



Theoretical study of Fe–Fe bonding in a Series of Iron Carbonyl clusters $[(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Mn}(\text{CO})_3]$, $[\text{Et}_4\text{N}][(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Fe}(\text{CO})_4]$ and $[\text{Et}_4\text{N}][\text{HAs}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-H})\}\{\text{Fe}(\text{CO})_4\}]$ by QTAIM Perspective

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THE bonding interactions such as Fe-Fe, Fe-H and Fe-CO, existing in the iron carbonyl clusters; $[(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Mn}(\text{CO})_3]$ (**1**), $[\text{Et}_4\text{N}][(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Fe}(\text{CO})_4]$ (**2**) and $[\text{Et}_4\text{N}][\text{HAs}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-H})\}\{\text{Fe}(\text{CO})_4\}]$ (**3**), have been studied using atoms in molecules (AIM) approach. Many topological parameters of the electron density for these clusters have been computed at bond critical points (bcp's). The conceptual framework of AIM theory indicates the absence of Fe-Fe direct bonding, since no bond critical point is found between Fe metals and therefore, no bond path connecting them in **1**, **2** and **3**. Also, from these results, a comparison was done for related but different interactions involving; different Fe...Fe interactions and bridged Fe-H bond versus other bridged Fe-ligand such as Fe-CO. An interaction of (Fe1-H1-Fe2-H2-Fe3) plan existing in each of cluster **1** and **2** is 5c-4e type. While in cluster **3**, an interaction core (Fe1-H1-Fe2) is 3c-2e. Finally, the existence of hydride bridging ligands has an efficient role to reduce the electron density delocalized between hydride bridged iron pairs oppositely with hydride unbridged ones.

Keywords: Iron Clusters, AIM2000, Topological properties, Delocalization Indices.

Introduction

The metal pnictides which composed of transition metals and group 15 elements, have been the object of scientific research, mainly due to the variety of physical and chemical properties observed among the high number of possible phases [1]. Additionally, some metal pnictide phases show good magnetic properties like magnetostrictive and magnetocaloric effects, while others are important catalysts in reactions of significant industries [2], the iron or iron/manganese clusters containing arsenic act as important single-source precursors for phases of metal pnictide [3, 4]. The Quantum Theory of Atoms in Molecules [5-7] is a widely insightful tool using the charge density analysis for different molecules. During the last years, under the perspective of the quantum theory AIM [7-10], the topological calculations of the electron density become widely used for studying the chemical bonding. More recently; there are significant number of researches about light atoms systems (periods 1-3) which give useful relations between

electron density properties and bonding modes, [9,11,12]. But, these relations are not easily extended to involve transition metal complexes, especially these containing multinuclear compounds for the interaction of M-M atoms [13-15].

There are just limited systematic researches on these types of interactions depending on QTAIM concepts [16-18]. These studies elucidated that a small electron density is shared in unsupported M-M bonds with bond order (≤ 1). However, it is possible for M-M bond path to be exist in the complexes when they don't include supporting ligands in their structure. Also, in order to focus on the M-M bonding fragments and their electron density topology, a lot of QTAIM studies are required for this purpose [19,20]. It is found by the QTAIM features some of an important topological characters for iron clusters (prepared by Schipper *et. al.* 2016)[3]; $[(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Mn}(\text{CO})_3]$ (**1**), $[\text{Et}_4\text{N}][(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Fe}(\text{CO})_4]$ (**2**) and $[\text{Et}_4\text{N}][\text{HAs}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-H})\}\{\text{Fe}(\text{CO})_4\}]$ (**3**) (Fig. 1).

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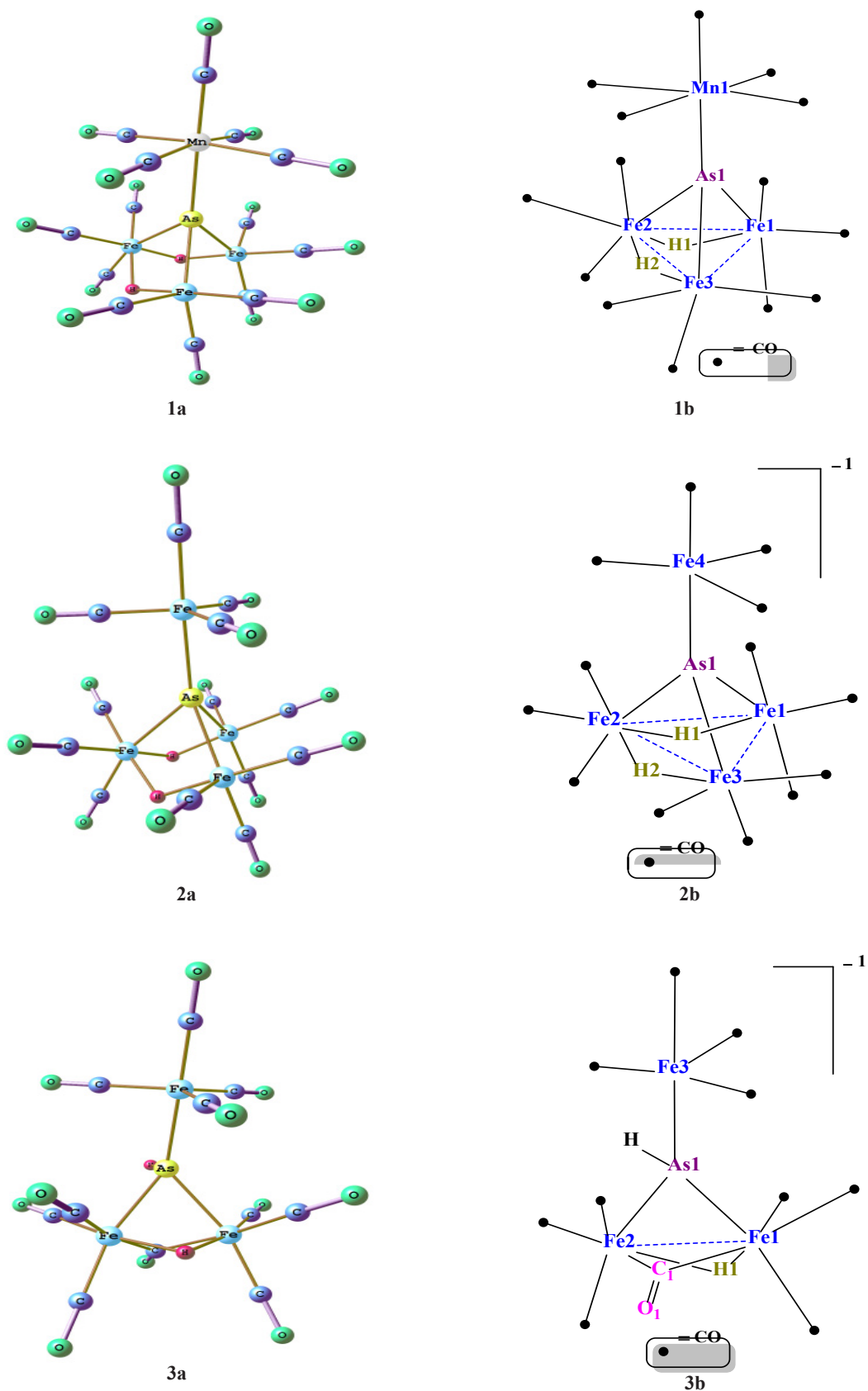


Fig.1. (a): X-ray structure, (b): Schematic structure of clusters: $[\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Mn}(\text{CO})_5]$ (1), $[\text{Et}_4\text{N}][\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Fe}(\text{CO})_4]$ (2), and $[\text{Et}_4\text{N}][\text{HAs}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-H})\}\{\text{Fe}(\text{CO})_4\}]$ (3)

These complexes [3] have been interested because there are no previous QTAIM studies about them hitherto reported and a comparison between topological properties is established. This comparison exhibits the features of different metal-metal bonds such as Fe-Fe bond order, H-bridged versus CO-bridged and ligand-unbridged Fe...Fe interactions, as well as Fe-CO.

Computational Details

Density functional theory (DFT) with nonrelativistic wave functions computations were applied with GAUSSIAN09 [21] packages to calculate the geometry optimization starting with the X-ray diffraction [3]. The PBE1PBE [22] functional has been used with the 6-31G (d, p) [16] as a basis set for H, C, N and O atoms in addition to the basis set LANL2DZ [11] which is based to calculate Fe and Mn elements. The PBE1PBE/6-31G(d,p)/WTBS model [23] were utilized to further topological calculations. The topological parameters for the clusters under study is investigated within QTAIM including both local and integral properties which are performed with the AIM2000 programs [24]. The previously reported X-ray diffraction structures of $[(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Mn}(\text{CO})_5]$, $[\text{Et}_4\text{N}][(\mu\text{-H})_2\text{Fe}_3(\text{CO})_9(\mu^3\text{-As})\text{Fe}(\text{CO})_4]$ and $[\text{Et}_4\text{N}][\text{HAs}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-H})\}\{\text{Fe}(\text{CO})_4\}]$ [3] have been used as starting points to find optimized geometries. These complexes were found to be of

C1 point group (coordinates of atoms are existing in the Supplementary Information of Schipper and Whitmire study) [3].

Results

Recently, by using QTAIM decided to compute the electron density $\rho(r)$ with AIM2000 package, many information about the bonding situation can be found, such as electron density $\rho(b)$, local kinetic energy density $G(b)$, Laplacian $\nabla^2\rho(b)$, local potential energy density $V(b)$, local energy density $H(b)$, and ellipticity $\varepsilon(b)$ were estimated at bcp's. The interaction of M-M bonds available was studied in bulk metals [25] and in organometallic compounds [26-30], as examples; Bader and coworkers [31], also other groups [32]. Additionally, there are a number of studies [25,33], explained an ionic interaction type involving M-L and M-M bonds.

By Fig. 2, the complexes 1-3 were depicted which are resulted from QTAIM perspective to clusters under study, these images display the whole set of bond (bcp's) and ring (rcp's) critical points in addition to bond paths (bp's). The bcp's and corresponding bp's were detected for Fe-C, Fe-H, C-O and Fe-As bonds in all systems. But there is no bcp and bp indicating the existence of direct Fe-Fe bond in these clusters, this may be attributed to arsenic and hydride bridging ligands effects which destroy these Fe-Fe bonds [34].

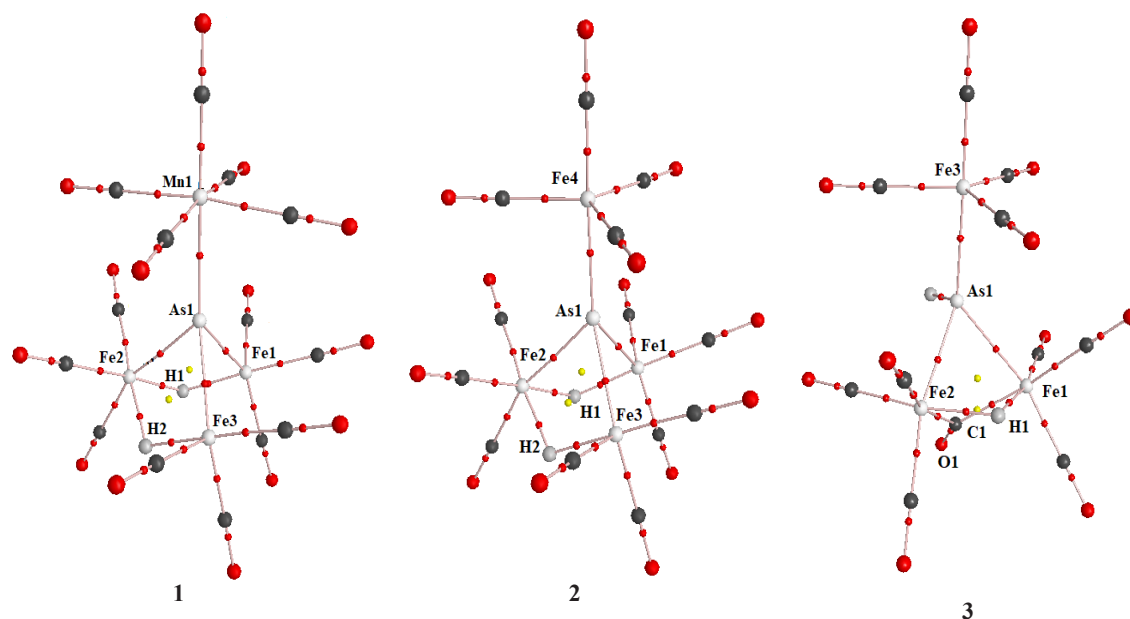


Fig. 2. Molecular structure of (1), (2) and (3) clusters, gray lines describe bp, bond red points (bcp) and ring yellow points (rcp).

Also, it was found two rcp's of Fe1-H1-Fe2-As1 and Fe2-H2-Fe3-As1 in complex **1**, two rcp's of Fe1-H1-Fe2-As1 and Fe2-H2-Fe3-As1 in complex **2** and only one rcp of Fe1-H1-Fe2-As1 in complex **3**. It is important to take into account the resultant effective information from these studies about the absence bps of Fe-Fe in the compounds supporting with hydride bridging [35]. But, these observations have been frequently found with another bridging species; bridging CO [14,36], bridging alkynes [34, 38-40] and recently, bridging borylenes [41]. Therefore, as a result, it has been concluded that the properties of supporting hydride to Fe...Fe in the atomic basin can be similar in these clusters [19].

The iron-hydride bps was determined, but the bps between Fe atoms cannot exist, so, they lack Fe-Fe bonding. Gradient trajectory maps shown in **Fig. 3** detect the electron density of atomic basins of iron atoms for the clusters **1-3**, in addition to the bp's, bcp's and rcp's located in the Fe atoms plane interactions. Clusters **2** and **3** maps are similar as we expected.

The electron density at the Fe atoms plane is shown in **Fig. 3** indicating the core interaction of iron atoms for **1**, **2** and **3** complexes respectively, of the atomic basins. It has been shown that there are no bp's and bcp's between iron atoms in each compound, but conversely with Fe bonded to carbonyl, arsenic and hydride ligands existing in the atomic basin of plane which were found.

Topological Analysis

Many local and integral topological properties for the **1**, **2** and **3** complexes (**Table 1**, **2**) have been calculated on the basis of QTAIM. These parameters are important to analyze the bonding in clusters containing iron transition metal.

Local Parameters of Fe...Fe and Fe-Ligand Interactions

The high magnitudes ρ_{BCP} , with $\rho_{bcp} < 0$, $H_{bcp} < 0$ indicate that the bonding has covalent character, while low magnitudes ρ_{BCP} with $\rho_{BCP} > 0$, $H_{BCP} > 0$ indicate ionic character or hydrogen bonding as well as van der Waals forces [42]. Some studies [43] were recently introduced, in which H_{BCP} , rather than ρ_{BCP} , exhibit higher efficiency index to explain an interaction. From our resultant calculations, it is found that no

direct bcp can be connecting the Fe...Fe atoms in all clusters **1-3**. By some previous literatures on complexes with supported hydride ligands M-H bonds (M: transition metal) [16,33,44]. We can get a comparison of M-H topological properties of previously studied complexes with these of complexes **1-3** in this work, for example; $[(\mu-H)_2Fe_3(\mu^3-Q)(CO)_9]$ [45] in which, the averaged values of M-H interaction electron density and Laplacian are (0.080 and 0.158) compared with corresponding Fe-H values in **1-3** clusters (**Table 1**) which are (0.075 and 0.248), (0.076 and 0.244) and (0.073 and 0.226) respectively. This indicate that there is a comparison between this bonding strength (M-H) with opposite single covalent bonds of non-metal atoms [25,46]. Additionally, the ellipticity values (0.041 and 0.054), (0.036 and 0.053) and (0.042) corresponding to Fe-H bonds in **1**, **2** and **3** respectively can be compared with those of $[Fe_3(\mu-H)(\mu-COMe)(CO)_{10}]$ (0.06) [19]. Also as shown in **Table 2**, the delocalization index (which is referred to pairs of electron in any A-B atoms in system) of this part $\delta(Fe-H)$ in **1** (0.354), **2** (0.341), and **3** (0.321) are slightly lower than (0.448) of $\delta(Os-H)$ in $[Os_3(\mu-H)(\mu-OH)(CO)_{10}]$ and (0.380) of $\delta(Cr-H)$ in $[Cr_2(\mu-H)(CO)_{10}]^-$ [33]. Accordingly, $\delta(Fe-H)$ magnitudes show that, about less than half electron pairs are shared in this interaction kind.

It is also can explaining the bonding nature of $Fe_2(\mu-H)$ fragment in these clusters (**1-3**) based on Laplacian graphical representations (**Fig. 4**) in which, the electron density indicates a bit polarization of surrounding Valance Shell Charge Concentration (VSCC) across Fe...Fe interaction midpoint. This feature is similar for bridging hydride in these complexes, the polarization gives positive Laplacian value.

In addition to the previous description, the resultant parameters of topology for Fe-CO bonds propose relatively higher magnitudes in and , this was approximate for **1** (0.146 and 0.666), **2** (0.148 and 0.666), and **3** (0.139 and 0.606) respectively. Additionally, the ellipticity of Fe-CO at bcp have small positive magnitudes, 0.043, 0.039 and 0.064 for **1**, **2**, and **3** respectively. Also, as shown in **Table 1**, the relatively small and negative magnitudes of index H_{bcp} in this three systems indicate the covalent character of Fe-C bond relatively.

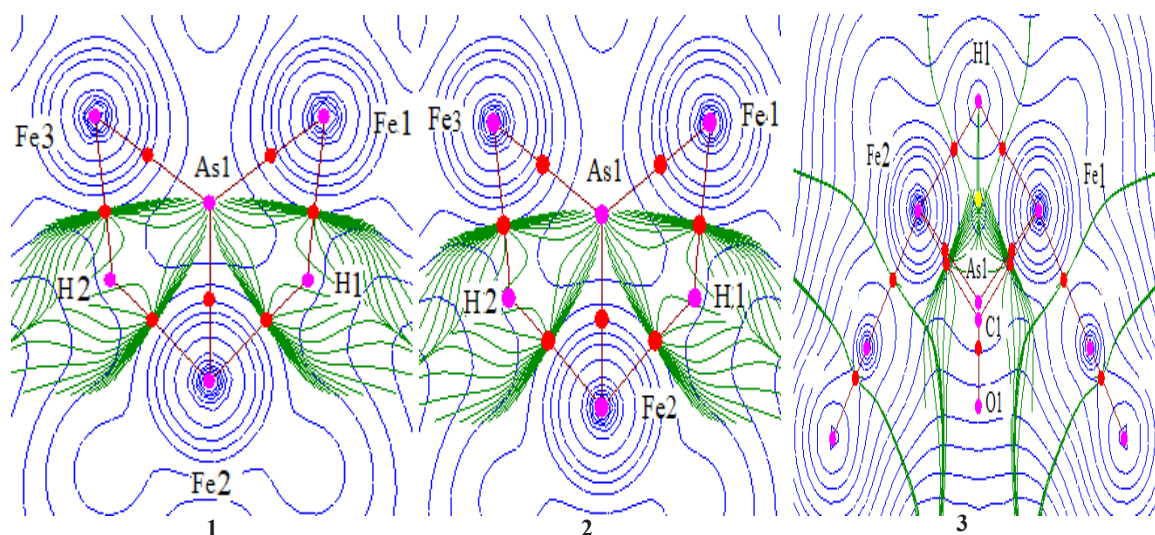


Fig. 3. Electron density mapping plot in 1: Fe1-Fe2-Fe3, 2: Fe1-Fe2-Fe3 and 3: Fe1-Fe2 planes of atomic basins in compounds indicating bp's and bcp's .

TABLE 1. Some features of topology at bcps for the three clusters .

Bond ^a						
Cluster 1						
Fe1-H1, Fe3-H2	0.073	0.244	0.076	-0.015	0.091	0.040
(Fe2-H1, H2) _{(av.)*}	0.078	0.251	0.081	-0.018	0.099	0.054
(As1-Fe1, Fe3) _{(av.)*}	0.082	0.146	0.065	-0.028	0.093	0.057
As1-Fe2	0.074	0.130	0.056	-0.023	0.079	0.006
Fe-CO _{(av.)*}	0.145	0.666	0.219	-0.052	0.272	0.043
C-O _{(av.)*}	0.459	1.392	1.096	-0.748	1.845	0.006
Mn1-As1	0.059	0.078	0.034	-0.014	0.049	0.006
Mn-CO _{(av.)*}	0.130	0.549	0.183	-0.046	0.230	0.007
Cluster 2						
Fe1-H1, Fe3-H2	0.073	0.241	0.076	-0.015	0.092	0.036
(Fe2-H1, H2)	0.078	0.246	0.080	-0.018	0.098	0.053
Fe1-As1, Fe3-As1	0.083	0.129	0.062	-0.029	0.091	0.037
Fe2-As1	0.074	0.118	0.053	-0.023	0.076	0.010
Fe4-As1	0.061	0.158	0.052	-0.012	0.064	0.013
Fe-CO _{(av.)*}	0.148	0.666	0.222	-0.055	0.278	0.039
C-O _{(av.)*}	0.452	1.320	1.068	-0.738	1.806	0.016
Cluster 3						
Fe1-H1, Fe2-H1	0.073	0.226	0.072	-0.015	0.088	0.042
(As1-Fe1, Fe2) _{(av.)*}	0.070	0.124	0.051	-0.020	0.071	0.053
As1-Fe3	0.062	0.146	0.050	-0.013	0.064	0.016
Fe-CO _{(av.)*}	0.139	0.605	0.200	-0.049	0.250	0.064
C-O _{(av.)*}	0.449	1.287	1.054	-0.732	1.787	0.032

*mean of magnitudes, (a) Electron density, (b) Laplacian values, (c) total kinetic energy density, (d) electronic energy density, (e) potential energy density, (f) ellipticity, all at bcps.

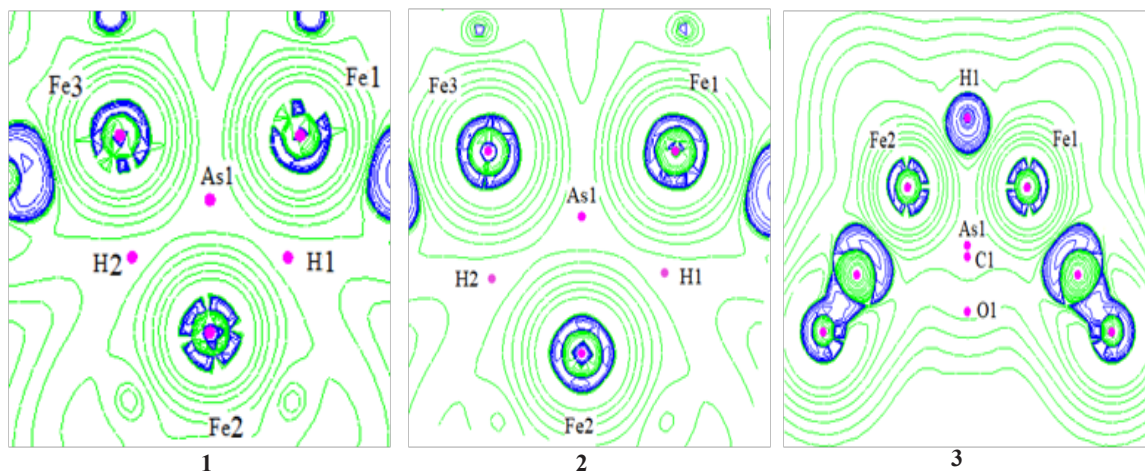


TABLE 2. Some Important Indices of Particular Atomic Delocalized $\delta(a,b)$ density relations in 1, 2 and 3. (* averaged magnitudes of Fe atom only with its coordinated carbonyls).

atoms (a, b)	$\delta(a, b)$	atoms (a, b)	$\delta(a, b)$
Cluster 1			
Fe1...Fe3	0.251	Fe1-C _(av.) *	1.173
Fe2...Fe1,Fe3	0.124	Fe3-C _(av.) *	1.174
Fe1-H1	0.343	Fe2-C _(av.) *	1.127
Fe3-H2	0.343	Fe-O _{CO(av.)}	0.160
Fe2-H1,H2	0.368	Mn1-CO _(av.)	0.894
As1-Fe2	0.638	C-O(Mn) _(av.)	1.524
As1-Fe1,3 _(av.)	0.718	C-O(core) _(av.)	1.353
Cluster 2			
Fe2...Fe3,Fe1	0.120	Fe4-C _(av.) *	1.107
Fe3...Fe1	0.230	Fe2-C _(av.) *	1.096
Fe2-H1,H2	0.359	Fe3-C _(av.) *	1.163
Fe3-H2	0.335	Fe1-C _(av.) *	1.161
Fe1-H1	0.335	Fe-O _{CO(av.)}	0.169
As1-Fe2	0.594	C-O(core) _(av.)	1.329
As1-Fe1,3 _(av.)	0.709		
Cluster 3			
Fe1...Fe2	0.147	Fe3-C _(av.) *	1.110
Fe1-H1	0.320	Fe1-C _(av.) *	1.101
Fe2-H1	0.321	Fe2-C _(av.) *	1.110
As1-Fe3	0.501	Fe-O _{CO(av.)}	0.163
As1-Fe1,2 _(av.)	0.548	C-O(core) _(av.)	0.368
Fe1,Fe2- μ CO	0.626		

The Laplacian of electron density at Fe1-As1-Fe2, Fe1-H1-Fe2, Fe2-As1-Fe3 and Fe2-H2-Fe3 planes of **1** were shown in **Fig. 4**, in which, a VSCC of supporting H1 ligand has a polarization to point middling in Fe1...Fe2 edges, and of bridging H2 atom toward the midpoint of the Fe2...Fe3 edge. Also for **2**, the VSCC of tow bridging hydride has polarized to point middling in Fe2...Fe3 edge. The positive Laplacian value (0.226) of Fe1-H1 and Fe2-H1 bonds in **3** indicates a small polarization. It is also observed for complex **3**, that the bridging ligands (hydride and carbonyl) are polarized toward a midpoint Fe1...Fe2 edge.

Delocalization Indices

Fermi correlation has been also concerning the existence of electron pairs delocalization symboling by $\delta(a,b)$ index, which computed for electrons shared with two atomic basins (a) and (b). Such an integral feature is very important to use in this field for each two bonded or non-bonded directly atoms in system according to QTAIM calculations [19]. All calculated delocalization values are summarized in **Table 2**.

Fe-Fe Delocalization Indices

These delocalization indices of **1**, **2** and **3** are summarized in **Table 2**. From data it is observed that these indices for Fe...Fe interactions in all complexes were about 0.120 - 0.251, these low values (as compared with corresponding in other studies) attributed to the effect of bridging ligands (hydride, carbonyl and As bridging ligands) bonded to Fe...Fe edges then destroying this M-M bonds [34]. So, an agreement was get with another examples proposed in the previous researches, as example; Fe-Fe bonding has mean value as 0.398 of $[\text{Fe}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}]$ [19], and Ru bonding magnitude is 0.458 of complex $[\text{Ru}_3(\mu\text{-H})_2(\mu^3\text{MeImCH})(\text{CO})_9]$ [16]. Also, two hydrides unbridged Fe1-Fe3 (in cluster **1**) and Fe1-Fe3 (in cluster **2**) bonds have higher delocalization indices values (0.251 and 0.230 respectively) than hydride bridged Fe2...Fe1, Fe3 (0.124 in cluster **1** and 0.120 in cluster **2**), and 0.147 for Fe1-H-Fe2 in cluster **3** which could give confirmation for sharing the bridging ligand with Fe...Fe interaction. The participations of $\delta(\text{Fe2}, \text{Fe3})$ related orbital have been tested to demonstrate that the planes of centered $\text{Fe}(\mu\text{-H})\text{Fe}$ (in **1**, **2** and **3**) and $\text{Fe}(\mu\text{-C})\text{Fe}$ (in **3**) relations indeed promote principal electron sharing between atoms of Fe [19].

Fe-H and Fe-As Delocalization Indices

By looking at the $\delta(\text{Fe-H})$ averaged value in **Table 2** for clusters, which was 0.345, we find that it is closed to corresponding of $\delta(\text{Ru-H})$ (0.474) in $[\text{Ru}_3(\mu\text{-H})_2(\mu^3\text{MeImCH})(\text{CO})_9]$ system [16] and of $\delta(\text{M-H})$ where; (M = Mn, Tc and Re respectively) in $[\text{M}_3(\mu\text{-H})_3(\text{CO})_{12}]$ [13] which are (0.430, 0.473 and 0.477 respectively). Another similar example produced about metal-hydride relations [33]. Furthermore, the $\delta(\text{Fe-H})$ index for Fe1-H1, Fe2-H1, Fe2-H2 and Fe3-H2 (in both **1**, **2** clusters) and Fe1-H1, Fe2-H1 (in cluster **3**) has confirmed one observation that a half pair of electrons was contributed in two Fe-H bonds. The 3c-2e interaction in $\text{Fe}_2(\mu\text{-H})$ is exist.

Also, the combination of delocalization indices magnitudes was nearly 1.890 pairs of electrons in Fe1-($\mu\text{-CO}$)-Fe2-As1 plane and 1.732 electron pairs in Fe1-As1-Fe2-H1 plane indicating the 4c-4e exist in both parts of complex **3**.

Fe-CO Delocalization Indices:

The π -back-donation from metal to carbonyl is complicated to detect, this can be interpreted by M-CO cylindrical symmetry of electron density along this bond (M-CO), which conceals the preferential accumulation planes and the polarity effect of the M-CO charges [16].

The interactions $\delta(\text{M-O})$ have been listed in **Table 2** in order to test π -bonding of Fe-CO fragment. Consequently, the 0.164 value represents the average value of $\delta(\text{Fe...O})$, this magnitude is comparable with $\delta(\text{M-O})$ of Ru, Ni, Fe, Co, and Os carbonyl clusters which about (0.150 - 0.250) [11,30,45]. So we can conclude that there is an important π -back-donation to CO ligand. The average values of Fe-CO delocalization indices 1.150 in **1**, 1.120 in **2** and 1.103 in **3** were significantly higher than average $\delta(\text{Fe-H})$ value (0.340) and average $\delta(\text{Fe...Fe})$ value (0.174). As depicted in **fig. 4**, it is clearly observed in all complexes that, the VSCC of carbonyl carbon atom is polarized directly toward Fe connected with.

Conclusion

The QTAIM calculations has established several essential concluded points:

(1) It has been demonstrated that, the QTAIM analysis method is an effective tool to constitute an extensive elucidation for testing and explaining the M-M and M-Ligand interatomic interactions.

(2) For Fe...Fe interaction, the distribution of an electron density is considerably effected by the existence of supporting hydride ligands. Consequently, calculated local and integral properties of hydride unbridged Fe...Fe for **1** and **2** clusters are significantly different from those of hydride bridged Fe...Fe.

(3) The hydride bridging ligand contribution to the Fe...Fe delocalization of electron density in complex **2** (0.120) was lower than that for complex **1** (0.124), while the presence of carbonyl bridging ligand supported to the Fe...Fe leads to reduce the hydride effect in complex **3**, so the delocalization of related Fe...Fe interaction was higher relatively (0.147).

(4) In contrast, the unsupported Fe...Fe delocalization (0.251 in complex **1** and 0.230 in complex **2**) was higher than those for supported one (0.124 in complex **1**, 0.120 in complex **2** and 0.147 in complex **3**).

(5) From $\delta(\text{Fe}\cdots\text{O}_{\text{CO}})$ delocalization value (0.164), one can conclude that the π -back-donation from iron to carbonyl is occurred in all complexes.

(6) we can describe the delocalization of an important fragments interaction in core such as; 5c-4e for Fe1-H1-Fe2-H2-Fe3 plane in each of **1** and **2** complexes, while in cluster **3**, Fe1-H1-Fe2 interaction is of 3c-2e type.

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