



Electronic structure study of clusters containing triiron metal atoms: QTAIM Approach

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Abstract

The bridging Fe-S-Fe, bridging Fe-CO-Fe, and terminal Fe-CO bonds of mono-chalcogenide triiron carbonyl cluster $[\text{Fe}_3(\text{CO})_7(\mu_3\text{-CO})(\mu_3\text{-S})(\mu\text{-dppm})][\text{dppm}; \text{diphosphine bis(diphenylphosphino)methane}]$ were characterized utilizing the quantum theory of atoms in a molecule (QTAIM) topological analysis. To our knowledge, there are a few studies investigating Fe-Fe and Fe-S bonds using QTAIM topological analysis. Analysis of the Fe1-s1-Fe2-C3-Fe3 moiety, which is the core of the bridged cluster, showed that there is no bonding pathway between the bonding critical point and the Fe atoms. The parameters electron density $\rho(r)$ and its Laplacian $\nabla^2\rho(r)$ calculated for Fe-s and Fe-C showed a pronounced pure σ -bonding of this interaction.

Keywords: Aim program, DFT calculations, Delocalization, Iron- cluster, Laplacian

Introduction

In the last two decades, crystal structures of [iron-iron]-hydrogenase have shown that the active site involves a diiron subunit other than thiolate as a bridging ligand and an additional cyanide and carbonyl ligands bound to the Fe₄S₄ ferredoxin unit (Volbeda et al., 1995) (Volbeda et al., 1996). This has been a major catalyst for the growth of synthetic active site analogs and a variety of iron biomimetics that have been tested as a deprotonation catalyst (Capon et al., 2009; Tard et al., 2009). One of the main characteristics of electrocatalysts for deprotonation is the capability to bind one or more protons and reduce them easily. Both are known features of low-valence metal clusters (M.G. Richmond et al., 2003) (A. Volbeda et al., 2004). Therefore, multicore clusters are promising as catalysts for hydrogen production by deprotonation (S. Ghosh et al., 2015; Ghosh et al., 2017; Ghosh et al., 2018; Rahaman et al., 2018).

In the present work, we use the topological analysis of the quantum theory of atoms in molecules, QTAIM approach, (Bader et al., 1984) to precisely characterize the chemical bonds within the triiron cluster. This method is a unique

theoretical tool for analyzing chemical bonds (Silvi et al., 2005; Lepetit et al., 2017). This work focuses on Fe-Fe, Fe-S, and Fe-CO bonds, in mono-chalcogenide triiron carbonyl clusters $[\text{Fe}_3(\text{CO})_7(\mu_3\text{-CO})(\mu_3\text{-S})(\mu\text{-dppm})][\text{dppm}; \text{diphosphinebis(diphenylphosphino)methane}]$ (Rahaman et al., 2019). Fig.1, in comparison with his QTAIM topological analysis of known intermetallic clusters whose experimental structures and theoretical properties have been reported in the literature.

Computational details

The PBE1PBE functional (Zhang et al., 1998) with the Gaussian 2009 software (Frisch et al., 2009) was used for all calculations. The SDD basis set (Wadt et al., 1985) was used for Fe metal atoms whereas for the lighter atoms, C, O, and S all-electron 6-31G* basis sets were used. The calculations using WTBS (Hehre et al., 2002) basis set for Fe atoms and 6-31G* for other remaining atoms were performed within the AIM2000 program package (Bader et al., 2002).

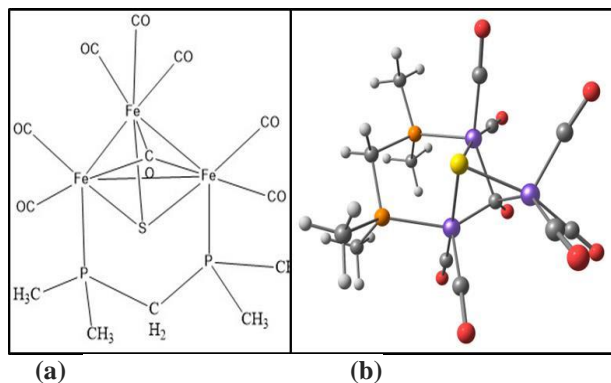


Fig. 1 (a) Molecular structure, (b) Geometry optimization for cluster

Results and Discussion

Topological analysis of electron densities allows detailed studies on the nature of interactions within clusters. According to this analysis, chemical bonds are represented by lines called bond paths (bp) that connect the two bonded nuclei atoms via a bond critical point (bcp). Fig. 2 present the molecular diagram of the cluster acquired by the QTAIM approach. This diagram makes it easy to see the critical points of bond paths, bonds and rings. Interestingly, all Fe-ligands Bcp and BPS were present, except for Fe...Fe interactions, which were not observed. In addition, three-ring critical points (rcpt) were observed corresponding to Fe1-S-Fe2-C1, Fe1-S-Fe3-C1, and Fe2-S-Fe3-C1.

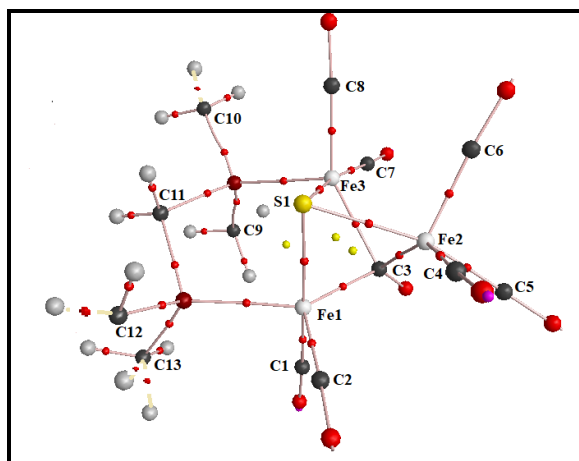


Fig. 2 QTAIM molecular graph of the triiron cluster. The BCPs are positioned as small red spheres while the yellow circles represent a tipping point in the ring

Gradient trajectory map of electron densities for Fe1-S-Fe2-C1, Fe1-S-Fe3-C1 and Fe2-S-Fe3-C1 surfaces are shown in Fig. 3. This map shows the expected bcp and bp between Fe-s and Fe-C with atom basins, but no corresponding bcp and bp between Fe...Fe metal atoms.

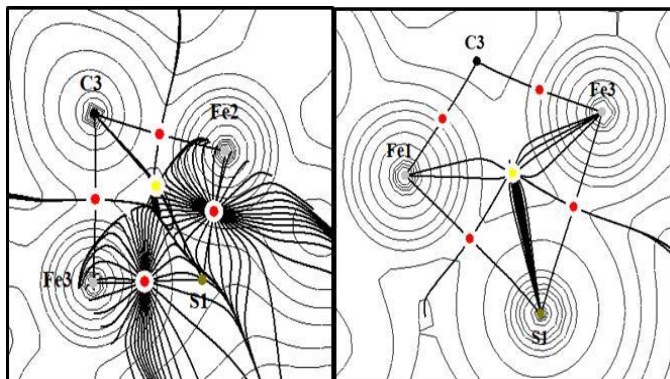


Fig. 3 Trajectory plot of the gradients in the plane passing through the Fe2-C3-Fe3-S1 and Fe1-C3-Fe3-S1.in Clusters

As shown in Fig. 4, the methyl diphosphine ligand map shows a hexagonal ring with one critical point of the ring and two critical points of the Fe-CO bonds, two P-CH₂ and two Fe-P bonds.

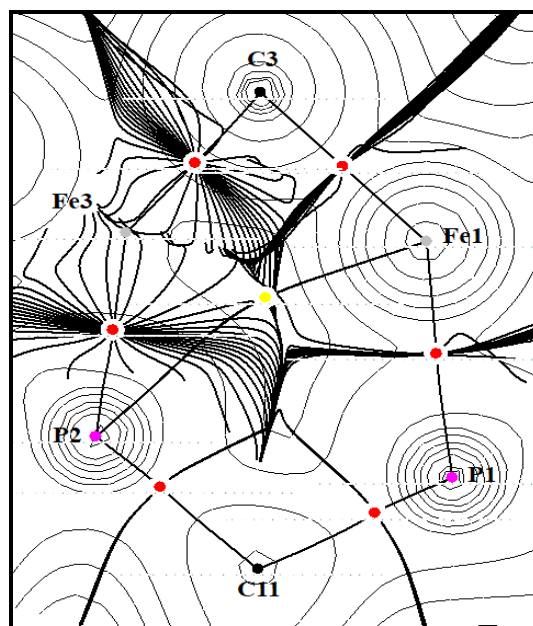


Fig. 4 Trajectory plot of the gradients in the plane passing through the diphosphine methyl in Clusters

Table 1. is calculated using Bader's approach to the QTAIM, giving the study of atomic bonding using charge density analysis. Topological analysis is recommended to reduce the difference between experiment and theory. The electron density (ρ) and Laplacian $\nabla^2\rho(r)$, kinetic energy, $G(r)$, potential energy, $V(r)$ and total energy densities, $H(r)$ were calculated (Stiefel et al., 1998). The charge density concentration for atomic interaction, denoted $\nabla^2\rho_b < 0 >$ indicates electron density-concentrated around atom nucleus, to classify the interaction as ionic or covalent and the closed shell compared with the open shell by the Laplacian sign can be best characterized by the method $H(r) = G(r) + V(r)$

(Rickard et al., 2007; Sourisseau et al., 1991). According to our electron density (ED) results for all bonds of the clusters under study, the interaction is nominated as a

closed-shell transport interaction between covalent and ionic bonds based on local characteristics of the data and power topologies (Moreau et al., 2011).

Table 1. QTAIM descriptors of the bond critical points in the cluster

Bond	ρ_{rb} (eÅ)	$\nabla^2\rho_{rb}$ (eÅ)	$G_{rb}(he)$	$H_{rb}(he)$	$V_{rb}(he)$	ϵT_b
Fe ₁ -S ₁	0.0876	0.3624	0.1145	0.0239	-0.0239	0.0254
Fe ₂ -S ₁	0.0864	0.3588	0.1127	0.0229	-0.0229	0.0272
Fe ₃ -S ₁	0.0873	0.3616	0.1140	0.0235	-0.0235	0.0102
Fe ₁ -C*	0.1595	0.7627	0.2687	0.0779	-0.0779	0.0161
Fe ₂ -C*	0.1520	0.7299	0.2542	0.0717	-0.0717	0.0207
Fe ₃ -C*	0.1526	0.7248	0.2537	0.0724	-0.0724	0.0155
Fe ₁ -P ₁	0.0951	0.3108	0.1123	0.0345	-0.0345	0.0482
Fe ₃ -P ₂	0.0983	0.3236	0.1180	0.0371	-0.0371	0.0282
P ₁ -C*	0.1531	0.0440	0.1524	0.1415	-0.1415	0.5788
P ₂ -C*	0.1527	0.0495	0.1535	0.1319	-0.1319	0.6983

*average

As shown in Table 1, the Fe-S and Fe-C bonds have values greater than 0 for the electron densities [0.0864 to 0.0876 (eÅ)] and [0.1520-0.1595 (eÅ)] respectively. Furthermore, these interactions have positive Laplacian values [0.3588–0.3624(eÅ)] and [0.572–0.662(eÅ)] respectively. These results, with H(r) at negative values ranging from [-0.0239 to -0.0229(he-1)] and [-0.122 to -0.022(he-1)], are equivalent and are consistent with the typical open shell interactions, mediated by purely ionic and covalent bonds between non-metallic atoms (Xu et al., 2011). The estimated ellipticity (ϵ_{rb}) for these bonds revealed that the Fe-S and Fe-C(bridging CO) bonds are close to zero, which means that the ellipticity (ϵ_{rb}) is low.

Laplacian topology is an important concept in molecular research. This is related to the area of local charge concentration or depletion. Globular nodes form a shell surrounding the area of concentration or fatigue. This is the so-called valence shell charge concentration (VSCC) term. The spherical symmetry of VSCC is broken when atoms contribute to bonds. The computed Laplace map of the plane containing Fe-C-Fe-S is useful for the analysis of Fe...Fe interactions, as shown in Fig. 5.

As mentioned above, the lack of critical bonding points between Fe atoms in the core is specifically filled by related S atoms. This is an interesting finding as there is no evidence of

local electron density between Fe atoms. As a result, within the core, no chemical bonding between pairs of iron atoms are observed (Nielsen et al., 2019). The topological Fe...Fe contacts are broken by the strong S-bridge interactions of the ligands. Important binding sites and pathways have been discovered between supported and unsupported metal atom interactions. The Fe-S interaction is classified as a closed transport shell metal-metal interaction model.

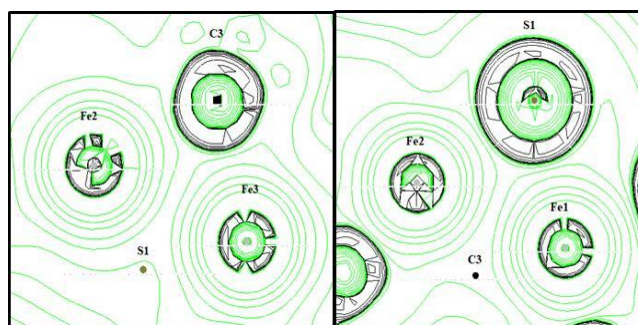


Fig. 5 Laplacian map of electron density in the clusters within (a) Fe2-C3-Fe3-S1 and (b) Fe1-S1-Fe2-C3 planes

Moreover, the calculated AIM ellipticities of the Fe-S bonds are very weak and close to zero, suggesting that these interactions resemble linear bonds. A Laplacian map of the cluster core shows that the valence shell charge concentration of the bridging sulfur is inconsistent with the Fe metal atom.

In contrast, the VSCC of the carbon atom of the bridging carbonyl ligand is slightly polarized towards the intermediate region between the Fe1 and Fe2 atoms Fig. 5 (Al-Ibadi et al., 2020).

Fig. 6 is consistent with our AIM results. The most remarkable feature of the topological analysis of M–P interactions in the cluster is the origin of the binding pathway between the M and P atoms of the methyl diphosphine group. It is, therefore, true that there are real bonds between the Fe and phosphene atoms of the methyl diphosphine ligand, rather than a simple "interaction".

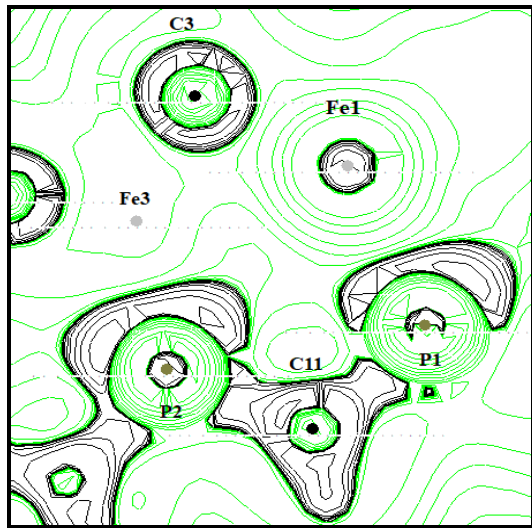


Fig. 6 Laplacian electron density image of a cluster of Fe-imidazole ligands

Delocalization Indices

Bond order is the total of electron pairs shared by two bonding atoms. QTAIM provides superior bond order analysis by uniquely combining the exchange densities of each atomic group. δ (A-B) is one of the most effective methods widely used in theoretical studies to determine the total of delocalized electron pairs between A and B atoms in topological features. Table 2. shows the calculated localization index δ (A-B) of Fe clusters. The values of (Fe, Fe) range from 1.433 to 1.546, which are higher than those of Fe obtained in previous studies for Fe (0.074–0.329) forms bridges with S atoms (Helal et al., 2018; Lewis et al., 1979). According to this study, there are multiple electron pairs between Fe atoms, but the lack of bonding between Fe atoms is due to the cluster configuration. According to our data, the mean value of the Fe–CO bond (0.152 Å⁻³) estimated in BCP is much higher than this intermetallic bond and lower than the atomic covalent bond. The computed delocalization indices were adopted to determine the presence of π -back bonding in metal-CO interactions due to inverse contributions, including M...CO interactions.

Table 2. Delocalization indexes for selected interactions in cluster

atom pairs (A, B)	δ (A, B)	atom pairs (A, B)	δ (A, B)
Fe(1)...Fe(2)	1.546	Fe2-C3	0.392
Fe(1)...Fe(3)	1.498	Fe2...C11	0.003
Fe(2)...Fe(3)	1,433	Fe3-C3	6.308
Fe(1)-S(1)	6.036	Fe3...C11	0.466
Fe(2)-S(1)	0,434	Fe1-P*	4,531
Fe(3)-S(1)	6.088	Fe2-P*	0.007
Fe1-C3	7.118	Fe3...P*	4.257
Fe1...C11	0.537	-	-

Conclusion

The structure of iron sulfide carbonyl clusters [Fe₃(CO)₁₀S] has been studied by computational density functional theory studies. Various bridging Fe-S-Fe, bridging Fe-CO-Fe and terminal Fe-CO bonds are characterized in detail using the quantum theory of atoms in a molecule (QTAIM) topological analysis. The results are compared to the date of topological analysis of other trimetallic clusters for which experimental and theoretical structures have already been reported. the core Fe1-s1-Fe2-C1-Fe3. As expected, within the Fe1-s1-Fe2-C1-Fe3 core, the bond critical points and bond baths disappear when the S and C atoms are bridged with Fe atoms. All topological parameters calculated for Fe-s and Fe-C bonds confirm that these interactions are purely σ -bonds.

Conflict of Interest

The author hereby declares no conflict of interest.

Consent for publication

The author declares that the work has consent for publication.

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