

QTAIM analysis for Metal - Metal and Metal- Non-metal Bonds in Tri-Osmium cluster

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Abstract:

Electron density of the interaction of the compound's chemical bonding has been computed using topological analysis. The findings suggest that **Os-Os**, **Os-N**, and **Os-H** bonds have experienced bond critical points (BCP) with corresponding bonds paths (BP). The presence of **N-C** bridging atoms is significantly impacted by electron density of **Os₂-Os₃** bond distribution therefore no critical point found and bond path. So, due to their positive electron density $\rho(\mathbf{b})$, negative laplacian $\nabla^2(\mathbf{b})$, and positive the total energy density $\mathbf{H}(\mathbf{b})$ values, the **Os-NC**, **Os-H**, and **Os-CO** bonds all have transit closed-shell topological properties.

Keywords: - QTAIM Theory, DFT calculations, Delocalization, Osmium cluster, Laplacian,

Introduction:

Triosmium complexes with reduced electron density has received a lot of attention^{1,2}. Additionally, these clusters have extensively employed to produce stable heterocyclic compound, allowing for synthesizing of novel and important chemicals. that are difficult for getting using traditional organic techniques³.

Earlier Introductory transition metals, which are abundant on Earth, usually exhibit unique structures and orthogonal reactivity when compared to late transition metals, are excellent alternatives for the creation and application of new catalytic processes⁴. However, complexes in high-valent forms have traditionally been dominated the organometallic chemistry of early transition metals because of their electropositive, oxophilic structure^{5,6}.

The topographic analysis of electron density within the structure of the Quantum Theory of Atoms in Molecules (QTAIM) has progressed into an effective technique for studying chemical bonding.^{7,8} Studies on light-atom systems (transition metal 1-3 periodic table) made it possible to establish important connections between the charged particle charge's structural features, bonding styles, and Laplacian^{9,10}. Such relationships cannot, however, be directly applied to transition metal atom complexes because these molecules show a distinctive and much smaller range of topological indices. Specifically, the QTAIM approach typically only detects M-M bond pathways in the absence of bridging bonds, compounds with bonds between transition-metal atoms^{11, 12,13}.

Few studies on the electron density of chemical structures containing three or more transition metal atoms bound to other transition metal atoms have been reported^{14,15}. More QTAIM research on this type of compounds are thus needed to better understand the interactions between their metal atoms^{16, 17}.

This research provide a important and interesting comparability between the various topological facets of the interaction of Os-Os metals. Os-Os interactions, and analyses of several topological qualities with other bonds in this compound, such as Os-N and Os-H interactions.

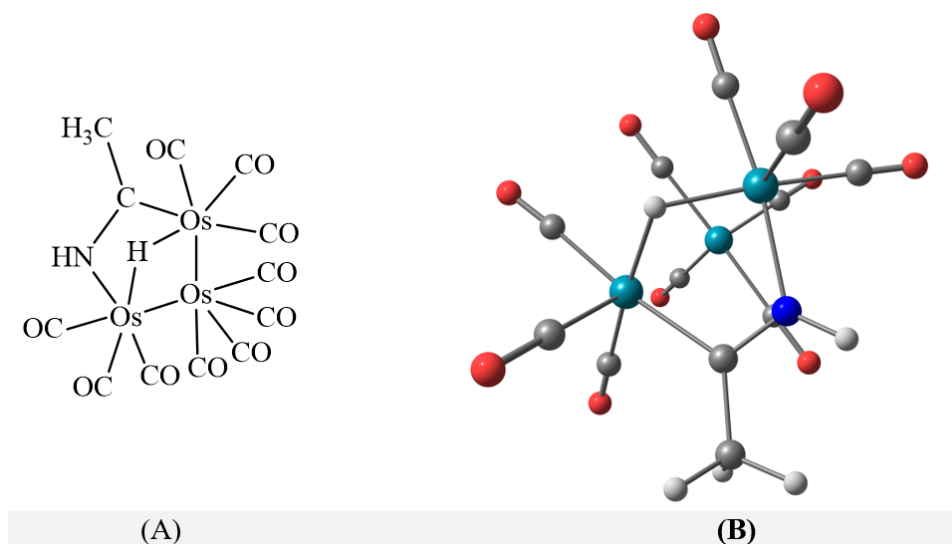


Figure 1: (A) Chemical Structure and (B) Enhancement for Morphology of “[Os₃(CO)₁₀(μ-C₂H₃-NH)(μ-H)]”.

Theoretical Methods

By utilizing one of computing theories (DFT)¹⁸, the triosmium cluster's form in the gas phase was optimized. It was identified as minimum on the surface of energy potential. A PBE1PBE¹⁹ functionality was applied using the Gaussian 09 program^{20, 21}, along while 6-31G(d, p) for C, N, H, with O atoms, and SDD²² efficient core potential (ECP) for Os basis sets. Using AIM2000²³ software package, the topological characters were calculated at PBE1PBE /WTBS²⁴ for Os and (6-31G^{**}) for the others.

Results and discussions:

The triosmium geometry cluster under investigation were optimizing, as **Figure 1** depicts a model system. The AIM software was applied to examine bond paths, bond and ring critical points in the clusters connected graph, as depicted in **Figure 2**. Analysis of this connected graph reveals. Also, (i) when BCP with the bond path between Os₂-Os₃ was not appear, indicating the absence of a chemical bonds (ii) Bond pathways between the Os1-Os2 and Os1-Os3 bonds were found using bond critical points. (iii) Bond critical points and bond pathways were found between

Os-C, Os-CO, C-O, C-N, and C-C bonds, as well as five ring critical points associated with $Os_1-Os_2-H_1-Os_3$, $Os_1-Os_2-C_8-N_1-Os_3$ rings.

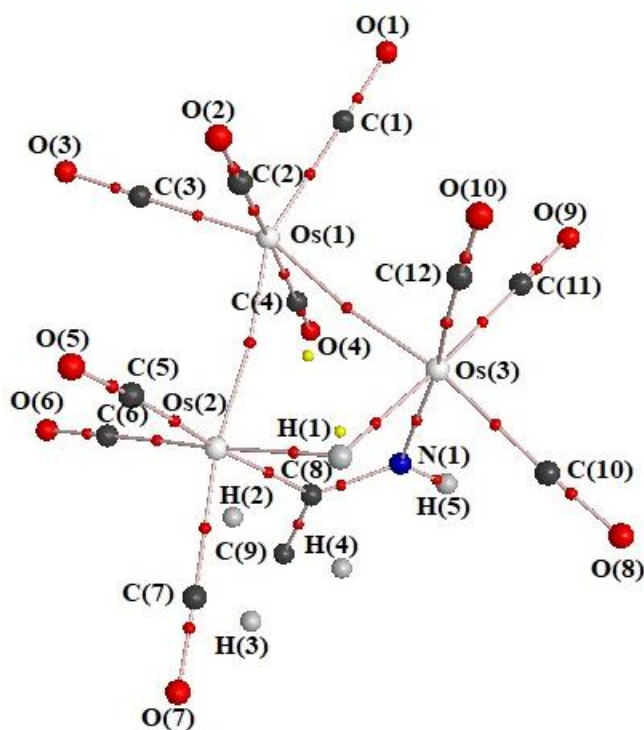


Figure 2: Depicts the cluster's molecular diagram of bond critical points (red circles) as well as the ring critical points (yellow circles).

Figure 3 depicts gradient trajectory images of the Tri-Osmium central plane $Os_1-Os_2-Os_3-H_1$. The presence of bond lines, bond critical points, and atomic basins can be seen by analyzing the Os_1-Os_2 and Os_1-Os_3 bonds. In Os_2-Os_3 no bond critical point, as well as bond line, is detected. In addition, one bridged Carbon H_1 with BCPs is apparent in the plot.

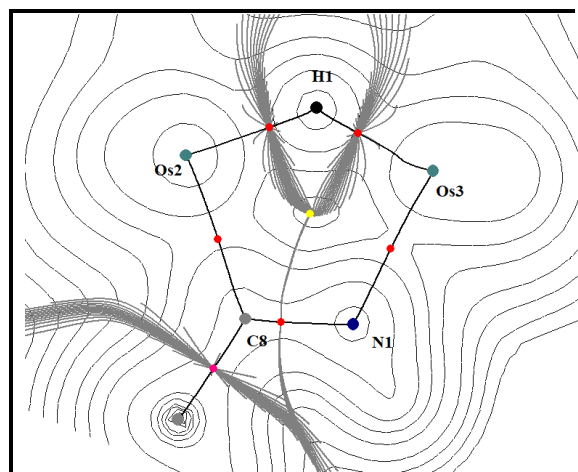


Figure: Diagram of gradient trajectories in the plane $Os_1-Os_2-Os_3-H_1$ cross compound.

The core's image illustrates a five-membered cyclic with a single ring critical point. This ring forming from the essential sites for the Os-C, N-Os, two Os-H, and N-C bonds. In furthermore, the BP and BCPs between the interactions of Os_1-Os_2 , Os_1-Os_3 , Os_3-H , Os_3-N , Os_2-H , and Os_2-C are illustrated in figure 4. While Os_2-Os_3 were not detected.

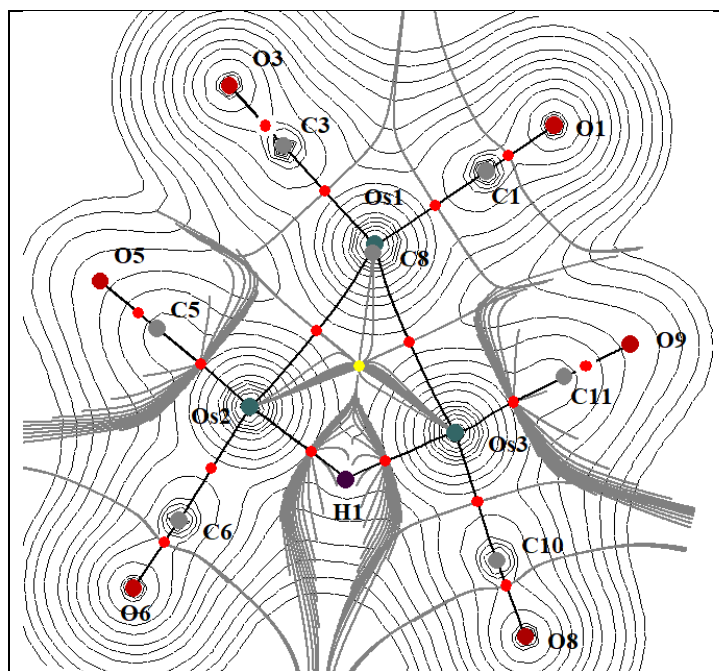


Figure 4: Diagram of gradient trajectories in the plane $Os_2-C_8-Os_3-H_1$ cross compound.

Referring to our investigation of the electron density for the cluster under analysis **Table 1**, the metal-metal interaction was classed as transit closed-shell interactions

between covalent and ionic bonds based on the topological and energetic local features of the data²⁵. These findings are consistent with previous research on Os-CO molecules²⁶.

The 'metallic' bonds exhibit structural features that are similar to covalent and ionic bonding¹⁵. This is obvious in the positive Laplacian $\nabla^2\rho_{rb}(e\text{\AA}^{-5})$ values, and the low $\rho_{rb}(e\text{\AA}^{-3})$ values are consistent with an ionic bond, but the negative $V_{rb}(e\text{e}^{-1})$ is consistent with a covalent bond.

Table 1:- The computed topological properties at the bonds critical points (electron density ρ_{rb}), Laplacian of the electron densities ($\nabla^2\rho$), Kinetic energy densities (G), Potential energy densities (V_{rb}), Total energy densities (H_{rb}), Ellipticities (ϵ_b) and Delocalization $\delta(A-B)$ for the Cluster.

| Bonds | $\rho_{rb}(e\text{\AA}^{-3})$ | $\nabla^2\rho_{rb}(e\text{\AA}^{-5})$ | $G_{rb}(e\text{e}^{-1})$ | $H_{rb}(e\text{e}^{-1})$ | $V_{rb}(e\text{e}^{-1})$ | ϵ_{rb} | $\delta(A-B)$ |
|----------------|-------------------------------|---------------------------------------|--------------------------|--------------------------|--------------------------|-----------------|---------------|
| Os (1)- Os (2) | 0.032 | -0.128 | 0.017 | 0.004 | -0.004 | 0.060 | 0.461 |
| Os (1)- Os (3) | 0.033 | -0.132 | 0.017 | 0.004 | -0.004 | 0.026 | 0.462 |
| Os (2)-H(1) | 0.076 | -0.306 | 0.073 | 0.019 | -0.018 | 0.109 | 0.448 |
| Os (2)-C(8) | 0.110 | -0.441 | 0.117 | 0.034 | -0.035 | 0.109 | 0.432 |
| Os (3)-H(1) | 0.078 | -0.313 | 0.074 | 0.019 | -0.019 | 0.060 | 0.443 |
| Os(3)-N(1) | 0.087 | -0.352 | 0.122 | 0.008 | -0.008 | 0.104 | 0.506 |
| Os*-CO* | 0.152 | -0.609 | 0.195 | 0.062 | -0.064 | 0.018 | 1.055 |
| N(1)-C(8) | 0.367 | -1.47 | 0.523 | 0.635 | -0.635 | 0.017 | 0.506 |

*average

Table 1 illustrates that Os-Os, Os-H, and Os-C bonds have positive ED values. Furthermore, these bonds have positive Laplacian values. These findings for nonmetal atoms with negative $V(r)$ values go between pure covalent and ionic interactions and agree with the typical open-shell interaction. The estimated elliptics (ϵ_{rb}) for these bonds indicated that the Os-Os, Os-C, and Os-H bonds are negative, suggesting that the ellipticities (ϵ_{rb}) are growing.

-Electron density Laplacian in BCP ($\nabla^2\rho_b$)

The concept of laplacian topology is essential to molecular science. This has a connection with the small regions for electronic charge builds up or depletes.

Globular endpoints form an envelope all over an intensity or depletion region. This is referred to as valence shell charge concentration (VSCC). When one atom constitutes to the bond, the VSCC's globular symmetry is broke²⁷. As shown in **Fig. 5(A, B)**, the Laplacian diagram measured for planes that included the Os₂-Os₃-C₈-N₁ is very important in studying Os...Os bonds.

The Laplacian distribution between Os₂-Os₃ atoms does not have a bond path with critical points, which means that there are no bond formation electron pairs between these transition metal atoms.

All Os-CO connections have the same mechanism, that is the typical donor-acceptor interaction between both the atoms of a transition metal (Os) and a nonmetal (C). Each carbon atom has a VSCC that points directly at a VSCD for the Os atom, which is also referred to as (ligand-opposed charge concentration)²⁸.

Furthermore, because the calculated AIM ellipticities of the **Os-H**, **Os-C**, and **Os-N** interactions are greater than zero (positive values), they mimic linear bonds. The Laplacian map of the cluster core shows that the bridging Os-N valence shell charge densities (VSCC) are polarized in the straight path of the connection's center between Os and Os²⁹.

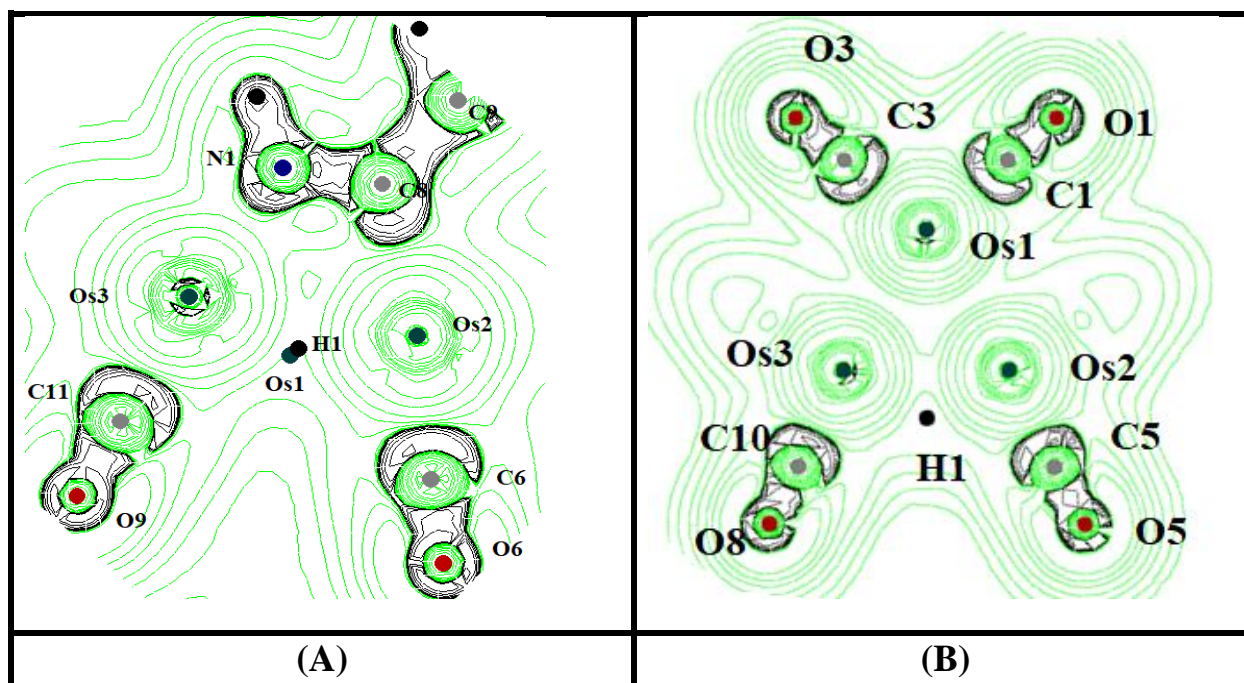


Figure 5: An illustration of the clusters in (A) $\text{Os}_2\text{-Os}_3\text{-C}_8\text{-N}_1$ (B) $\text{Os}_1\text{-Os}_2\text{-Os}_3$ and CO of the Laplacian electron density.

Delocalization Indices.

The bond order is the multitude of two electrons shared between two connected atoms. QTAIM provides a good study for bond order by unifying the interchange density once over each of the two atomic basins³⁰. One of the most effective methods for estimating The number of two electrons that are uniformly distributed between atoms A and B in a topographic property is expressed as $\delta(\text{A-B})$, which has been used primarily in theoretical research.

The value of $\delta(\text{Os...Os})$ with $\delta(\text{Os...H})$ and $\delta(\text{Os...N})$ bonds that computed for clustering the results consider the bonds a weak **M...M** interaction. **Table 1.** These values increase with the appearance of nonmetal (N, H) atoms in the molecule and are consistent with the values for **Os...Os** bonding interactions in several carbonyl compounds. For example, $[\text{Os}_3(\text{CO})_{10}]$ equals 0.350^{11} .

A delocalization index, $\delta(\text{Os-C})$ refers to first order for the bond by one pair electron shared between them, as illustrated in **table 1**. It is difficult to identify the pi-back donation from the Os to the CO binding site. due to the cylindrical symmetry of the density for the Os-CO bond path, which obscures any vestige of plans.^{31,32}.

Conclusions:

Topological characteristics of the electron density for $[\text{Os}_3(\text{CO})_{10}(-\text{C}_2\text{H}_3\text{-NH})(-\text{H})]$ compound utilizing atom quantum theory in compounds (QTAIMs) has computed.

These topological reveals important details of the **Os-Os**, **Os-H**, and **Os-N** interactions, as well as the compound's extra topological properties.

The core **Os₃H** and **Os₃NC** AIM analyses are the core **Os₃H** and **Os₃NC** However, no BCP and BP are observed between any pair of $\text{Os}_2\text{-Os}_3$ bonds; thus, has gained an important delocalization index.

Os_3H has a multicenter (4c-5e) interaction, whereas Os_3NC has a single center (5c-8e). The topological data of the Os-Os, Os-H, and Os-N bonds were analyzed. All of the bonds are typically transit closed-shell metal-metal interaction bonds.

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