Abstract
The topological features of the Triosmium cluster \([\text{Os}_3(\text{CO})_9(\mu-\eta^2-\text{C}_7\text{H}_3(2-\text{CH}_3)\text{NS})(\mu-\text{CH}_2)\text{CH}_3]\), containing carbonyl and 2-methylbenzothiazolide ligands, has been examined using density functional theory (DFT) and QTAIM-based "Quantum Theory Atoms in Molecules". The topological parameters of the electron density in the cluster have been calculated. The QTAIM analysis of the topological features demonstrated that the core part Os3C1 in the cluster is significantly absence a bond critical point and its bond path between Os1-Os3. Whereas, the analysis Os1-Os2 and Os2-Os3 interactions revealed the occurrence of bond paths and bond critical points between these atoms. A multicentre 4c–5e interaction for the Os3C1 core has been proposed. The topological parameters calculation show that the interactions in the bridging 2-methylbenzothiazolide Ligand are a typical for shared shell with the existence of some double-bond character.

Keywords:- DFT calculations, QTAIM, Metal–metal bonds, Organometallic complexes, Topological analysis.

Introduction
Electron-deficient benzoheterocyclic triosmium clusters has been of special interest in the area of recent organometallic chemistry[1].The structures and reactivity of electron-deficient compound and their product are very sensitive on the nature of the substituent group of the heterocyclic ring[2-5].Chemistry of electron-deficient triosmium clusters has been widely studied in recent years because of their high reactive comparative to their electron precise counterparts[2,6,7]. Quantum theory of atoms in molecules(QTAIM) are an important methodology to describe the bonding in the organometallic system[8]. The core of this methodology is defining and characterizing a chemical bond through bond critical point (bcp) along of an atomic interaction line in an equilibrium geometry(bond bath)[9-11]. At this bond critical point, computing the topological parameters, such as electron density ($\rho$), the Laplacian ($\nabla^2 \rho$) and the electronic energy density ($H_b$) give us a useful information about the bonding situation in chemical compounds[12-16]. The aim of our study is to exploring of the M–M and M–ligand interactions properties in "[\text{Os}_3(\text{CO})_9(\mu-\eta^2\text{C}_7\text{H}_3(2-\text{CH}_3)\text{NS})(\mu-\text{CH}_2)\text{CH}_3]\"[17] as shown in Figure 1. Our results might be important due to an interesting comparisons between the different topological features of the
interaction between Os-Os metals, the influence of bridging ligand (μ²-CH₂ and 2-methylbenzothiazolide) in the Os-Os interactions, and comparison several topological properties with the other interaction such Os-N and Os-C bonds in the cluster. Additionally, the interactions in the bridging 2-methylbenzothiazolide ligand were discussed in detail.

Theoretical Methods

The structure of Triosmium cluster in the gas phase was fully optimized using Density functional theory (DFT). Frequency calculations confirmed it as minima on the potential energy surface. By using Gaussian 09 program[18], a PBE1PBE[19] functional was used, associated with all-electron 6-31G(d,p) for C, H, N, S and O atoms and SDD[20] effective core potential (ECP) for Os basis sets. The topological parameters were computed, at PBE1PBE /WTBS[23] for Os /6-31G (d, p)[21] for other atoms, using AIM2000 program package[22].

Results and Discussion

The geometry structure of triosmium cluster species under study is optimized and a representative structure is shown in Figure 1-b. Using AIM program, the molecular graph of the cluster is illustrated in Figure 2, where addressed a bond paths and bond and ring critical points. Inspection on this molecular graph finds that: (i) The bond critical point with its bond path between Os₁-Os₃ is not found which is an indicator of absence a chemical bond (ii) The bond paths with a bond critical points corresponding to Os₁-Os₂ and Os₂-Os₃ bonds are exist. (iii) A set of bond paths and bond critical points within Os-C, C-O, C-S, C-N and C-C bonds and four ring critical points related Os₁-Os₂-Os₃-C₁, Os₂-C₃-C₄-N₁-Os₃, C₃-C₄-C₅-C₆-C₇-C₈, C₇-C₈-N₁-C₉-S₁ rings were found.

Gradient trajectory maps of the triosmium core plane Os₁-Os₂-Os₃-C₁ are plotted in Figure 3. Inspecting the Os₁-Os₂ and Os₂-Os₃ bonds reveals the existence bond paths, bond critical points, and atomic basins. Differently, no bond critical point or bond path is observed for Os₁-Os₃. Additionally, in the plot, one bridged Carbon C₁ with bond critical points and bond paths are visible.

Additionally, the map of 2-methylbenzothiazolide ligand display a six-membered cyclic with one ring critical point and five-membered ring having one ring critical point and one C=C, two N=C, and two S-C bond critical points as seen in Figure 4. Also, in this figure, the bond paths and bond critical points between the interaction of Os₃ and Os₂ with N₁ and C₃ respectively, are observed.
methylbenzothiazolide ligand led to lowering the electron density and the laplacian values (positive values) and then lowering of the covalent contribution to both Os1-Os2 and Os2-Os3 bonds. Regarding to the bridged Os1 and Os3 atoms, a key point is the nonexistence of a bond path with its bond critical point. Thus pointing out that there is no localized electron concentration between these two Osmium atoms led to conclude that the strong interactions of bridging C ligand destroy the topological Os1–Os3 bond.

From the literature, the bond critical points with its bond path have been found between unsupported M-M bond, for example Co-Co and Mn-Mn in "Co2(CO)8(Asph)2,"[32] and Mn2(CO)10[33] respectively. Conversely, a bond path and bond critical point have also been found for the interaction a transition metal with strong bridging ligand, for instance, Mo-Mo in "[MO3(μ2-S)(μ2-S)Cl2(φH)3]"[34]. The laplacian map for the core Os3(C1), as seen in Figure5, show the VSCCs of bridging carbon are obviously shifted across a midpoint of the Os-Os interaction.

We also calculated the delocalization indices for the interactions in the Os3C (1) core, Table 2. The calculated delocalization indices values for the Os1-Os2 and Os2-Os3 bonds (0.328 and 0.471, respectively) are comparable to the Ru-Ru bond (0.458 on average) in "[Ru3(μ-H)2(μ2-MelImCH)(CO)8]"[35]. Os-Os bonds (within the range 0.350 -0.461) in "[Os8(μ2-H)(μ-C)(CO)12], [Os8(μ2-H)(μ-OH)(CO)10], and Os8(μ2-H)(CO)10]"[31] and Fe-Fe bond (0.398 on average) in [Fe6(μ-H)(μ-COMe)(CO)10][36]. Furthermore, the obtained values are correlated with computed values for other M-M interactions[37]. By reasons of nonbonding interaction, small Os1...Os3 delocalization indices was obtained (0.277) Table 2. This calculated value was consistent with the hydride-bridged metal...metal non-bonding interactions Ru...Ru (within range 0.169-0.246) in "[Ru3(μ-H)2(μ2-MelImCH)(CO)8]"[35], Os...Os (0.177) in Os8(μ-H)(μ-Cl)(CO)10][31], and Fe...Fe (0.208) in Fe6(μ-H)(μ-COMe)(CO)10][38] and compare well to those found for other organometallic compounds[38,39,40]. From other side, the nonbonding Os1...Os3 delocalization indices is correlated to other studies reported for unbridged M-M interaction ex. Co-Co interaction in [Co2(CO)8] (0.460)[41]. As the bridged Os1...Os3 interaction, the delocalization index value is smaller than that of unbridged Os-Os interaction. Regarding to Os-C1 bonds, the topological properties will discussed in next section. When we sum up the delocalization indexes δ(A–B) for bonding and nonbonding interactions in the core, shown in Table. 3, are equal to the value of 2.581. Therefore, the interaction

**Figure 4:** Gradient trajectories map in the plane through 2-methylbenzothiazolide ligand in complex.

Within the conceptual framework of the QTAIM Theory, the Laplacian ($\nabla^2 \rho_b$) is an indicator for classification of the interactions between atoms in two types: shared (covalent bond) and closed-shell interactions (ionic bond). For the former interactions, the electronic charge is concentrated towards the line of interaction running between two nuclei ($\nabla^2 \rho_b < 0$), whereas for later interactions electronic charge is depleted toward each of the interacting nuclei ($\nabla^2 \rho_b > 0$). On the other hand, the total electronic energy densities ($H_b = G_b + V_b$) kinetic energy densities ($V_b$), potential energy [dewhere[25-27]. Consequently, $H_b < 0$ with $\nabla^2 \rho_b < 0$ for covalent bonds $H_b > 0$ with $\nabla^2 \rho_b > 0$ for ionic bonds and $H_r < 0$ with $\nabla^2 \rho_r > 0$ for transit-closed interaction[28-30].

The calculated of local properties of electron density at the bond critical points for the triosmium cluster are given in Table 1.

For the core part Os3C(1), as seen from Table 1, the BCP Laplacian of the Os1-Os2 and Os2-Os3 bonds are small positive values (0.037 and 0.093, respectively). Additionally, the small BCP electron density values (0.032 and 0.049, respectively) with the small negative values of $H_b$ (-0.004 and -0.009, respectively) are corresponding to a metal-metal open-shell interaction. Comparison of the BCP electron density and its laplacian for Os1-Os2 and Os2-Os3 bonds with the electron density and laplacian at the unbridged Os-Os bonds for the compounds "[Os3(CO)12], [Os3(μ2-H)2(CO)10], [Os3(μ-H)(μ-OH)(CO)10], and [Os3(μ-H)(μ-Cl)(CO)10][31]." Showed that the strong interaction between Os1 and Os2 metal atoms with 2-

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in the core part Os3C(1) of the cluster is essentially explained by 4c–5e.

Table 1. The local properties of electron density at critical points of the bonds of Cluster.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\rho_{\text{r}}$(eÅ)</th>
<th>$\nabla^2\rho_{\text{r}}$(eÅ)</th>
<th>$G_{\text{r}}$(he)</th>
<th>$H_{\text{r}}$(he)</th>
<th>$V_{\text{r}}$(he)</th>
<th>$\varepsilon_{\text{r}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os1-Os2</td>
<td>0.032</td>
<td>0.037</td>
<td>0.013</td>
<td>-0.004</td>
<td>-0.018</td>
<td>0.652</td>
</tr>
<tr>
<td>Os2-Os3</td>
<td>0.049</td>
<td>0.093</td>
<td>0.032</td>
<td>-0.009</td>
<td>-0.042</td>
<td>0.039</td>
</tr>
<tr>
<td>Os1-C1</td>
<td>0.079</td>
<td>0.132</td>
<td>0.055</td>
<td>-0.022</td>
<td>-0.077</td>
<td>0.105</td>
</tr>
<tr>
<td>Os3-C1</td>
<td>0.129</td>
<td>0.243</td>
<td>0.113</td>
<td>-0.052</td>
<td>-0.165</td>
<td>0.037</td>
</tr>
<tr>
<td>Os-C(CO)*</td>
<td>0.148</td>
<td>0.483</td>
<td>0.184</td>
<td>-0.063</td>
<td>-0.247</td>
<td>0.055</td>
</tr>
<tr>
<td>Os2-C3</td>
<td>0.108</td>
<td>0.209</td>
<td>0.089</td>
<td>-0.037</td>
<td>-0.126</td>
<td>0.042</td>
</tr>
<tr>
<td>Os3-N1</td>
<td>0.074</td>
<td>0.361</td>
<td>0.099</td>
<td>-0.008</td>
<td>-0.108</td>
<td>0.085</td>
</tr>
<tr>
<td>N1-C8</td>
<td>0.293</td>
<td>-0.796</td>
<td>0.190</td>
<td>-0.389</td>
<td>-0.579</td>
<td>0.108</td>
</tr>
<tr>
<td>N1-C9</td>
<td>0.353</td>
<td>-0.889</td>
<td>0.308</td>
<td>-0.531</td>
<td>-0.839</td>
<td>0.231</td>
</tr>
<tr>
<td>S1-C7</td>
<td>0.208</td>
<td>-0.397</td>
<td>0.063</td>
<td>-0.162</td>
<td>-0.226</td>
<td>0.187</td>
</tr>
<tr>
<td>S1-C9</td>
<td>0.210</td>
<td>-0.404</td>
<td>0.067</td>
<td>-0.168</td>
<td>-0.236</td>
<td>0.261</td>
</tr>
<tr>
<td>C9-C10</td>
<td>0.255</td>
<td>-0.618</td>
<td>0.067</td>
<td>-0.222</td>
<td>-0.289</td>
<td>0.037</td>
</tr>
<tr>
<td>C-O*</td>
<td>0.460</td>
<td>0.521</td>
<td>0.930</td>
<td>-0.8</td>
<td>-1.731</td>
<td>0.002</td>
</tr>
</tbody>
</table>

* Average

Figure 5. shows the plots of the Laplacian distribution in the core(Os3C(1)) plane.

Table 2. Delocalization indexes for selected interactions.

<table>
<thead>
<tr>
<th>Atom (A, B)</th>
<th>$\delta$(A, B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os2-Os2</td>
<td>0.328</td>
</tr>
<tr>
<td>Os1-Os3</td>
<td>0.277</td>
</tr>
<tr>
<td>Os2-Os3</td>
<td>0.471</td>
</tr>
<tr>
<td>Os1-C1</td>
<td>0.599</td>
</tr>
<tr>
<td>Os3-C1</td>
<td>0.029</td>
</tr>
<tr>
<td>Os2-C2</td>
<td>0.877</td>
</tr>
<tr>
<td>Os2-N1</td>
<td>0.012</td>
</tr>
<tr>
<td>Os2-N2</td>
<td>0.015</td>
</tr>
<tr>
<td>Os3-N1</td>
<td>0.418</td>
</tr>
</tbody>
</table>

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For Os-C\textsubscript{1} bonds, given in Tables 1, the computed BCP electron density, Laplacian and electronic energy density H properties for both Os-C\textsubscript{1} bonds showed that both bonding have lower \( \rho_b \) (0.079 and 0.129 Å\textsuperscript{-3}), positive \( \nabla^2 \rho_b \) (0.132 and 0.243 Å\textsuperscript{-3}) and negative \( H_b \) (-0.022 and -0.052he\textsuperscript{-1}) values which is typical for open-shell coordination bonding. The results obtained were in line with the computed data for bridging ligands such as CO, H and CH\textsubscript{3}. In comparison with the Os-C(co) bonds, the BCP topological values of Os-C(co) bonds are higher than the Os-C\textsubscript{1} bonds might be explained by their higher polarity of CO group. Regarding to the bonds between Os atoms with the 2-methylbenzothiazolide ligand the BCP Laplacians of all bonds within the methylbenzothiazolide ligand atoms are listed in the bonding interaction within the bridging 2-methylbenzothiazolide ligand in the cluster. As expected for polar bonds, excepting C-C bonds, the BCPs are arranged in the middle of the bond path, the BCPs on the C-N and C-S bonds are displaced to the less electronegative atom. The BCP characteristics of the bonding interaction within the bridging 2-methylbenzothiazolide ligand atoms are listed in Tables 1. The BCP Laplacians of all bonds within the bridging 2-methylbenzothiazolide ligand are negative as expected, for sharing coordination bonding (covalent bonds). Interestingly, The BCP ellipticity values of C-S bonds are higher than C-N indicate that the C-S bonds have a \( \pi \)-character more than C-N bonds.

Figure 6. Shows the plots of the Laplacian distribution of the Os-Os-Ni plane

The nature of the interactions of the 2-methylbenzothiazolide ligand bonds are shown in the map of the Laplacian (Figure 7). The electron cloud in the VSCCs of C\textsubscript{1} atom is polarised to the Os\textsubscript{2}, whereas the N\textsubscript{i} atom polarised to the Os\textsubscript{3}.

Conclusion

A topological properties of the electron density distribution for triosmium cluster \([\text{Os}_3(\text{CO})_9(\mu-\eta^2-C_2H_2(2-CH_3)NS)(\mu-CH_2CH_3)]\) have been calculated and interpreted by QTAIM theory. The topological properties of the bonding interaction was analyzed and compared with the previous studies. The QTAIM analyses of the Os3C(1) core part reveal, on one hand, existence the bond paths and bond critical points in the Os\textsubscript{2}-Os\textsubscript{3} and Os\textsubscript{2}-Os\textsubscript{3} interactions. On the other hand, neither bond path nor bond critical point between Os\textsubscript{1}-Os\textsubscript{3} interaction is observed, although for these non-bonding interactions, a non-negligible delocalization index has been computed. Consequently, the interaction in the core part can be described as multiple 4\textendash{}5\textendash{}e bonding interaction. Inspection of the topological features of the bonding interactions in the bridging 2-methylbenzothiazolide ligand finds that all these bonds are typical for shared shell with the presence of some double-bond character.

Acknowledgement

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Reference