

STUDY OF THE LITHIUM CATION-FERROCENE INTERACTION BY DFT CALCULATIONS: AN IN-DEPTH ANALYSIS OF THE EXISTENCE OF A PLANETARY SYSTEM

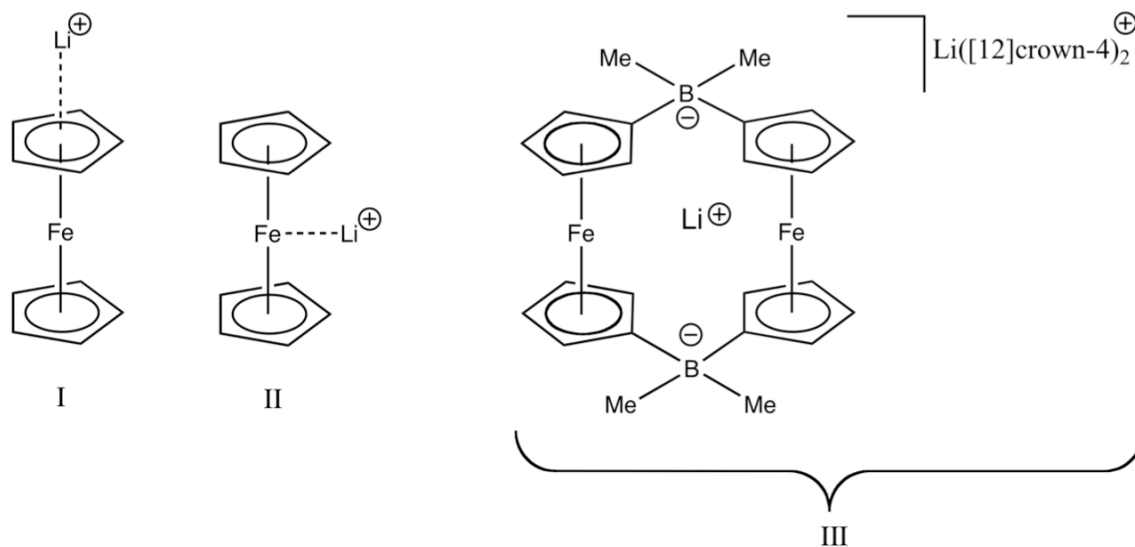
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The term *planetary system* was proposed by Abboud et al. to refer to complexes between Li^+ and a neutral species where the cation has closed, thermally accessible paths resembling orbits, revolving around the central neutral species.¹ Afterwards, Irigoras et al. found a *planetary system* for the complex between Li^+ and ferrocene by DFT calculations.² The peculiarity of this system is that the cation orbits around the ferrocene on a planar orbit (with a radius of about 2.4 - 2.5 Å), so it is the first *planetary system* having one and only one planar orbit. According to their calculations the ferrocene-lithium cation complex has two isomers (scheme 1). The most stable isomer of this complex has Li^+ on-top of one of the cyclopentadienyls (I), while in the least stable isomer Li^+ binds to the central iron metal (II). This later isomer lies 8.52 kcal/mol higher in energy than the ring-bonded isomer. In structure II the lithium cation is at a distance of 2.4 Å from the central iron atom in a staggered arrangement with respect to both cyclopentadienyl rings. The transition state connecting any two adjacent equivalent forms of II is separated by a barrier of only 2.6 kcal/mol through structure $\text{TS}_{\text{II-II}}$, in which the lithium cation is at 2.53 Å from the central iron atom and eclipsed with respect to both cyclopentadienyl rings. This isomer II has been characterized as a

planetary system in the sense that Li^+ has one thermally accessible planar orbit around the central ferrocene moiety.



scheme 1

Afterwards, Scheibitz *et al.* have claimed to provide experimental evidence for the existence of structure II.³ However, their experimental proof is indirect, since it is only based in the synthesis of the compound III of scheme 1, $[3\text{-Li}]\text{Li}([\text{12}]\text{crown-4})_2$. In our opinion, the existence of the anion of compound III does not represent a conclusive proof, because the Li^+ placement in this compound could be due to different effects to those of complex II: at first glance, the two negatively charged boron atoms could constitute a better explanation of the *confinement* of Li^+ in the central position.

In order to analyze in depth this subject, we have carried out a comprehensive DFT study of the ferrocene- Li^+ interaction in this kind of compounds.

Computational Methods

Geometries of all complexes studied in this study were fully optimized at the B3LYP/6-31+G* level of theory by using the Gaussian03 software package.⁴ Interaction energies of the complexes were calculated by means of the supermolecule method and employing the Boys-Bernardi counterpoise method to avoid Basis Set Superposition Error, BSSE.⁵ It is a well known fact that some of the most employed functionals, such as B3LYP, give an incorrect description of

interactions when these have an important dispersive component. However, it is well established that the gas-phase interactions between neutral molecules and alkali-metal cations are essentially electrostatic, also in complexes stabilized by cation- π interactions.⁶⁻⁹ Moreover, Coriani et al. have found that, unlike the MP2 model, the B3LYP model gives a reasonably accurate description of the ferrocene molecule (when both CCSD(T) and experiment results are taken as reference).¹⁰

Results and discussion

The molecular electrostatic potential (MEP) maps are a very useful tool to explain intermolecular interactions. For ferrocene, iso-valued electrostatic potential surfaces and the electrostatic potential distribution on a plane going through the iron atom and perpendicular to the cyclopentadienyls are shown in figures 1 and 2, respectively. According to these figures, MEP can explain the two possible places of Li^+ when this ion binds to ferrocene: top/bottom (I) and “planetary” (II), being preferential the first one. So, around the ferrocene structure there are two regions with clearly negative MEP values: -0.031 a.u. is the minimum value in the top/bottom region and only -0.016 a.u. in the radial one.

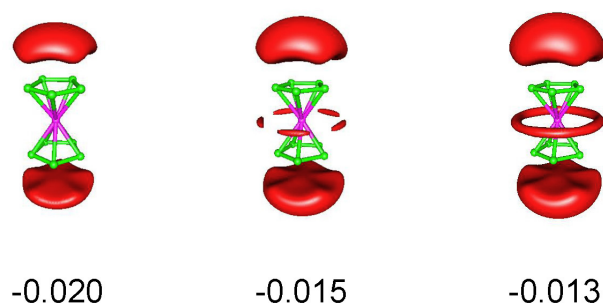


Figure 1. Iso-valued electrostatic potential surfaces for ferrocene (a.u.).

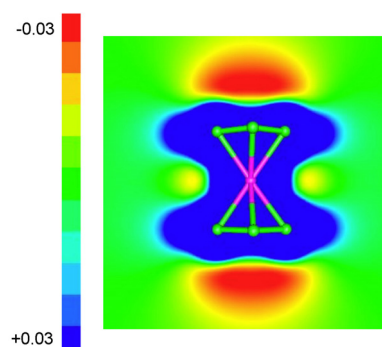


Figure 2. Map of the electrostatic potential distribution (a.u.) on a plane of ferrocene.

Figure 3 shows the obtained structures and relative energy values for the lithium cation-ferrocene interaction. It is worth noting that our values are very similar to those of Irigoras et al.² obtained with a much more large basis set. The calculated interaction energy for structures I and II are very strong: -46.08 kcal/mol and -39.16 kcal/mol, respectively. So, comparison between MEP and

energetic values confirm the electrostatic character of the interaction Li^+ -ferrocene, as expected.

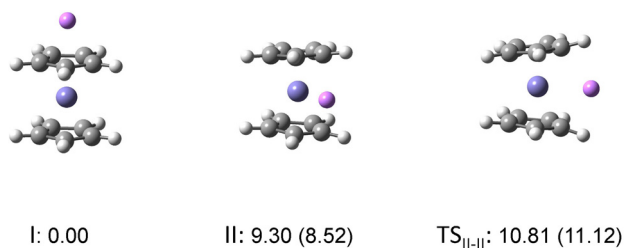


Figure 3. Lithium cation-ferrocene complexes. $\text{TS}_{\text{II-II}}$ corresponds to transition structure between two equivalent isomers II. Relative energies in kcal/mol. Values calculated by Irigoras et al.² are included in parentheses.

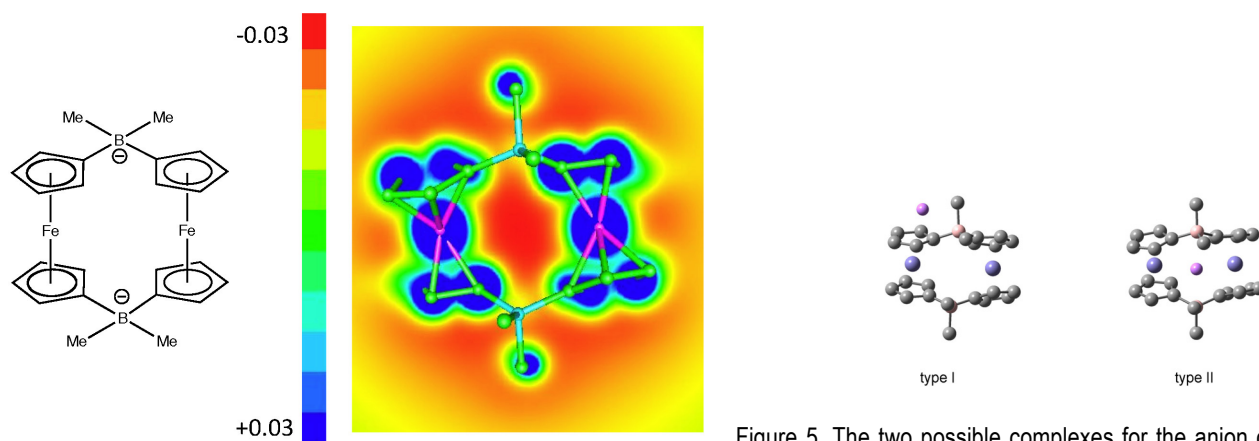


Figure 4. Map of the electrostatic potential distribution (a.u.) on a plane of structure III (without Li^+).

Figure 5. The two possible complexes for the anion of structure III. Type I corresponds to isomer where Li^+ is placed on top/bottom of one of the cyclopentadienyls. Type II corresponds to isomer where Li^+ binds to the central iron metal. This second complex was synthesized by Scheibitz et al.³

Figure 4 shows the electrostatic potential distribution on a plane for the anion of compound III (without Li^+). In this case, a huge negative MEP value (-0.305 a.u.) is obtained in the central region and a some smaller value in the top/bottom regions (-0.268 a.u.). These MEP values (very large, as expected for an anion) agree with the calculated energetic values when Li^+ is incorporated (figure 5). So, in this case, the type II complex is 39.57 kcal/mol more stable than the type I one. The calculated interaction energy for these two structures leads to the same conclusion: -198.65 and -236.02 kcal/mol for type I and II, respectively. Therefore, in the anion of compound III the favored complex is that in which the lithium cation is located in an orbital position around the central ferrocene moiety. This fact agrees with the experimental studies of Scheibitz et al.³ These authors

argue that this fact represents an experimental proof for the existence of structure II in the lithium cation-ferrocene complex. However, we think that there are too many structural differences between the lithium cation-ferrocene complex and the anion of compound III to reach this conclusion. So, in our opinion, the main question is: the preferential *orbital* placement of lithium cation in III is generated by the additive effect of two ferrocene moieties or by the double anion B⁻? In order to try to answer this question, MEP and energetic calculations were carried for the two following structures: (a) a structure with B⁻ but removing the two ferrocene moieties. (b) a structure IV, totally equivalent to III but without negative charge (the two B⁻ were substituted for two neutral carbon atoms).

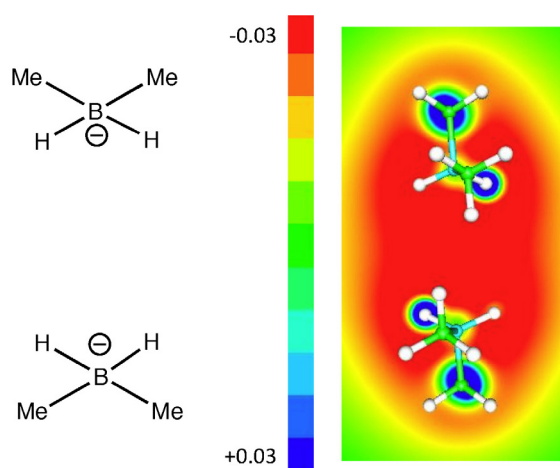


Figure 6. Map of the electrostatic potential distribution (a.u.) on a plane of structure III without the two ferrocene moieties and without Li⁺ (case (a) in text).

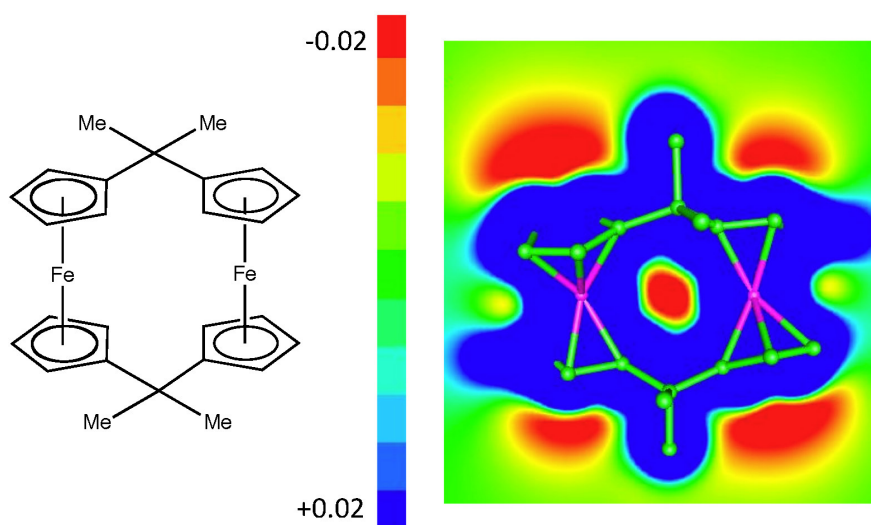


Figure 7. Map of the electrostatic potential distribution (a.u.) on a plane of structure IV without Li⁺ (case (b) in text).

Obviously, in the former case (a), calculations were performed keeping frozen the geometry of III and without geometric relaxation. For this case (removing Li^+) MEP calculations (figure 6) show that a huge negative value is obtained in the central region (-0.380 a.u.). Therefore, according to this calculation, it looks as if only the two B^- were responsible for the central large negative region in III. However, calculations of case b) show that this is not absolutely true. So, in this case (figure 7) a significant negative value MEP is obtained in the central region too (-0.030 a.u.). It is worth noting that this value is virtually twice as large as that of the same region of a single ferrocene moiety (-0.016 a.u.). The minimum value in the top/bottom regions is only slightly more negative (-0.032 a.u.). This very small electrostatic advantage of the top/bottom region does not result in a more favorable complex for the lithium cation in this region. So, on the contrary, type II complex is more stable (11.50 kcal/mol). The same trend is obtained for the interaction energy in the complex: -51.59 and -64.39 kcal/mol for complex type I and II, respectively. Therefore, in this case b) the comparison between MEP and energetic values of the Li^+ complexes show that interaction is not absolutely of electrostatic character.

Taking into account the results of these last cases, we can state that the two B^- are the main responsible for the favored central placement of lithium cation in the anion of structure III. Therefore the existence of the anion of this compound cannot be considered a conclusive proof for the existence of structure II of ferrocene. However, the calculations performed on structure IV (totally similar to structure III, but removing the two B^-), allow us to confirm that the additive effect of two ferrocene moieties is able to give an *orbital* placement of Li^+ (type II) more favorable than top/bottom placement (type I), which preferentially takes place in a single ferrocene. So, although in III the main effect is caused by the negative charges, a significant contribution comes from the above commented additive effect.

In summary, a much better experimental evidence to confirm the existence of a *planetary system* in the Li^+ -ferrocene complex would be the synthesis of a structure similar to IV: this would be the experimental challenge.

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