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Study of the ferrocene–lithium cation interaction by DFT calculations: an in-depth analysis of the existence of a *planetary system*

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ABSTRACT

Irigoras et al. found two isomers of the ferrocene–lithium cation complex by DFT calculations [Irigoras, A.; Mercero, J. M.; Silanes, I.; Ugalde, J. *J. Am. Chem. Soc.* **2001**, *123*, 5040–5043]. The most stable isomer (I) of this complex has Li^+ on top of one of the cyclopentadienyls, while in the least stable isomer (II) Li^+ binds to the central iron metal. The latter isomer has been characterized as a *planetary system* in the sense that Li^+ has one thermally accessible planar orbit around the central ferrocene moiety. Afterwards, Scheibitz et al. have provided experimental indication for the existence of structure II [Scheibitz, M.; Winter, R. F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 924–927]. However, their experimental proof is indirect, since it is only based on the synthesis of $[3\text{-Li}]\text{Li}([12]\text{crown-4})_2$, a crystalline solid, which anion (structure A) has a lithium cation bound to the iron atoms. As these authors have indicated, the existence of structure A could not represent a conclusive proof, because the Li^+ placement in this structure could be due to different effects to those of complex II (specifically, the electrostatic field originating from the two anionic dimethylborate bridges). To analyze this subject we have carried out a comprehensive DFT study of the ferrocene–Li^+ interaction in this kind of compounds.

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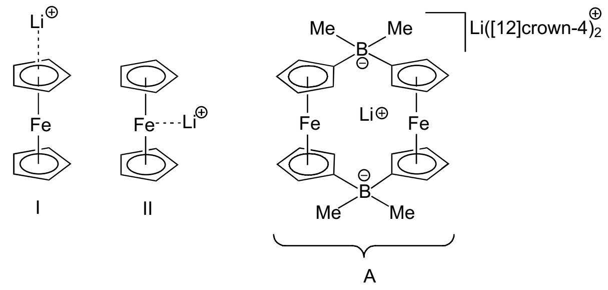
1. Introduction

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 (I) of this complex has Li^+ on top of one of the cyclopentadienyls, while in the least stable isomer (II) Li^+ binds to the central iron metal. This latter 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 $TS_{II–II}$, in which the lithium cation is at 2.53 Å from the central iron atom and eclipsed with respect to both cyclopentadienyl rings. The 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 provided experimental indication for the existence of structure II.[3] However, their

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experimental proof is indirect, since it is only based on the existence of structure A, the anion of the crystalline solid [3-Li]Li([12]crown-4)$_2$ (Scheme 1). Therefore, the existence of structure A does not represent a conclusive proof, because the Li^+ placement in this structure could be due to different effects to those of complex II: at first glance, the two negatively charged boron atoms could constitute a good 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.

2. 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,[6,7] also in complexes stabilized by cation–π interactions.[8–12] 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 experimental results are taken as reference).[13] Furthermore, according to our calculations for ferrocene, the 6-31+G* basis set provide even better results than those obtained for Xu et al. using for carbon and hydrogen atoms a DZP basis set and for iron atom augmented by two sets of *p* functions and one set of *d* functions and contracted (designated 14s11p6d/10s8p3d).[14]

3. Results and discussion

The molecular electrostatic potential (MEP) maps are a very useful tool to explain intermolecular interactions, especially when these have a significant electrostatic contribution. 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 locations of Li^+ when this ion binds to ferrocene: top (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 region and only −0.016 a.u. in the radial one (Table 1).

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 larger basis set. The calculated interaction energy for structures I and II are very large: −46.08 kcal/mol and −39.16 kcal/mol, respectively (Table 2). So, comparison between MEP and energetic values confirms the electrostatic character of the ferrocene–Li^+ interaction, as expected.

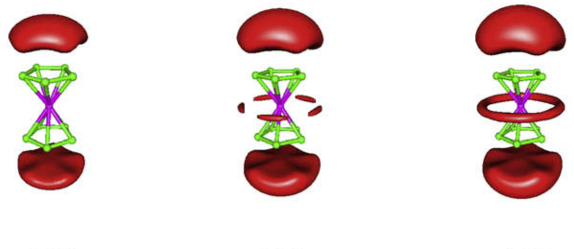

Figure 1. Iso-valued electrostatic potential surfaces for ferrocene (a.u.).

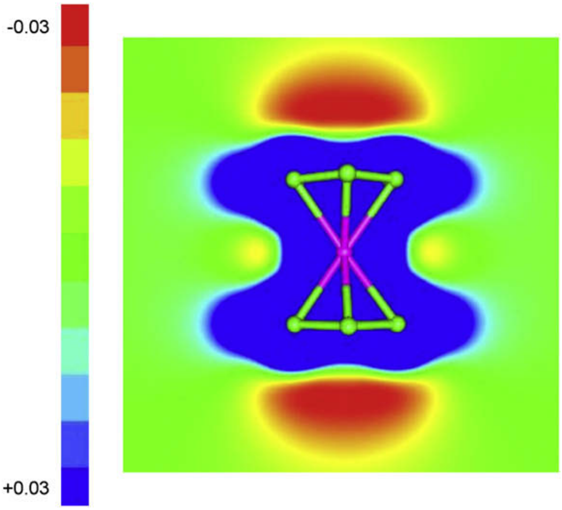

Figure 2. Map of the electrostatic potential distribution (a.u.) on a plane of ferrocene.

Figure 4 shows the electrostatic potential distribution on a plane for structure A (without Li^+). In this case, a huge negative MEP value (−0.305 a.u.) is obtained in the central region and a something smaller value in the top/bottom regions (−0.268 a.u.) (Table 1). These MEP values (very large, as expected for an anion) agree with the calculated energetic values when Li^+ is incorporated. So, in this case, the complex type II is 39.57 kcal/mol more stable than the type I one (Table 2). The calculated geometry for the complex type II agrees quite well with the experimental one,[3] although this comparison is not absolutely right since experimental data corresponds to solid state (X-ray crystallography). Table 3 shows values for several selected distances and angles. The calculated interaction energy for the two complexes leads to the same conclusion that relative energies. Therefore, in A the favored complex is that in which the lithium cation is located in an orbital position around the ferrocene moieties. This fact agrees with the experimental studies of Scheibitz et al. and it could represent an experimental evidence for the existence of structure II in the ferrocene–lithium cation complex (Fig. 5).[3] However, there are too many structural differences between the ferrocene–lithium cation complex and the anion A to reach this conclusion. So, the main question, as Scheibitz et al. have stated, is: the preferential *orbital* placement of lithium cation in A is generated by the additive effect of two ferrocene moieties or by the two B^- anions? In order to try to answer this question, MEP and energetic calculations were carried out for the two following structures: (a) a structure like A but removing the two ferrocene moieties, (b) a structure A2, totally equivalent to A but without negative charge (the two B^- were substituted for two neutral carbon atoms). Obviously, in the former case, calculations were performed keeping frozen the geometry of A and without geometric relaxation. For this case (removing Li^+) MEP calculations (Fig. 6)

Table 1
Calculated minimum values of MEP (a.u.) in two regions: top of cyclopentadienyls and radial relative to iron atoms (*orbital*)

	Top	Orbital
Ferrocene	−0.031	−0.016
A (without Li^+)	−0.268	−0.305
A (without Li^+ and ferrocenes)		−0.380
A2 (without Li^+)	−0.032	−0.030

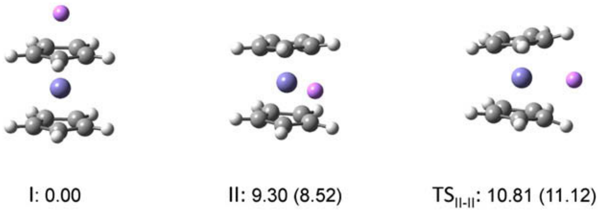

Figure 3. Ferrocene–lithium cation complexes. TS$_{II-II}$ corresponds to transition structure between two equivalent isomers II. Relative energies in kcal/mol. Values calculated by Irigoras et al[2] are included in parentheses.

Table 2
Calculated energetic values for the complexes with Li$^+$ (kcal/mol). Relative energy of the two possible isomers: Li$^+$ on top of cyclopentadienyls (type I) and Li$^+$ bound to Fe (type II). Interaction energies are included in parentheses

	Type I	Type II
Ferrocene	0.00 (−46.08)	9.30 (−39.16)
A	39.57 (−198.65)	0.00 (−236.02)
A (without the two ferrocenes)		(−255.50)
A2	11.57 (−51.59)	0.00 (−64.39)

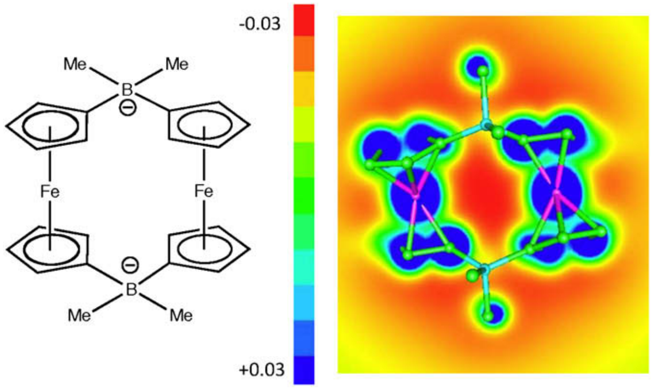

Figure 4. Map of the electrostatic potential distribution (a.u.) on a plane of the anion A (without Li$^+$).

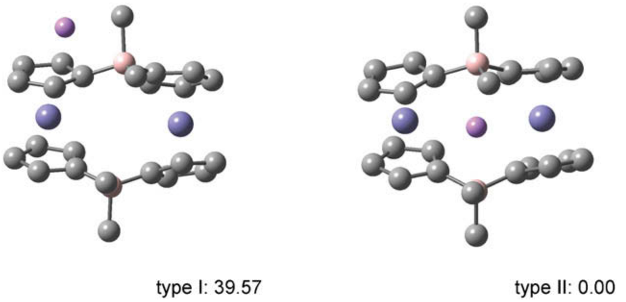

Figure 5. The two possible complexes for structure A. Type I corresponds to isomer where Li$^+$ is placed on top of one of the cyclopentadienyls. Type II corresponds to isomer where Li$^+$ binds to the central iron metal. This second complex was synthesized by Scheibitz et al.[3] Relative energies in kcal/mol.

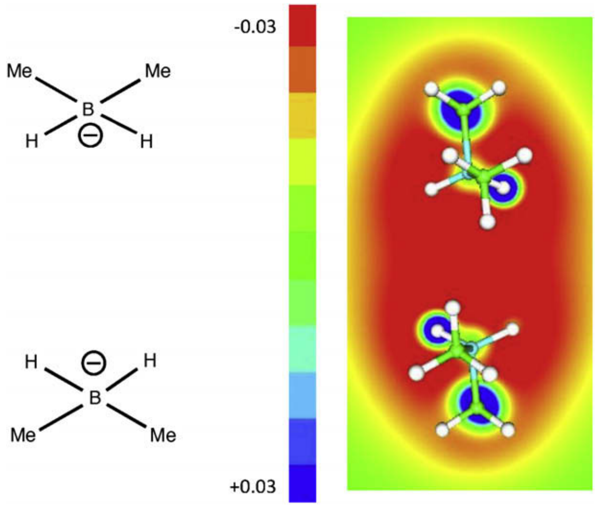

Figure 6. Map of the electrostatic potential distribution (a.u.) on a plane of structure A without the two ferrocene moieties and without Li$^+$ (case (a) in text).

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 A. However, calculations of case (b) show that this is not absolutely true. So, in this case (Fig. 7) a significant negative value of MEP is obtained in the central region too (−0.030 a.u.) (Table 1). 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 regions is only slightly more negative (−0.032 a.u.). This very small electrostatic advantage of the top 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 (Table 2). Therefore, in this case (b) the comparison between MEP and energetic values of the Li$^+$ complexes shows that interaction is not absolutely of electrostatic character.

Table 3
Comparison between calculated and experimental geometry for the complex type II of structure A (on the right-hand side of Fig. 5). Selected interatomic distances (Å) and angles (°). The indicated carbon atoms refer to that of ferrocene moieties, not to that of methyl groups

	Experimental[a]	Calculated
Li–B	2.309, 2.314	2.317, 2.318
Li–Fe	2.706, 2.720	2.647, 2.648
B–C	1.646–1.659	1.654–1.659
C–B–C	114.8, 115.7	114.4, 114.5
B–Li–B	179.2	173.5
Fe–Li–Fe	128.2	132.1

[a] See Ref. 3.

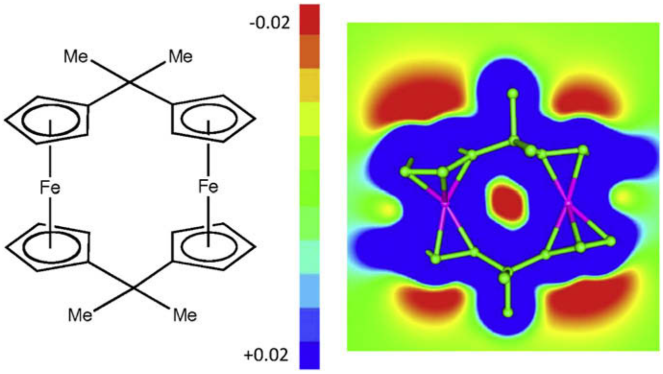

Figure 7. Map of the electrostatic potential distribution (a.u.) on a plane of structure A2 without Li$^+$ (case (b) in text).

Taking into account the results of these last cases, we can state that the two B$^-$ are mainly responsible for the favored central placement of lithium cation in structure A. Therefore, the existence of this structure cannot be considered a conclusive proof for the existence of isomer II of the ferrocene–lithium cation complex. However, the calculations performed on structure A2 (totally similar to structure A, 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 placement (type I), which preferentially takes place in a single ferrocene. So, although in A the main effect is caused by the negative charges, a significant contribution comes from the above commented additive effect.

4. Conclusions

Our calculations represent a confirmation of the Scheibitz et al. assumptions. So, the additive effect of two ferrocene moieties produces a significant enhancement of the negative character of MEP in the *orbital* region. In structure A this fact is important but it is practically outshone by the strong effect of the two negative charges on the boron atoms. For that reason the synthesis of A is a very good indication but it cannot be considered a conclusive proof for the existence of the *planetary system* in the ferrocene–lithium cation complex (isomer II, where Li$^+$ binds to the central iron metal). However, in structure A2 (where the two B$^-$ are substituted by two neutral carbon atoms) this additive effect is strong enough to favor the placement of Li$^+$ in the central region, so a change in the order of stabilities of the two types of ferrocene–Li$^+$ complexes takes place. Therefore, an especially suitable experimental proof to confirm the existence of a *planetary system* in the ferrocene–Li$^+$ complex would be the synthesis of a structure similar to A2: this would be the experimental challenge.

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