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DFT Study of the Interaction of Cu(II), Zn(II), Sn(II) with Carbohydrates in Aqueous Solution

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Abstract: In the present work, authors studied the interaction between carbohydrates as ligands such as L_1: fructose, L_2: glucose and L_3: sucrose with metal(II) halides such as $CuCl_2$, $ZnCl_2$, $SnCl_2$. Also authors compare the stability of the metal-ligand bond strength. DFT (density functional theory) was utilized using the B3LYP functional and the 6-31G(d) basis set. This level of calculation was used for optimization of geometry of ligands and exploring electronic properties such as ionization potential (I), electron affinity (A), chemical potential (μ), hardness (η), band gap (HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital)). The local reactivity was analyzed by the fukui function indices and the indices local of nucleophilicity in order to predict the sites of attack of carbohydrates. In addition, the strength of interaction has been evaluated by energy lowering and charge transfer using DFT at the B3LYP level employing the basis set Lan2DZ. As a result, the sequence of high stability of metal-ligand bond for ligands is in the following order; sucrose > glucose > fructose. Furthermore, the sequence of high stability for metal halides is in the following order, $CuCl_2$ > $SnCl_2$ > $ZnCl_2$. We advise person who carries a dental amalgam do not exceed the consommation of monosaccharides, because their complexes are not sufficiently stable and hence these ions are not ejected easily outside the human body.

Key words: Carbohydrates, metals, interactions, DFT, energy lowering, charge transfer.

1. Introduction

The interaction between metal ions released from amalgam and carbohydrates in oral cavity is very interesting, it resolves corrosion problem [1-6] related to dental restorations in systems where such data are not available. Also it plays a major role in many biochemical processes such as toxic metal metabolism [7]. The abundance of electronegative functional groups make saccharides potentially interesting ligands for the binding of metal ions in natural systems [8], and the understanding of such interactions remains one of the main objectives of carbohydrates coordination chemistry [9]. For this, authors consider the interaction between ligand and metal ion as acid-base reaction.

$A + :B \leftrightarrow A:B$, where, A is Lewis acid or electron acceptor, and B is a base or electron donor. Since the acid-base complex, A:B can be an organic molecule, an inorganic molecule or a complex ion [10]. The properties of the acids and bases in the various boxes were such that it seemed reasonable to label the boxes as hard or soft [11]. A modern version of metal ion classification differing slightly from Pearson's classification is presented here for some of the 82 ions considered in the study [12] (Table 1).

Some hard/soft acids and bases are given in Tables 1 and 2.

With this nomenclature, it is possible to make a simple statement "hard acids prefer to coordinate to hard bases, and soft acids prefer to coordinate to soft bases", this is the principle of HSAB (hard and soft acids) and bases (principle) [10], and classify the interaction between acids and bases in terms of global softness. This is an extremely useful qualitative theory that enables predictions of what adducts will form in a complex mixture of potential Lewis acids and bases.

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Table 1 Some hard, borderline and soft of acids.

Hard ions	Borderline ions	Soft ions
Al^{3+}, Be^{2+}, Ca^{2+}, Ce^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, H^+ In^{3+}, La^{3+}, Mg^{2+}, Mn^{2+}, Na^+, Sc^{3+}, Sn^{4+}, K^+,Ti^{4+}, U^{4+} , Zr^{4+}	Bi^{3+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Ir^{3+}, Ni^{2+}, Pb^{2+}, Ru^{2+}, Sn^{2+}, Zn^{2+}	Ag^+, Au^+, Cd^{2+}, Cu^+, Hg^+ Hg^{2+}, Pd^{2+}, Pt^{2+}, Tl^+, Tl^{3+}

Table 2 Some hard, borderline and soft bases.

Hard base	Borderline base	Soft base
H_2O, F^-, ROH, RO^-, R_2O, NH_3, Cl^-, ClO_4^-, SO_4^-	N_2, Br^-, $C_6H_5NH_2$, N_3^-	H^-, R^-, I^- , CN^-, CO, RNC, R_3P, R_2S

Furthermore, chemical hardness is associated with chemical reactivity of molecules [13].

DFT (density functional theory) derived reactivity descriptors have been recently and intensively used in the field of organic chemistry, either as global reactivity indices or as a tool for describing the local reactivity in molecules [14, 15], in terms of popular qualitative chemical concepts like electronegativity (χ), chemical potential (μ) [16], ionisation potential (I), electron affinity (A) [17], electrophilicity index (ω) and local reactivity descriptors such as local hardness [18], Fukui function and local softness [19].

Metal ligand bond strength has recently been evaluated with the help of quantum chemical parameters [20-22]. In this paper, density functional theory calculations at B3LYP/6-31G(d) and B3LYP/Lan2DZ have been performed to investigate geometry, stability, reactivity and electronic structure properties of model molecules. The stabilities of metal-carbohydrates interaction are determined from the frontier molecular orbital energies and their gaps and evaluated to the energy lowering and charge transfer.

2. Basic Concepts

2.1 Global Quantities

Density functional theory has developed the concept of chemical potential (μ) and absolute electronegativity (χ) [16]:

$$\mu = (\delta E \;/\; \delta N)v(r) = -\chi \qquad (1)$$

where, E is the total energy, N is the number of electrons, and $v(r)$ is the external potential of the system.

Hardness (η) is defined [23] as the corresponding second derivative.

$$\eta = (\delta^2 E \;/\; \delta N^2)v(r) = (\delta\mu \;/\; \delta N)v(r) \qquad (2)$$

Ionization potential (I) and electron affinity (A), the electronegativity (χ), global hardness (η) and softness (S), may be defined in terms of the energy of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) according to Koopman's theorem [24].

Softness (σ) is the inverse of hardness and is given as follows:

$$\sigma = 1/\eta \qquad (3)$$

Ionization potential (I) is defined as the amount of energy required to remove an electron from a molecule [25]. It is related to the energy of the E_{HOMO} through Eq. (4):

$$I = -E_{HOMO} \qquad (4)$$

Electron affinity (A) is defined as the energy released when a proton is added to a system [25]. It is related to E_{LUMO} through Eq. (5):

$$A = -E_{LUMO} \qquad (5)$$

Using a finite difference method working equations for the calculations of χ and η may be given as:

$$\chi = (I + A) \;/\; 2 \qquad (6)$$

$$\eta = I - A \qquad (7)$$

where, I is the ionization potential and A is the electron affinity. If ε_{HOMO} and ε_{LUMO} are the energies of the HOMO and LUMO, respectively, the Eqs. (5) and (6) can rewritten using Koopman's theorem [24]:

$$\chi = (\varepsilon_{LUMO} - \varepsilon_{HOMO}) \;/\; 2 \qquad (8)$$

$$\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO} \qquad (9)$$

2.2 Local Quantities

The Fukui function defined the reactivity/selectivity of a specific site in a molecule. The change in electron density is the nucleophilic $f^{+}(r)$ and electrophilic $f(r)$ Fukui functions, which can be calculated using the finite difference approximation as follows [26]:

$$f^{+}_{\mathrm{K}} = q_{N+1} - q_{N} \quad \text{for nucleophilic attack} \quad (10)$$

$$f_{\mathrm{K}} = q_{N} - q_{N-1} \quad \text{for electrophilic attack} \quad (11)$$

where, q_N, q_{N+1} and q_{N-1} are the electronic population of the atom K in neutral, anionic and cationic systems.

According to Domingo et al. [27, 28], the global nucleophilicity index, N is defined by Eq. (12):

$$N = \varepsilon_{HOMO(Nu)} - \varepsilon_{HOMO(TCE)} \quad (12)$$

where, $\varepsilon_{HOMO(Nu)}$ is associated to the HOMO energy within the Kohn-Sham scheme [29, 30] and $\varepsilon_{HOMO(TCE)}$ corresponds to the HOMO energy of the TCE (tetracyanoethylene) taken as reference. Satisfactory linear correlation has been found between experimental ionization potentials and calculated nucleophilicities for a large series of molecules.

The local nucleophilicity index N_k, the global nucleophilicity index (N) can be expressed as the sum of local nucleophilicities condensed to all atoms of the molecule:

$$N = \Sigma N_k \quad (13)$$

From the above definition of the global nucleophilicity, it is possible to define the local nucleophilicity condensed to an atom k through the nucleophilic Fukui function, f^{-}_{k} [31].

$$N_k = N f_k \quad (14)$$

DFT provided a quantitative measure for a qualitative concept that was so successfully used in a description of Lewis acids and bases [32]. Parr and Pearson also derived simple expressions for the amount of charge transfer ΔN and energy change ΔE which accompany the formation of A:B complex from acid A and base B. These expressions are:

$$\Delta E = -(\chi_A - \chi_B)^2 / 4(\eta_A + \eta_B) \quad (15)$$

$$\Delta N = (\chi_A - \chi_B) / 2(\eta_A + \eta_B) \quad (16)$$

3. Materials and Methods

All calculations were performed using the Gaussian 03W series of program [33]. The geometry optimization of the free carbohydrates $L_{1\text{-}3}$ (Fig. 1) was optimized by the density functional theory DFT [34] with the Becke's three parameter exchange functional and the Lee Yang Parr correlation functional (B3LYP) [35]. The calculations were based on 6-31G(d) basis set. Various reactivity and selectivity descriptors such as chemical hardness, chemical potential, nucleophicity, and electrophilicity and the appropriate local quantities employing NPA (natural population analysis) [36, 37] scheme are calculated. The significance of interaction has been evaluated by lowering of energy and transfer charge, by solving the Eqs. (15) and (16), respectively.

4. Results and Discussion

4.1 Frontier Molecular Orbital Energies

The frontier molecular orbital such as HOMO and LUMO of the chemical species are very important in defining organic compounds reactivity [38, 39], transition of electron is due to interaction between HOMO and LUMO of reacting species [40]. The 3D of the frontier orbitals HOMO and LUMO for three ligands are shown in Fig. 2. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [41]. HOMO-LUMO gap is an important stability index, a molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [42].

The high stability in turn indicates low chemical reactivity and large band gap. In other words, the smaller band gap between HOMO and LUMO, which indicates a less stability of the compound, the easier the electron transition and lesser the stability of the compound will be. The band gaps of molecules vary from -0.2948 to -0.3037 a.u with the level of calculation and also with the size of the molecule. The ligand L_3 is the most stable and L_1 is the least stable reflected from the band gap values.

4.2 Fukui Indices

There is a general consensus by several authors that the more negatively charged a heteroatom, the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [43]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [44]. Hence the greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.

The analysis of the local nucleophilicity N_k and local electrophilicity indices and Fukui function values f^-_k, f^+_k given in Table 4, show that the oxygen numbering atom indicate the highest value of the local nucleophilicity N_k for each sites attack privileged of ligand are characterized by indices and Fukui function values f^-_k. (Table 4).

4.3 Molecular Electrostatic Potential

The MEP (molecular electrostatic potential) is related to the electronic density and a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions (Fig. 3), whereas electrophilic reactivity has been presented by negative (red) regions, nucleophilic reactivity has been shown by the positive (blue) regions of MEP. As seen from the Fig. 3, the red region has been localized on the vicinity of oxygen atoms. On the other hand, nucleophilic reactivity of the molecule has been localized on the hydrogen atoms. In this respect, the compound is useful to both bond metallically and the blue region that does not correspond to the interact intermoleculary. This result has also been supported by the evidences of charge analyses part.

4.4 Charge Transfer ΔN and Energy Lowering ΔE

The values of ΔN and ΔE for interaction of donors (ligands) with acceptor ($CuCl_2$, $ZnCl_2$, $SnCl_2$) have been evaluated and reported in Table 5.

Metal bond strength between interaction of acceptor (metal(II) halides) and donor (ligand) increases as the charge transfer (ΔN) increases [45]. The values of charge transfer indicate that the least stable complex formation is between L_1 and $CuCl_2$ as the value of charge transfer is lowest. Bond strength of donors with $CuCl_2$ based on the values of ΔN is in the following order: $L_1 > L_2 > L_3$. It is the same sequence of stability of metal-ligand bond for ligands (L_1, L_2, L_3) with $ZnCl_2$ and with $SnCl_2$.

Metal bond strength between interaction of acceptor (metal(II) halides) and donor (ligand) increases as the energy lowering (ΔE) decreases [46]. Strongest bond strength has been observed between L_3 and $CuCl_2$ in which case the value of ΔE is the lowest (-0.5632 eV). Bond strength of donors with $CuCl_2$ based on the values of ΔE is in the following order: $L_3 > L_2 > L_1$. It is the same sequence of stability of metal-ligand bond for ligands (L_1, L_2, L_3) with $ZnCl_2$ and with $SnCl_2$.

A higher value of electronegativity is indicative of a better acceptor character (11). The χ value indicates that the acceptor strength is in the order: $CuCl_2 > SnCl_2 > ZnCl_2$ (0.2877 > 0.2658 > 0.2181, respectively).

It is clear that both ΔE and ΔN provide the same sequence of stability of metal-ligand bond. These results are in total agreement with the experimental results [47].

Table 3 HOMO and LUMO energies, chemical potential (*μ*), potential ionization (*I*), electron affinities (*A*), global nucleophilicity (*N*) and energy gap.

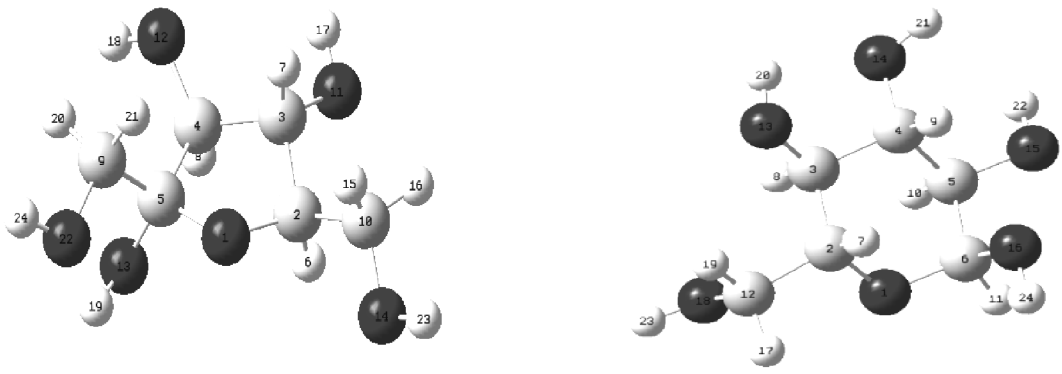
Ligands	HOMO	LUMO	μ	I	A	N	Energy gap
L_1	-0.25170	0.05208	-0.09981	0.25170	-0.05208	2.641974	-0.30378
L_2	-0.24862	0.04622	-0.10120	0.24862	-0.04622	2.725785	-0.29484
L_3	-0.25219	0.04359	-0.10430	0.25219	-0.04359	2.628640	-0.29578

Table 4 Fukui indices, local nucleophilicity N_k and local electrophilicity W^+.

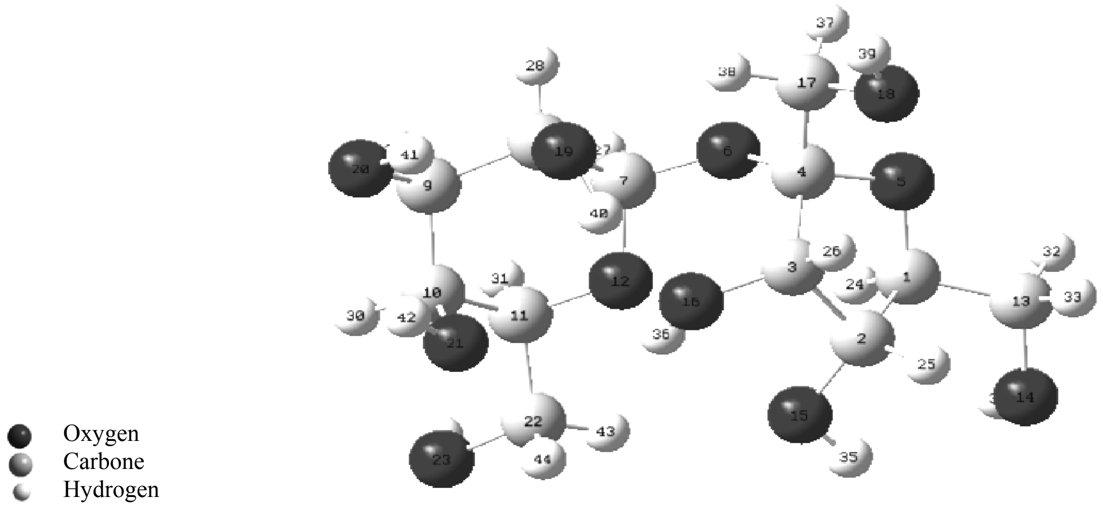
Ligand		f^{-}_k	f^{+}_k	W^+	N_k
L_1	O_{14}	0.51584	-0.29612	-0.01219268	1.36283599
	O_1	0.52457	-0.37823	-0.01557354	1.38590043
L_2	O_{15}	-0.38047	0.57252	-0.01563119	1.56056698
	O_{13}	-0.38467	0.54516	-0.01580374	1.48598948
L_3	O_{19}	-0.37860	0.47339	-0.01657456	1.24437215
	O_{18}	-0.38372	0.52612	-0.01679871	1.38298037

Table 5 The absolute hardness and electronegativity of acid (A), base (B), ΔN and ΔE.

Acid	Base	η_A	η_B	χ_A	χ_B	ΔN	ΔE
$CuCl_2$	L_1	0.0653	0.3035	0.2877	0.1197	0.2278	-0.5197
$ZnCl_2$	L_1	0.2115	0.3035	0.2181	0.1197	0.0955	-0.1278
$SnCl_2$	L_1	0.1107	0.3035	0.2658	0.1197	0.1763	-0.3483
$CuCl_2$	L_2	0.0653	0.3003	0.2877	0.1176	0.2326	-0.5360
$ZnCl_2$	L_2	0.2115	0.3003	0.2181	0.1176	0.0981	-0.1333
$SnCl_2$	L_2	0.1107	0.3003	0.2658	0.1176	0.1802	-0.3619
$CuCl_2$	L_3	0.0653	0.2883	0.2877	0.1163	0.4849	-0.5632
$ZnCl_2$	L_3	0.2118	0.2883	0.2186	0.1163	0.1018	-0.1415
$SnCl_2$	L_3	0.1107	0.2883	0.2658	0.1163	0.1873	-0.3809



L_1: fructose L_2: glucose



L_3 : sucrose

Fig. 1 Optimized structures of ligands $L_{1\text{-}3}$ calculated by B3LYP/6-31G(d) with atom numbering scheme.

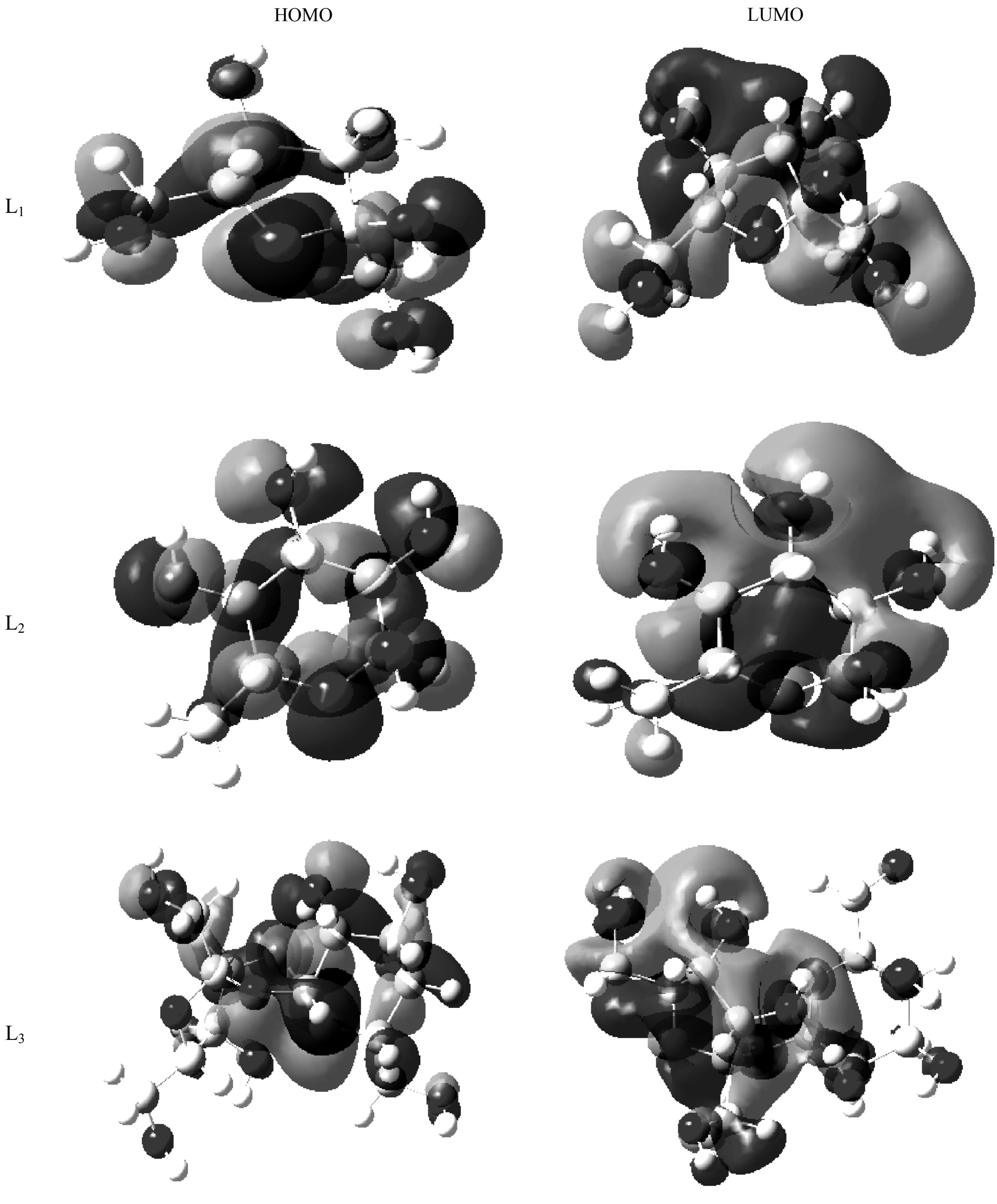


Fig. 2 The HOMO and LUMO molecular orbitals of $L_{1\text{-}3}$.

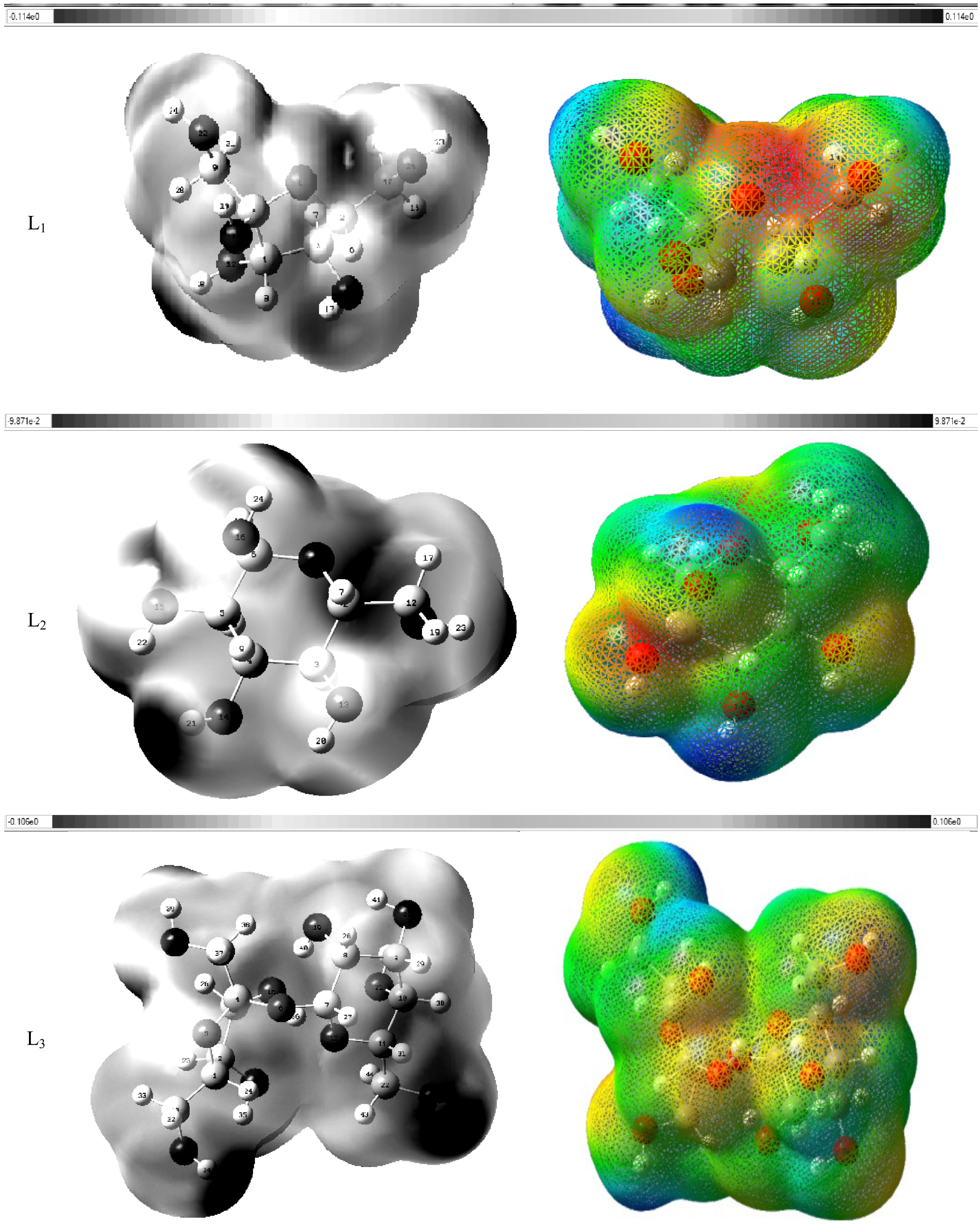


Fig. 3 **Molecular electrostatic potential of $L_{1\text{-}3}$.**

5. Conclusions

The aim of this work is to establish a comparison between the interaction of carbohydrates and metal ions. These are released from dental amalgam composing. For this, authors conducted a theoretical study by DFT to determine preferred sites attack using local indices nucleophilicity through Fukui indices. Moreover, the determination of ΔN and ΔE allowed the authors to establish a classification of stability, so the values of charge transfer (ΔN) and lowering of energy (ΔE) also indicate the same sequence of the stability of complexes formed by the donors (carbohydrates) with the acceptors (metal(II) halides), as a result, sucrose is more stable than glucose and fructose. However, the high value of energy gap (-0.29578) showed that sucrose is the most stable ligand. On the other hand, the sequence of high stability for metal halides is in following order: $CuCl_2$ > $SnCl_2$ > $ZnCl_2$.

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