



Diamondoid metallic complexes as an alternative to capture N₂: A DFT study



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ARTICLE INFO

Article history:

Received 17 January 2017

Received in revised form 8 March 2017

Accepted 29 March 2017

Available online 2 April 2017

ABSTRACT

Iron octahedral complexes in which four positions are occupied by nanodiamond carboxylate units (diamondoids) applied on the nitrogen fixation process are studied. The trans effect caused by different substituents play an important role in the formation of the theoretical complexes. The thermodynamic availability of different compounds as well as their respective structures were obtained with promising results. All the calculations were performed by means of Density Functional Theory (DFT) (B3PW91/6-31G(d,p)//B3PW91/6-31G(d,p)).

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1. Introduction

Searching for a cheap route for ammonia preparation, artificial nitrogen fixation, has been one of the most important challenges in chemistry in the XX century and until present days [1]. The fact that certain micro-organic beings perform this process has been an important incentive for these studies [2]. The problem can be divided in several objects of study. However, always the first and fundamental part is the trapping of the N₂ fragment by a complex molecule (generally a metallic derivative) [3]. It has been established that the mechanism followed by the nitrogenase enzyme contained in bacteria involves a complex center, which contains molybdenum and iron atoms [4,5]. Therefore, the study of possible N₂ successful interactions has been focused in a large way in iron organometallic and coordination complexes in which certain combination of substituents can account to reach one of these nitrogen trappers [6].

In other context, today, nanodiamond derivatives constitute a very important object of study [7], there is a large variety of different particles sizes which can suffer changes by functionalization or doping [8,9]. Therefore, it is possible to predict that these fragments can participate as chemical agents in reactions or be substituents on coordination complex compounds.

In the same sense, diamondoid complexes are coordination metal compounds, which include small carboxylic functionalized fragments of nanodiamond [8,9] with notorious characteristics. It

has been demonstrated that the presence of the two “diamondoid walls” in this kind of compounds generates a strong electronic activity region around the coordination sphere of the metal center. This feature gives place to a particular reactivity on the iron environment that can be used to design species with special structures.

The aim of this study is to design diamondoid complexes, which can capture the N₂ molecule. One part of the capability is obtained with the help of the “diamondoid walls” and the other is a consequence of the trans effect, but anyway, it seems the desired effect of nitrogen fixation can occur; therefore, all the factors, which can have an important influence on the incorporation of N₂ molecule, are analyzed including a reactivity study.

2. Methodology

The proposed methodology followed in previous works [10,11] was applied using the suit of programs of computational chemistry Gaussian 09 [12] (B3PW91/6-31G(d,p)//B3PW91/6-31G(d,p)). A detailed structure study for different Fe complex: FeC₄₆H₅₄ · LL' with L and L' = CN, H₂O, CO, N₂, NH₃, was done. The notation used in this work is L–Fe_d–L'. Fig. 1 shows a general scheme of all complexes studied. At the center there is an iron (Fe²⁺) ion surrounded by four oxygen atoms in octahedral conformation. The ligands are located perpendicular to the oxygen plane in apical positions.

A conformational search of possible local minima for all studied complexes was carried out using Spartan'14 code [13], the Systematic method and the MMFF Merck molecular force field [14] were employed for this task. 10,000 conformers were requested. After, structure optimization was done for all possible minima found in

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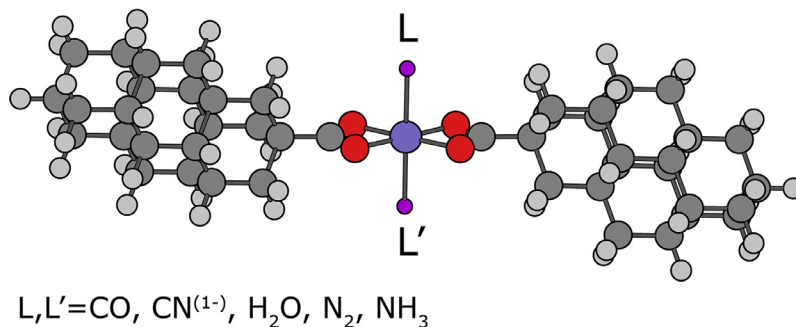


Fig. 1. Scheme of studied complexes.

Table 1

Formation energies for $\text{H}_2\text{O}-\text{Fe}_d-\text{L}$ complexes. The formation energies of previously reported complexes: $\text{L}-\text{Fe}_d-\text{L}$ for complexes with CO and CN [11] are given.

$\text{L}-\text{Fe}_d-\text{L}'$	E_f (kcal/mol)
$\text{CN}-\text{Fe}_d-\text{CN}$ [11]	-71.74
$\text{H}_2\text{O}-\text{Fe}_d-\text{CN}$	-97.31
$\text{CO}-\text{Fe}_d-\text{CO}$ [11]	-73.62
$\text{H}_2\text{O}-\text{Fe}_d-\text{CO}$	-74.01

Table 2

Enthalpies associated to ligand displacement.

Ligand	ΔH (kcal/mol)
CO	11.60
CN	-6.68

the conformational search (conformers within 20 kcal/mol of lowest energy were selected). The structures reported are those with minimum energy. All these structures were verified by vibrational frequencies analysis at normal conditions (1 atm and 298.15 K).

The electronic structure and several properties have been obtained and analyzed. These are frontier molecular orbitals (HOMO and LUMO), HOMO-LUMO energy gap ($\Delta_{\text{HOMO-LUMO}}$) as a measure of hardness, chemical potential, molecular electrostatic potential (MEP) and charge separation index (CSI) in conjunction with the global softness (σ). In addition, we estimate the energy of the reactions involved in the process of nitrogen fixation.

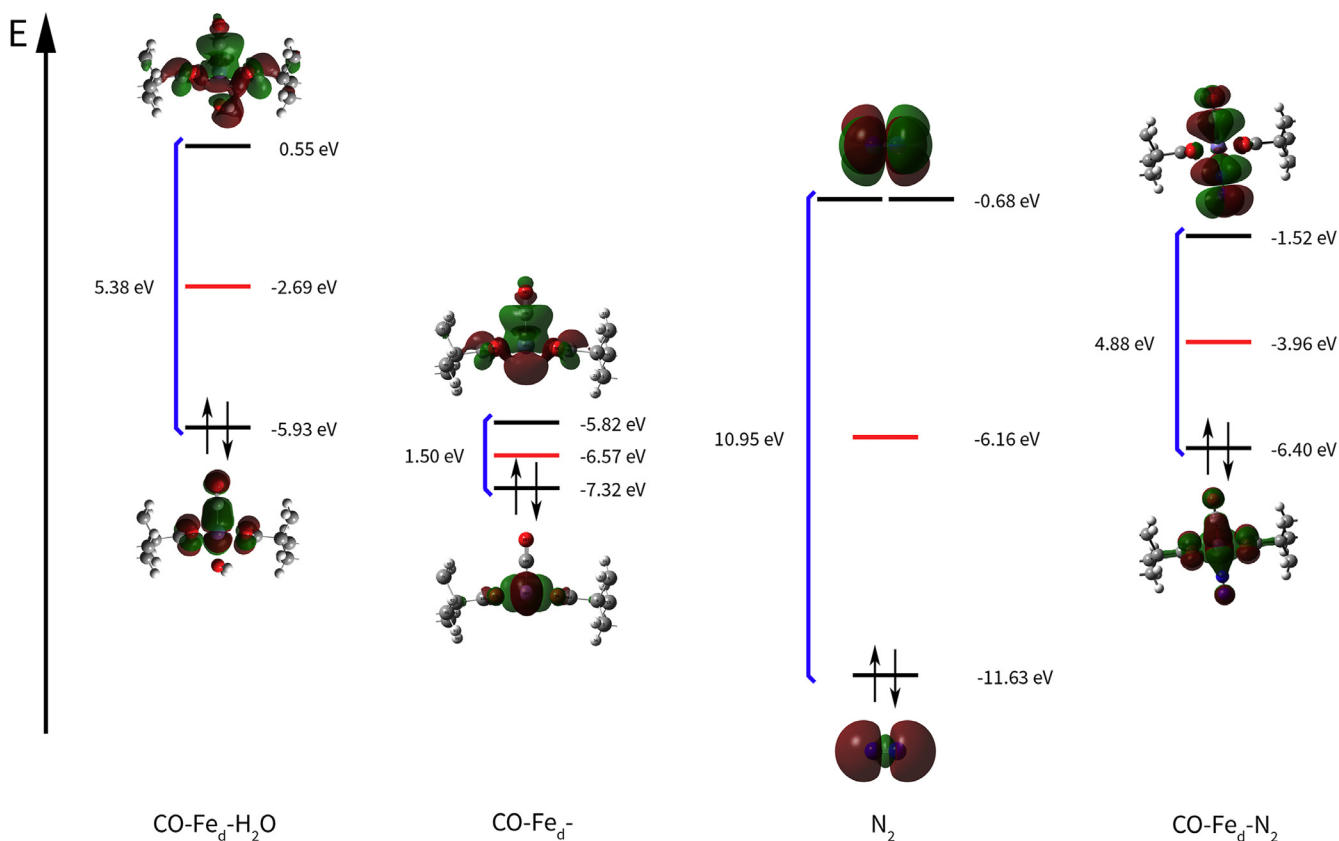


Fig. 2. FMO diagram for species arising from $\text{CO}-\text{Fe}_d-\text{H}_2\text{O}$, $\text{CO}-\text{Fe}_d-$, N_2 molecule and $\text{CO}-\text{Fe}_d-\text{N}_2$ compounds (red lines correspond to chemical potential and the blue parentheses to the hardness).

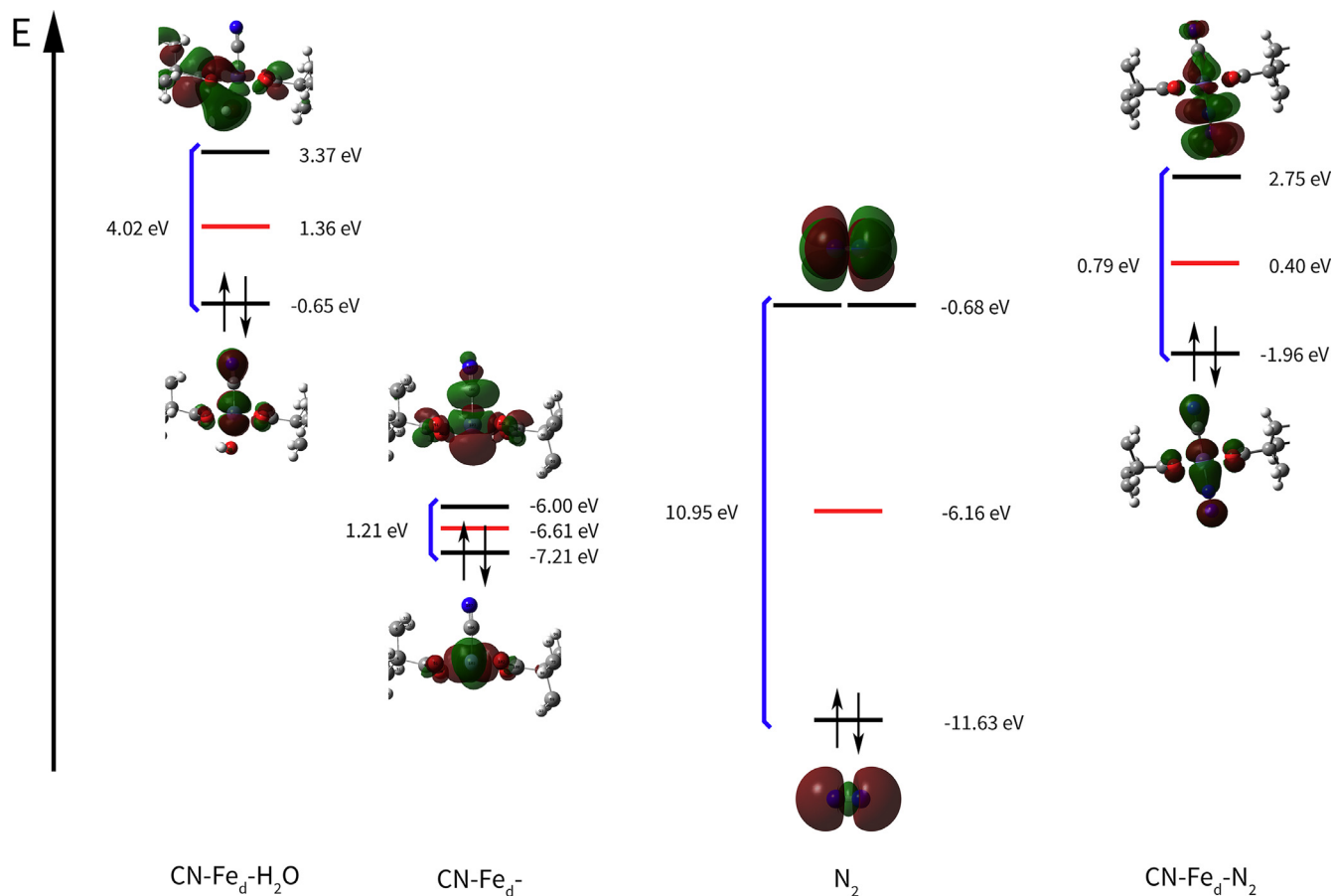


Fig. 3. FMO diagram for species arising from CN-Fe_d-H₂O, CN-Fe_d-, N₂ molecule and CN-Fe_d-N₂ compounds (red lines correspond to chemical potential and the blue parentheses to the hardness).

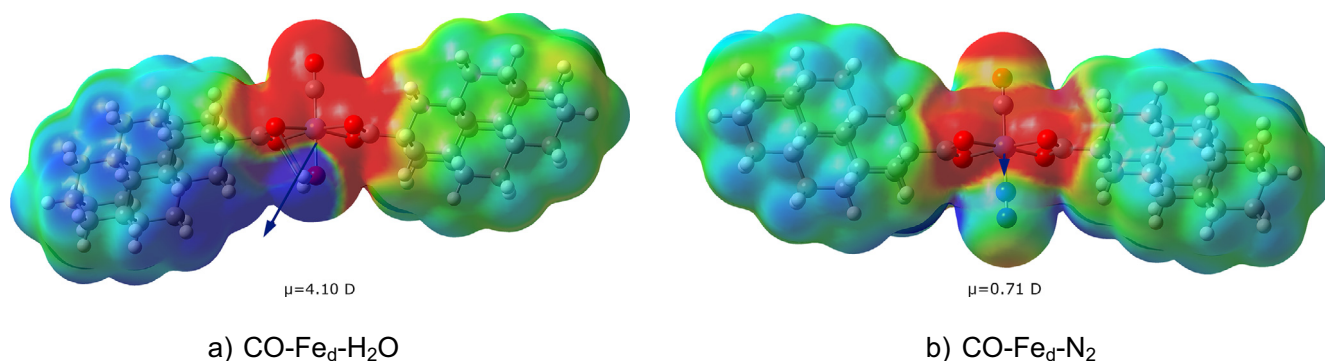


Fig. 4. Electrostatic potential map with dipole moment vector for CO derived complex.

The chemical potential and the hardness are calculated by means of conceptual DFT [15]; CSI is obtained from the sum of absolute values of the q charges of each i atom of the study region [16]:

$$CSI = \sum_i |q_i| \quad (1)$$

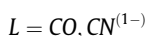
And it can be interpreted as the measure for the local polarity of the molecule [16].

Using the CSI index and σ , we calculated the local softness (S) as follows:

$$S = \sigma \cdot CSI \quad (2)$$

3. Results and discussion

Table 1 shows the formation energies (E_F) of diamondoid iron complexes H₂O-Fe_d-L, according to Eqs. (3) and (4). As reference, the E_F of L-Fe_d-L complexes with CO and CN studied previously [11] are also shown.



$$E_F = H_{L \cdot Fe_d \cdot H_2O} - (H_{Fe_d} + H_L + H_{H_2O}) \quad (4)$$

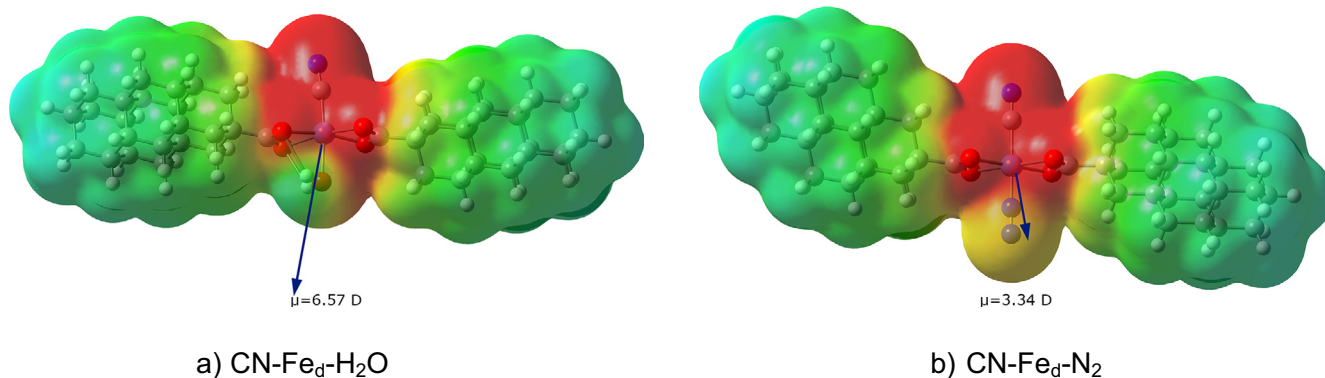


Fig. 5. Electrostatic potential map with dipole moment vector for CN derived complex.

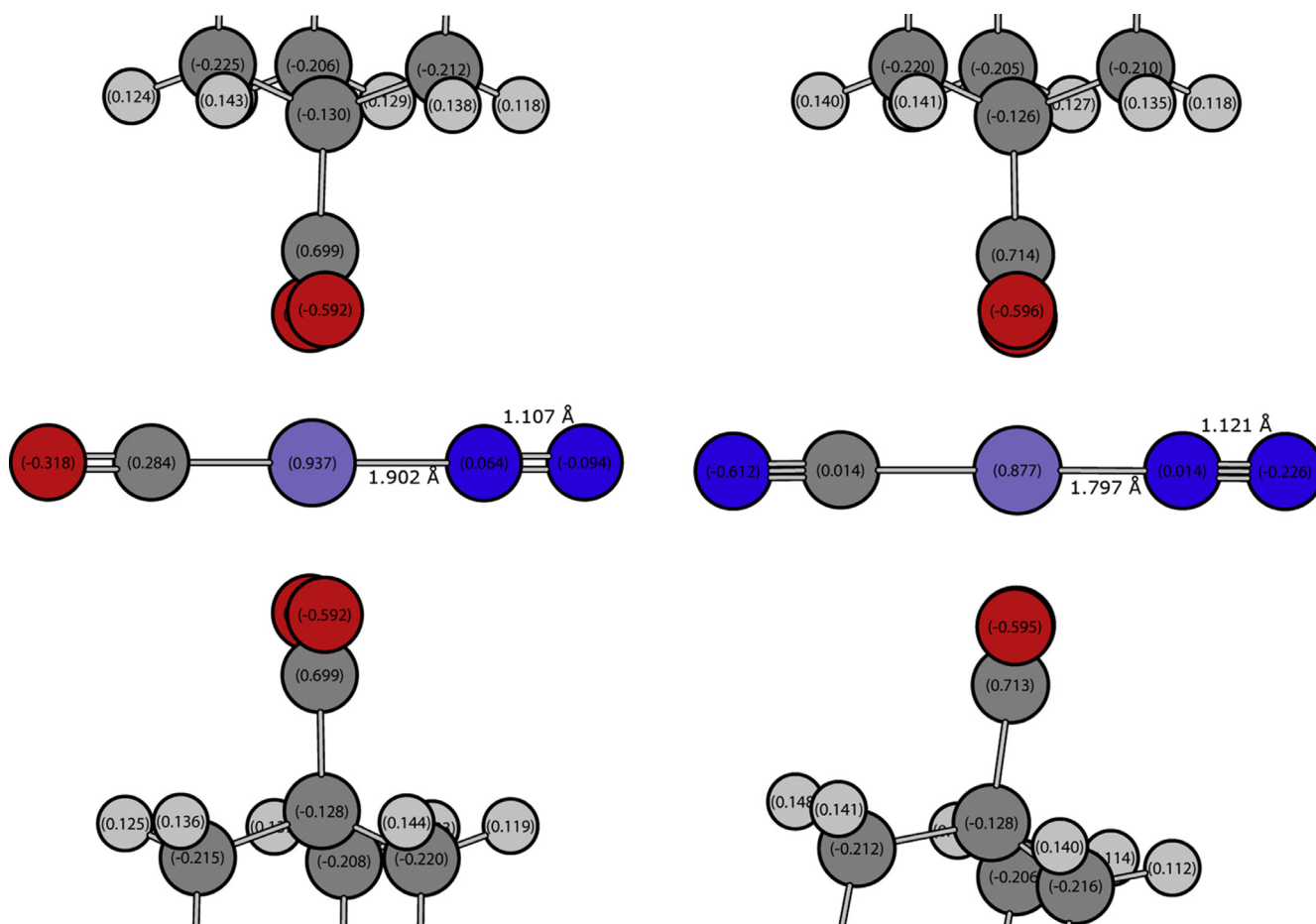
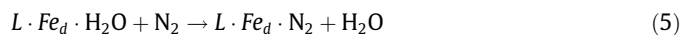


Fig. 6. Mulliken population analysis and distances (Fe-N and N-N) for L-Fe_d-N₂ complexes with L = CO (a) and CN (b).

As can be seen, the current compounds (H₂O-Fe_d-CN and H₂O-Fe_d-CO) and those reported previously (L-Fe_d-L) are thermodynamically stable. The formation energy suggests that it should be possible to synthesize these compounds.

To study the process by which the N₂ is trapped by the proposed compounds, we begin estimating the energy involved in the following global reaction:



Eq. (5) represents the energy for the H₂O displacement reaction by nitrogen in a L-Fe_d-H₂O complex (related to trans effect). The enthalpy of this equilibrium is estimated as:

$$\Delta H = (H_{L \cdot Fe_d \cdot N_2} + H_{H_2O}) - (H_{L \cdot Fe_d \cdot H_2O} + H_{N_2}) \quad (6)$$

where H 's represent the enthalpies of the reactants and products involved in Eq. (5).

Table 2 shows ΔH for the described processes. To estimate the reaction energies, it is supposed that the enthalpy is the major contribution.

As can be seen, the trans effect caused by CN ligand is reflected in a negative enthalpy value, as was expected. Moreover, the positive ΔH value for the CO ligand is small and can be reached at reasonable temperatures. Therefore, the proposed complexes represent an interesting possibility to capture N₂.

Table 3
Charge separation index (CSI) and local softness (S) for N–N bond in L-Fe_d-N₂ complexes.

Complex	CSI		S	
	L	N ₂	L	N ₂
CO-Fe _d -N ₂	0.602	0.134	0.165	0.037
CN-Fe _d -N ₂	0.626	0.240	0.178	0.068

To shed light on the proposed nitrogen capture process, an insight of some electronic properties of all complexes and molecules involved is relevant.

As mentioned before (Eq. (5)), to describe how the nitrogen molecule is trapped by the complexes, we assumed that at the beginning of the process, the water molecule is going to be displaced from the L-Fe_d-H₂O complex since the trans effect weakens the bonding between the H₂O and the iron ion. The trans effect is caused by the presence of CO and CN ligands. In order to analyze this, the Frontier Molecular Orbitals (FMO) diagrams for L-Fe_d-H₂O, L-Fe_d-, N₂ y L-Fe_d-N₂ are analyzed.

Figs. 2 and 3 show the FMO diagrams for CO and CN complexes, respectively, for the process above mentioned (for clarity, the region correspond to the diamondoids are omitted). Additionally, the chemical potential and molecular hardness are presented in the same figures. To complement the information provided by FMO diagrams, the molecular electrostatic potential (MEP) with electric dipole moment of each complex is shown in Figs. 4 and 5.

Comparing the FMO diagrams of CO-Fe_d-H₂O and CN-Fe_d-H₂O complexes, it can be observed that neither the HOMO nor the LUMO of the complexes can interact directly with the nitrogen molecule. Therefore, the water molecule must leave the complex in order to allow the interaction between the Fe and N₂. From the FMO of the complexes without water (L-Fe_d-), it can be observed that there is electronic density where the H₂O is missing. On the other hand, the N₂ LUMO and the L-Fe_d- HOMO are suitable for orbital overlap to form the L-Fe_d-N₂ complexes. Thereby, this indicates that the reaction between L-Fe_d- and N₂ is possible.

Furthermore, by means of the Hard and Soft Acid Bases (HSAB), Pearson's theory [15], the chemical potential drop associated with the trapping of N₂ by CN-Fe_d- (see Fig. 3) is larger in the CN case than in CO (see Fig. 2). This indicates that the process is more favorable in CN than in CO, in concordance with the enthalpies reported for the global process (see Table 2).

The charge separation in the CN complexes is greater than in the corresponding for CO. This can be associated with the fact that CN has a greater trans effect. This is reflected in the MEP (more negative regions in the CN complexes) and in the magnitude of dipole moment (greater magnitudes for CN complexes), as can be observed in Figs. 4 and 5. In all cases, it can be seen that the larger concentration of charge is located near the Fe atom and the CO or CN ligand, indicating that the interchange of ligands of the reaction proposed in Eq. (3) is possible.

From Figs. 2 and 3, it can be noticed that the CO-Fe_d-N₂ complex have a bigger hardness than that corresponding to CN, being an indicative that the lability of N₂ bonding is larger in CN-Fe_d-N₂. In order to have a better perception, a Mulliken population analysis for the nitrogen atoms of N₂ in relevant regions of the complexes is presented in Fig. 6. Table 3 gives the values of some chemical descriptors for this region.

With the purpose to analyze the lability of the N–N bond due to the chemical environment caused by the complex, the charge separation index (CSI) and a kind of local softness (S) (corresponding to the N₂ region) is used. In this work we estimated the softness using the global softness in conjunction with the CSI, obtaining

as a result the local softness (S) for the N–N region in the complex (as presented in Methodology section).

As shown in Fig. 6, there is a bigger loss of charge in the N–N region of CN-Fe_d-N₂ than in CO-Fe_d-N₂. This is due to the larger trans effect of CN, concentrating the charge in this group, thereby the bond between the nitrogen atoms of N₂ is weaker in CN-Fe_d-N₂ than in CO-Fe_d-N₂ (in accordance with the bond distance, Fig. 6). This is supported by the values shown in Table 3. Both indexes (CSI and S) tell us the charge concentration in the given region and, therefore, the polarizability of this region. As shown, N₂ in the complex with CN has larger values than that in the corresponding CO complex, showing how the trans effect of this ligand affects the bond in N₂. The charges and the indexes values agree with the larger dipole moment and MEP distribution of CN complex. Further work could be done in this direction, in order to elucidate the possible application of these complexes in the transmutation of N₂ to NH₃ [17], completing the nitrogen fixation process.

4. Conclusions

We have designed new theoretical diamondoid complexes, which have the potential to capture the nitrogen molecule. From the FMO analyses is clear that the water molecule must leave the complex to allow the N₂ capture. According to our results, one part of the capability of our complexes to capture this molecule is related with the trans effect associated with CO and CN groups.

Enthalpies estimations for the global reaction to trap N₂ (11.60 kcal/mol and –6.68 kcal/mol for CO-Fe_d-H₂O and CN-Fe_d-H₂O, respectively) indicates that the process is easier for the CN complex. This fact could be explained with the larger chemical potential falling when the water molecule outcomes of the CN complex.

Finally, with the MEPs, charge distribution and chemical reactivity indexes used, the proposed complexes represent an interesting possibility to capture N₂. For further work, the conversion of N₂ to NH₃ using these complexes could be studied. This research is currently underway in our group.

Acknowledgements

We thank Alberto López, Alejandro Pompa and Joaquín Morales for the technical support. I.G.C. acknowledges projects Y.61023 and D.61015 and to authorities from Instituto Mexicano del Petróleo for granting permission to publish this work. R.S. thanks projects DGAPA PAPIIT IN203816 and RN203816.

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