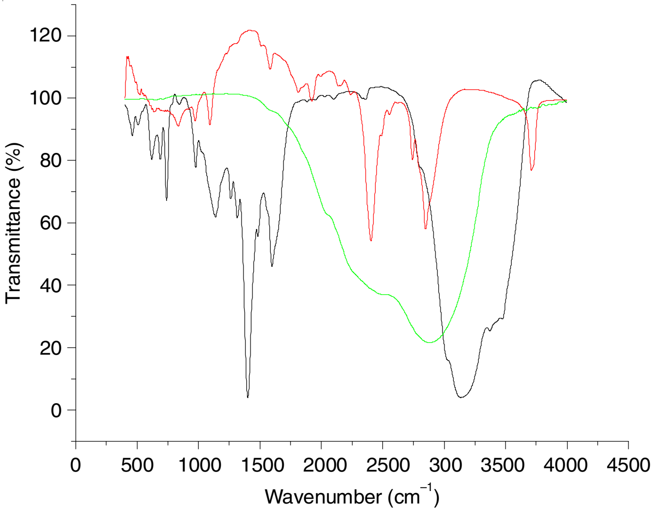

Fig. 3. IR spectra of Schiff base, Mn(II) and Hg(II) complexes

complex does not exhibit *d-d* electronic transition due to the completely filled *d*-orbital but it shows C-T band (LMCT & MLCT) at 327 nm and 394 nm confirmed the Hg(II) complex would have the tetrahedral geometry [18] (Fig. 2).

IR spectra: The IR spectra of Mn(II) and Hg(II) complexes were analyzed in comparison with that of their respective free Schiff base in the region of 4000-400 cm^{-1}. The IR spectra of the Schiff base ligand show a azomethine (C=N) absorption band at 1595 cm^{-1}, while on complexation these absorption band appears at 1639 and 1624 cm^{-1}, indicating that the Schiff base have undergone deprotonation on complexation and azomethine nitrogen coordination to the metal ion [19]. In the Schiff base, amine group (N-H) stretching frequency at 3500 cm^{-1} is shifted to 3446 and 3442 cm^{-1}, which give the evidence for the coordination of the Schiff base to the respective metal ions Mn(II) and Hg(II) *via* two nitrogen atoms of imine and amine [20]. The aromatic (C-H) frequencies at 3371 and 3142 cm^{-1} in Schiff base also appeared at 3290 and 3036 cm^{-1} in Mn(II) and at 3164 cm^{-1} in Hg(II) complexes. A band at 1398 cm^{-1} for the free ligand is assigned to the C-N stretching frequency, while on complexation it is shifted to 1401 cm^{-1} in Mn(II) whereas in Hg(II) it appears at same region [21,22]. In metal complexes, the SCN^{-} stretching frequency at 2055 cm^{-1} and 2101 cm^{-1} was confirmed by the coordination of metal ion through 'N' and 'S' atoms of thiocyanate ion, respectively (Fig. 3). The metal-chelates of metal complexes confirmed by Far-IR spectra, where the medium band at 542 and 526 cm^{-1} for M-N bond of amine group and 420 and 413 cm^{-1} for M-N bond of imine (C=N) group in Mn(II) and Hg(II) complexes. The additional anionic ligand M-N frequency at 494 cm^{-1} in Mn(II) complex but in Hg(II) complex it show at 414 cm^{-1} attributed to the M-S bond of metal chelates [23].

NMR spectra: The ^{1}H NMR spectrum of Schiff base and its metal(II)complexes were recorded in DMSO-d_6 at room temperature. The Schiff base shows the signals for imine H-C=N and NH_2 at δ 8.41 ppm to 8.43 ppm and δ 5.05 ppm, respectively, while in Hg(II) complex these values are shifted to downfield deshielded at δ 8.16 to 8.17 ppm and δ 5.44 ppm support the involvement of imine and amine nitrogen atoms on coordination of metal ions. The magnetic properties and geometry of the complex also confirmed by resonance peaks of ^{1}H NMR, the other resonance at δ 7.11 to 7.66 ppm for the aromatic ring of cinnamaldehyde moiety and at δ 6.69 to 7.03 ppm for the aniline moiety which were condensed in the Schiff base. In metal(II) complexes, these are shifted to down or upfield due to effective coordination of Schiff base to the metal(II) ion [24].

In ^{13}C NMR, Schiff base shows 127.98 ppm (C1), 129.43 ppm (C2), 129.82 ppm (C3), 136.20 ppm (C4), 136.10 ppm (C5), 115.17 ppm (C6), 158.79 ppm (C7=N), 143.10 ppm (C8), 144.02 ppm (C9-NH_2), 116.89 ppm (C10), 129.33 ppm (C11), 117.01 ppm (C12) and 127.85 ppm (C13), these resonance are shifted to downfield and upfield in Hg(II) complex except (C7=N) and (C9-NH_2), which is drastically changed to upfield at δ 153.76 ppm and downfield at δ 146.17 ppm due to the involvement of nitrogen atom of imine and amine group of Schiff base to metal(II) ion coordination [25].

Antibacterial activity: Antibacterial activities of the ligands and its metal(II) complexes were evaluated using well diffusion method on Mueller-Hinton agar (MHA) for bacteria. The inhibition zones were reported in millimeter (mm). Briefly, MHA agar plates were inoculated with bacterial strain under aseptic conditions and wells (diameter = 6 mm) were filled with 100 µL of the test samples and incubated at 37 ºC for 24 h. After the incubation period, the diameter of the growth inhibition zones was measured. Eighteen to 24 h single colonies on agar plates were used to prepare the bacterial suspension with the turbidity of 0.5 McFarland (equal to 1.5×10^{8} colony forming units (CFU)/mL).Turbidity of the bacterial suspension were measured at 600 nm. All the tests were performed in triplicate. The antibacterial activity of the Schiff base and its metal(II) complexes was assessed against *Staphylococcus aureus*, *Vibrio parahaemolyticus*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Enterococcus* and *Candida albicans* by agar well diffusion method. Each bacterial culture was grown in nutrient broth (bacterial) and potato dextrose broth (fungal) medium for 12 h at 37 ºC. Then, each grown cultures were swabbed on nutrient agar medium and well were cut about 5 mm using cork borer. Each well was added with 80 µL of sample and incubated at 37 ºC for 18 h. After incubation, the plates were observed for zone of inhibition and measured.

***in vitro* bio-potential study:** The *in vitro* bio-potential screening of the investigated compounds was tested against some bacterial and fungal strains by agar well diffusion method using chloramphenicol and fluconazole as standards and DMSO as control. The results (Table-2) showed that the metal(II) complexes posses higher activity than the Schiff base, which can explained by Tweedy Chelation theory and Overtone's concept [26,27]. Upon chelation of metal(II) complexes the permeability increase the polarity of the metal ions will be reduced, which will lead to the partial sharing of the positive charge to donor Schiff base. The delocalization of π-electrons on the whole chelates ring also enhances the lipophilicity also restrict the growth of microorganisms.

Antioxidant (DPPH free radical method): The free radical scavenging capacity was measured on the method reported by Brand-Williams *et al.* [28] with slight modification. A 1 mL of 0.1 mM DPPH solution in methanol was mixed with 1 mL of compound solution of varying concentrations (10, 100, 500 and 1000 µg/mL). Blank sample was also prepared and L-ascorbic acid was used as standard. The tubes were thoroughly mixed and kept in the dark for 30 min and their absorbance was measured at 517 nm using UV-vis-spectrophotometer. The inhibition % was calculated using the following formula:

$$\text{Inhibition (\%)} = \frac{A_c - A_s}{A_c} \times 100$$

The DPPH free radical scavenging activity results indicated that the antioxidant ability of metal(II) complex increases at the increasing concentrations due the chelation transition metal ions to the ligand [29,30]. The IC_{50} values of the Schiff base are lower than that of Mn(II) complex (Table-3).

Physico-chemical properties and general computational methodology: Using the online Swiss ADME software, one can calculate the number of physico-chemical descriptors, such as the molecular weight (MW), molecular refractivity (MR), count of specific atom types and the topological polar surface area (TPSA), estimation of membrane diffusion, pharmacokinetic behaviour. The lipophilicity was assessed by means of five alternative predictive models; *i.e.* Xlog P; Wlog P; Mlog P; SILICOS-IT and ilog P, together with consensus log P estimation based on the average value of the different computational parameters. The results indicate that the physico-chemical parameters are fit in their particular range (Table-4). In pharmacokinetics study, the lipophilicity of metal complexes increases than the free Schiff base confirming the better biological activity of the synthesized metal(II) complexes. For the drug likeliness properties of the metal(II) complex, it violate one of the Lipinski′s rule five but the Schiff base did not violate the rule of five so that in medicinal chemistry they are used as drug for the biovailability as 0.55, 0.56 and 0.56 for Schiff base, Mn(II) and Hg(II) complexes, respectively [31] (Table-5).

Quantum chemical calculations of Mn(II) complex: Geometry of the synthesized Mn(II) complex optimized by B3LYP/lanL2DZ using Gaussian 09W was studied. Using the same level of theory Mulliken's population analysis, HOMO-

TABLE-2
ANTIBACTERIAL AND ANTIFUNGAL ACTIVITIES OF THE SYNTHESIZED SCHIFF BASE AND ITS Mn(II) AND Hg(II) COMPLEXES

Compound	Zone of inhibition (mm)					
	S. aureus	*E.coli*	*Vibrio parahaemolyticus*	*P. aeruginosa*	*Enterococcus*	*C. albicans*
Schiff base	08	14	12	08	14	28
$[Mn(SB)_2(SCN)_2]$	10	10	04	08	10	40
$[Hg(SB)(SCN)_2]$	42	18	48	26	14	44

TABLE-3
in vitro ANTIOXIDANT ACTIVITY OF THE SYNTHESIZED SCHIFF BASE AND ITS Mn(II) COMPLEXES

Compounds	Concentration (µg/mL)				Inhibition (%)				IC_{50} value
	10	100	500	1000	10	100	500	1000	
Schiff base	1.249	0.917	0.651	0.437	26.0	45.7	61.4	74.1	359.3
Mn(II) complex	1.458	1.185	0.834	0.649	13.7	29.8	50.6	61.5	649.7

TABLE-4
PHYSICO-CHEMICAL PROPERTIES OF THE SYNTHESIZED SCHIFF BASE AND ITS Mn(II) AND Hg(II) COMPLEXES

Properties	Schiff base	Mn(II) complex	Hg(II) complex
Formula	$C_{15}H_{14}N_2$	$C_{32}H_{28}MnN_6S_2$	$C_{17}H_{14}HgN_4S_2$
Molecular weight	222.29 g/mol	615.67 g/mol	539.04 g/mol
Num. heavy atoms	17.0	41	24.0
Num. arom. heavy atoms	12.0	24	12.0
Fraction Csp3	0.00	0.00	0.00
Num. rotatable bonds	3.00	6.00	3.00
Num. H-bond acceptors	1.00	4.00	3.00
Num. H-bond donors	1.00	2.00	1.00
Molar Refractivity	74.47	174.90	100.43
TPSA	38.38 Å²	124.34 Å²	85.96 Å²

TABLE-5
COMPUTATIONAL METHODOLOGY FOR MEDICINAL CHEMISTRY OF THE SYNTHESIZED SCHIFF BASE AND ITS Mn(II) AND Hg(II) COMPLEXES

Lipophilicity	Schiff base	Mn(II) complex	Hg(II) complex
Log $P_{o/w}$ (iLOGP)	2.61	0.00	0.00
Log $P_{o/w}$ (XLOGP3)	2.97	7.06	4.10
Log $P_{o/w}$ (WLOGP)	3.58	7.20	3.61
Log $P_{o/w}$ (MLOGP)	3.05	3.15	1.66
Log $P_{o/w}$ (SILICOS-IT)	3.67	3.67	3.67
Consensus log $P_{o/w}$	3.18	4.22	2.61
Pharmacokinetics	**Schiff base**	**Mn(II) complex**	**Hg(II) complex**
GI absorption	High	Low	High
BBB permeant	Yes	No	No
P-gp substrate	No	No	No
CYP1A2 inhibitor	Yes	No	Yes
CYP2C19 inhibitor	Yes	Yes	Yes
CYP2C9 inhibitor	Yes	Yes	Yes
CYP2D6 inhibitor	No	No	No
CYP3A4 inhibitor	Yes	Yes	Yes
Log K_p (skin permeation)	-5.55 cm/s	-5.04 cm/s	-6.68 cm/s
Drug likeliness	**Schiff base**	**Mn(II) complex**	**Hg(II) complex**
Lipinski	Yes; 0 violation	Yes; 1 violation: MW>500	Yes; 1 violation: MW > 500
Ghose	Yes	No; 3 violations: MW > 480, WLOGP > 5.6, MR > 130	No; 1 violation: MW > 480
Veber	Yes	Yes	Yes
Egan	Yes	No; 1 violation: WLOGP > 5.88	Yes
Muegge	Yes	No; 2 violations: MW > 600, XLOGP3 > 5	Yes
Bioavailability score	0.55	0.56	0.56

LUMO analysis and molecular electrostatic potential analysis have been performed. Additionally global reactivity descriptors were also calculated [32].

Mulliken's population analysis: The bonding capability of a molecule depends on the electronic charges on the chelating atoms. The atomic charge values were obtained by the calculation on the Mulliken atomic charges of the studied complex using B3LYP method with lanL2DZ basis set. It is evident that the atomic charge populations are not evenly distributed in the whole molecule. Atoms such as nitrogen and carbon are negatively charged, while their directly bonded neighbouring atoms show obvious positive characteristics [33]. The uneven charge distribution of the studied compound is expected to present some interesting electron-transfer characteristics. The detailed Mulliken atomic charges of all atoms are listed in Table-6.

Frontier molecular orbital: Fig. 4 shows the distributions and energy levels of the FMOs computed for the Mn(II) complex. As seen from Fig. 5, the atomic π-electron orbital's are respon-

TABLE-6
GLOBAL AND LOCAL REACTIVITY DESCRIPTORS OF THE SYNTHESIZED SCHIFF BASE AND ITS Mn(II) AND Hg(II) COMPLEXES

Parameters	Values (a.u)
HOMO energy	-0.212782
LUMO energy	-0.209053
Energy gap	-0.003729
IP	122.61148
EA	-122.61148
η	-0.003729
S	-133.014
μ	0.2109175
χ	-0.2109175
ω	-61.57918
ΔN_{max}	56.561410
ΔE_n	-61.0323
ΔE_e	+61.0323

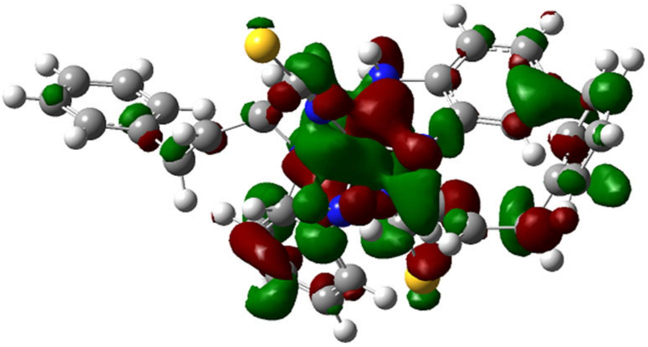

Fig. 4. HOMO structure of Mn(II) complex

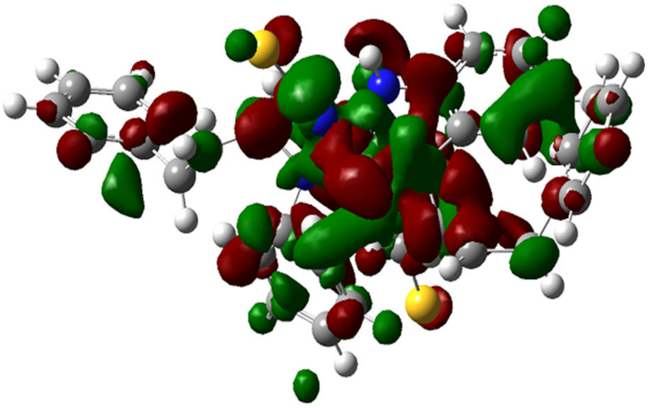

Fig. 5. LUMO structure of Mn(II) complex

sible for the FMOs. The lowest unoccupied molecular orbital (LUMO) are mainly localized on the central fragment and E_L. The highest occupied molecular orbital (HOMO) is localized mainly on central fragment. This shows that the charge transfer is taking place from central fragment to E_H. The small energy gap (LUMO-HOMO) is 0.0038 a.u. indicates that the Mn(II) complex has high excitation energy [34].

Global and local reactivity descriptors: Using Koopman's theorem for closed-shell compounds, η, μ and χ can be defined. Parr *et al.* [35] have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as follows:

$$\omega = \frac{\mu^2}{2\eta}$$

The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity. All the calculated values of hardness, potential, softness and electrophilicity index are shown in Table-6. The maximum amount of electronic charge is given by:

$$\Delta N_{max} = -\frac{\mu}{\eta}$$

Molecular electrostatic potentials (MEP): To predict reactive sites for electrophilic and nucleophilic attack for the investigated compounds, molecular electrostatic potential (MEP) was calculated at B3LYP/lanL2DZ optimized geometries. Red and blue areas in the MEP map refer to the regions of negative and positive potentials and correspond to the electron-rich and electron-poor regions, respectively, whereas the green colour signifies the neutral electrostatic potential. The electron total density on to which the electrostatic potential surface has been mapped as shown in Fig. 6 the electron density surface being 0.002 a.u. The negative regions V(r) were related to electrophilic reactivity and the positive ones to nucleophilic reactivity. The complex has several possible sites for electrophilic attack in which V(r) calculations have provided in-sights. It is found that the positive regions over the hydrogen atoms of Mn(II) complex, which indicate that these sites can be the most probably involved in nucleophilic processes.

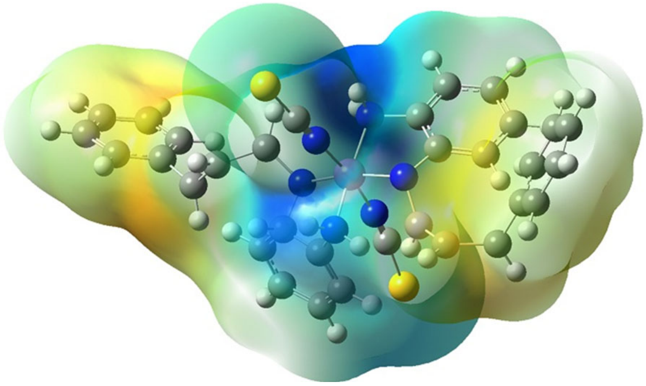

Fig. 6. Electrostatic potential of Mn(II) complex

Thermal study of Mn(II) complex: Thermogravimetric analysis and differential scanning colorimeter shows weight loss and transition temperature of synthesized Mn(II) complex. The thermogram curve at 319 °C is the starting decomposition of one Schiff base ligand from metal complex at 36.86%. This decomposition completed at 450 °C. The second decomposition start from 450 °C and continued to 500 °C, but at 490 °C there is a mass change of 6.0% due to the decomposition of sulphur atom from one of the mixed anionic thiocyanate ligand. The third step start from 500 °C continued to 720 °C and in between at 593 °C, a mass change of 43.24% was observed corresponds to the decomposition of second Schiff base and another thiocyanate ion (Fig. 7). After 740 °C, the solid residue was obtained which corresponds to metal oxide [36].

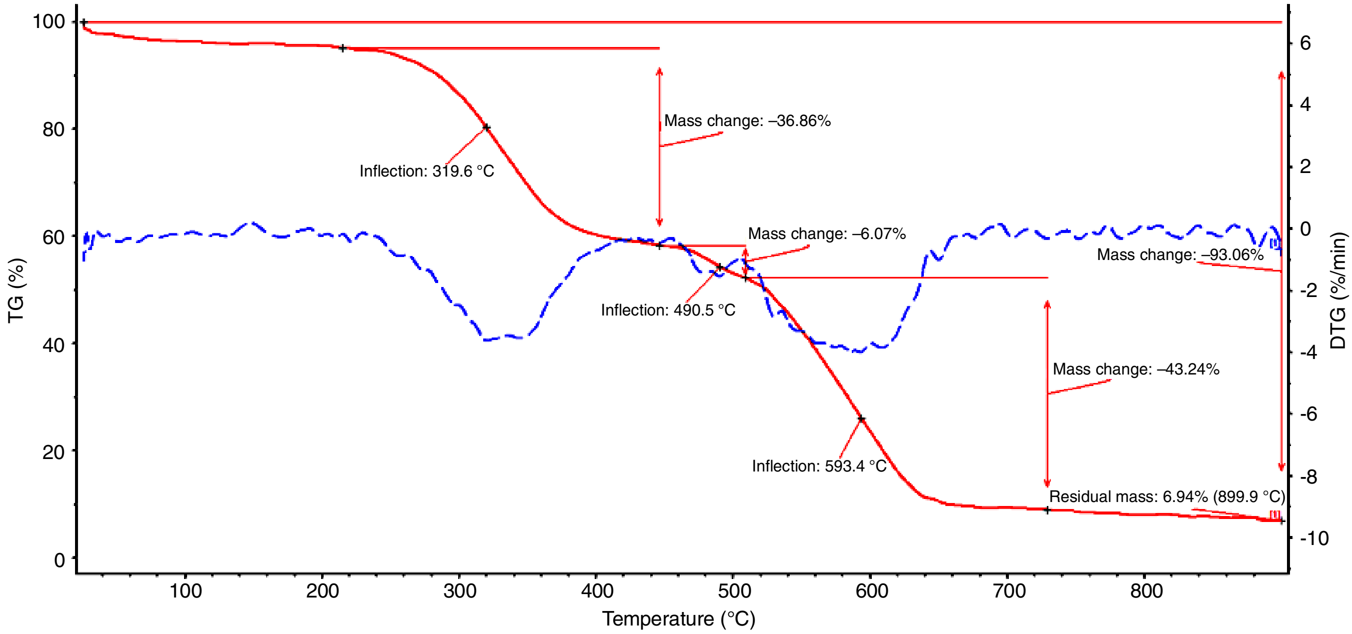

Fig. 7. TGA of Mn(II) complex

Conclusion

The Schiff base ligand and its Mn(II) and Hg(II) complexes were synthesized successfully using water as a solvent and characterized. The metal complexes were found to be stable under normal conditions and are non-electrolytic in nautre. Both the metal(II) complexes were biologically active against tested microorganisms and show a significant antioxidant activity which was further confirmed by the pharmacokinetics study using Swiss ADME software. From the DFT Mulliken's population analysis, FMO, Global and local reactivity descriptors and molecular electrostatic potentials (MEP) results, it indicates a small energy gap (LUMO-HOMO) for Mn(II) complex, which have high excitation energy and also posses nucleophilic reactivity and electrophilic attack. The electrostatic potentials were also confirmed by the biological recognition processes and the hydrogen bonding interactions.

ACKNOWLEDGEMENTS

The authors are grateful to The Director of SAIF Chennai, STIC Cochin and Harman Research Institute, for providing spectral and biological activities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, **43**, 6011 (2014); https://doi.org/10.1039/C4CS00094C
2. Md. Kudrat-E -Zahan, M.S. Islam and M.A. Baashar, *Russ. J. Gen. Chem.*, **85**, 667 (2015); https://doi.org/10.1134/S1070363215030238
3. P. Ikechukwu, A. Ejidike and P. Ajibade, *Bioinorg. Chem. Appl.*, **2015**, 890734 (2015); https://doi.org/10.1155/2015/890734
4. T.C. Amaral, F.B. Miguel, M.R.C. Couri, P.P. Corbi, M.A. Carvalho, D.L. Campos, F.R. Pavan and A. Cuin, *Polyhedron*, **146**, 166 (2018); https://doi.org/10.1016/j.poly.2018.02.024
5. H. Temel, S. Ilhan and M. Sekerci, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1625 (2002); https://doi.org/10.1081/SIM-120015083
6. R. Nair, A. Shah, S. Baluja and S. Chanda, *J. Serb. Chem. Soc.*, **71**, 733 (2006); https://doi.org/10.2298/JSC0607733N
7. S.S. Cheng, J.Y. Liu, K.H. Tsai, W.J. Chen and S.T. Chang, *J. Agric. Food Chem.*, **52**, 4395 (2004); https://doi.org/10.1021/jf0497152
8. T.M. Fasina, D. Ogundele, F.N. Ejiah and C.U. Dueke-Eze, *Int. J. Biol. Chem.*, **2012**, 1 (2012); https://doi.org/10.3923/ijbc.2012
9. P.V. Rao and S.-H. Gan, *Evid. Based Complement. Alternat. Med.*, **2014**, 642942 (2014); https://doi.org/10.1155/2014/642942
10. U.K. Sharma, A.K. Sharma and A.K. Pandey, *BMC Complement. Altern. Med.*, **16**, 156 (2016); https://doi.org/10.1186/s12906-016-1147-4
11. D. Gunawardena, N. Karunaweera, S. Lee, F. van Der Kooy, D.G. Harman, R. Raju, L. Bennett, E. Gyengesi, N.J. Sucher and G. Münch, *Food Funct.*, **6**, 910 (2015); https://doi.org/10.1039/C4FO00680A
12. G.C. Dismukes, *Chem. Rev.*, **96**, 2909 (1996); https://doi.org/10.1021/cr950053c
13. A. Morsali and M.Y. Masoomi, *Coord. Chem. Rev.*, **253**, 1882 (2009); https://doi.org/10.1016/j.ccr.2009.02.018
14. V.K. Rao, S.S. Reddy, B.S. Krishna, K.R.M. Naidu, C.N. Raju and S.K. Ghosh, *Green Chem. Lett. Rev.*, **3**, 217 (2010); https://doi.org/10.1080/17518251003716550
15. S.M. Jahromi, M. Montazerozohori and S.M. Jahromi, *J. Thermal Anal. Calorim.*, **120**, 591 (2015); https://doi.org/10.1007/s10973-015-4594-0
16. A.P. Mishra, R.K. Mishra and S.P. Shrivastava, *J. Serb. Chem. Soc.*, **74**, 523 (2009); https://doi.org/10.2298/JSC0905523M
17. M. Montazerozohori, M. Nasr-Esfahani, M. Hoseinpour, A. Naghiha and S. Zahedi, *Chem. Spec. Bioavail.*, **26**, 240 (2014); https://doi.org/10.3184/095422914X14145135824213
18. M.R.T.B. Olyai, *J. Appl. Chem. Res.*, **11**, 14 (2017).
19. M.A. Khalifa and A.M. Hassal, *Indian J. Chem.*, **34A**, 580 (1995).
20. N. Raman, Y.P. Raja and A. Kulandaisamy, *Proc. Indiana Acad. Sci.*, **113**, 183 (2001); https://doi.org/10.1007/BF02704068
21. E. Akila, M. Usharanai, S. Vimala and R. Rajavel, *Chem. Sci. Revs. Lett.*, **1**, 181 (2012).
22. M.S. Suresh and V. Prakash, *E-J. Chem.*, **8**, 1408 (2011); https://doi.org/10.1155/2011/254018
23. A. Ahmed, S.A. Benguzzi and A.E.L. Hadi, *J. Sci. Appl.*, **1**, 79 (2007).
24. M. Montazerozohori, H. Tavakol, S.A. Skheiri, S.A. Musavi and S. Joohari, *Bulg.. Chem. Commun.*, **46**, 96 (2014).
25. N. Raman, J.D. Raja and A. Sakthivel, *J. Chem. Sci.*, **119**, 303 (2007); https://doi.org/10.1007/s12039-007-0041-5
26. S.R. Gandhi, D.S. Kumar, S.S. Tajudeen and A.K.I. Sheriff, *Asian J. Chem.*, **29**, 1076 (2017); https://doi.org/10.14233/ajchem.2017.20416
27. A.A. Nejo, G.A. Kolawole and A.O. Nejo, *J. Coord. Chem.*, **63**, 4398 (2010); https://doi.org/10.1080/00958972.2010.532871
28. W. Brand-Williams, M.E. Cuvelier and C. Berset, *LWT-Food Sci. Technol.*, **28**, 25 (1995); https://doi.org/10.1016/S0023-6438(95)80008-5
29. Y. Harinath, D.H. Kumar Reddy, B.N. Kumar, C. Apparao and K. Seshaiah, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **101**, 264 (2013); https://doi.org/10.1016/j.saa.2012.09.085
30. A. Choudhary, R. Sharma, M. Nagar and M. Mohsin, *J. Enzyme Inhib. Med. Chem.*, **26**, 394 (2011); https://doi.org/10.3109/14756366.2010.518966
31. M. Hay, D.W. Thomas, J.L. Craighead, C. Economides and J. Rosenthal, *Nat. Biotechnol.*, **32**, 40 (2014); https://doi.org/10.1038/nbt.2786
32. M.J. Frisch *et al.*, GAUSSIAN 09, Revision A.02, Gaussian, Inc., Wallingford CT (2009).
33. L.H. Abdel-Rahman, N.M. Ismail, M. Ismael, A.M. Abu-Dief and E.A.-H. Ahmed, *J. Mol. Struct.*, **1134**, 851 (2017); https://doi.org/10.1016/j.molstruc.2017.01.036
34. J.-P. Costes, C. Duhayon, L. Vendier and A.J. Mota, *New J. Chem.*, **42**, 3683 (2018); https://doi.org/10.1039/C7NJ04347C
35. R.G. Parr, L.V. Szentpály and S. Liu, *J. Am. Chem. Soc.*, **121**, 1922 (1999); https://doi.org/10.1021/ja983494x
36. V. Nishal, D. Singh, A. Kumar, V. Tanwar, I. Singh, R. Srivastava and P.S. Kadyan, *J. Org. Semicond.*, **2**, 15 (2014); https://doi.org/10.1080/21606099.2014.942767