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Theoretical study of the guest···guest interactions of cobaltocene intercalated in metal sulfides

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The interaction between neighboring cobaltocene molecules is studied by means of density functional B3LYP and semiempirical PM3(tm) calculations, using bimolecular and heptamolecular aggregates. These calculations provide interesting information on the effect that guest···guest interactions may have on the orientation of intercalated metallocenes and may also be relevant for the study of the packing motifs in the crystals of unsubstituted metallocenes, as revealed by a structural database analysis.

Introduction

The versatility of the transition metal coordination sphere provides a wide catalog of molecular shapes that allows the assembly of molecules into a wealth of supramolecular arrays.[1–3] An example of the combination of an extended network with a molecular array is provided by the intercalation compounds. The intercalation of molecules within the layers of metal chalcogenides has been extensively studied due to the interesting physical and structural properties introduced in the host lattice by means of such a process.[4,5] In particular, examples of the intercalation of metallocenes in metal sulfides and selenides (Fig. 1) have abounded since the first report by Dines in 1975,[6] including cobaltocene or chromocene in TiS_2, $TiSe_2$, TaS_2, $TaSe_2$, ZrS_2, $NbSe_2$ or SnS_2, although in the last case chromocene reacts with the host lattice. In contrast, ferrocene shows less tendency to form intercalation compounds, and only its MoS_2 derivative has been reported.[7] The intercalation of bulkier sandwich complexes has also been achieved, including $[Mo(\eta^6\text{-}C_6H_6)_2]$, $[Mo(\eta^6\text{-}C_6H_5Me)_2]$, $[Mo(\eta^6\text{-}C_6H_3Me_3)_2]$, $[Cr(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)]$, $[Ti(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5H_5)_2]$ or $[Co(\eta^5\text{-}C_5H_4R_2)_2]$ (R = Me, ^{i}Pr, ^{n}Bu) within a ZrS_2 host lattice.[8]

Despite considerable advances in new characterization techniques that have allowed us to study the kinetic[9] and structural aspects of the intercalation process,[10,11] there are some aspects that still remain unclear from the experimental viewpoint. Among the aspects that require a better understanding we can mention the ability of the organometallic molecule to intercalate into the host lattice and the packing of the guest molecules inside the host, which is ultimately determined by host···guest and guest···guest interactions. Theoretical methods can be employed as a complementary tool to clarify the nature and strength of these interactions. Thus, we have recently reported a periodic *ab initio* study of the electronic properties of the host lattices focusing on the interlayer interaction and on the energetics of the electron transfer process between the metallocene and the metal chalcogenide.[12] Further work was devoted to the study of the host···guest interactions, in an attempt to predict and rationalize the position and orientation of the metallocene molecules within the host.[13] The aim of the present paper is to extend the analysis of the interactions present in such intercalation compounds by studying the guest···guest interactions within the metal chalcogenide layers and how they affect the relative orientation of neighboring metallocene molecules.

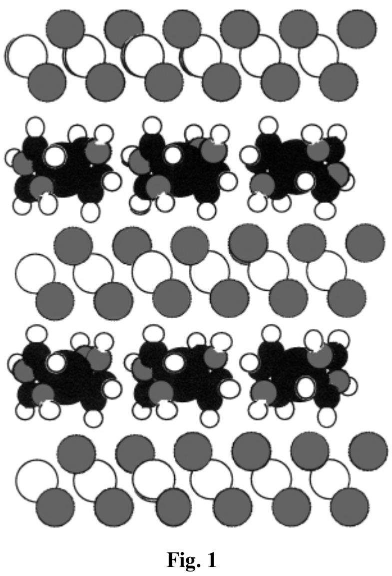

Fig. 1

Traditionally, *ab initio* methods have been employed to study weak interactions like hydrogen bonds but also density functional theory (DFT)[14] using hybrid methods[15] provides a good degree of accuracy to describe the electronic structure of systems with those kind of interactions.[16] In the present case, however, due to the large number of atoms in a metallocene, these methods are computationally too expensive for a system formed by a central metallocene with the whole set of neighboring molecules. To face this limitation one could use bimolecular models or carry out calculations with semiempirical methods on larger systems. We have selected for this study the cobaltocene molecule, the metallocene that is most frequently found in intercalation compounds. However, it seems reasonable to expect a similar behavior for other metallocenes, such as ferrocene or chromocene, because the intermolecular interactions involve mainly the Cp ring. Due to the weak nature of the interactions involved in the guest···guest contacts, the use of semiempirical methods is not straightforward and some validation tests are necessary. Thus, the first part of this paper is devoted to studying the interactions between cobaltocene molecules in a bimolecular model, using the hybrid B3LYP method, comparing the results with those obtained by means of the semiempirical PM3(tm) method.[17] In the second part, the semiempirical method is used for a larger model that comprises seven cobaltocene molecules. Finally, we present a structural

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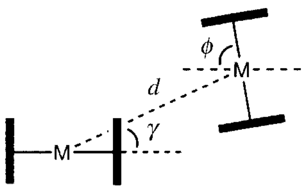

Fig. 2

database study of the relative orientations of metallocene molecules in the crystal structures of isolated metallocenes to verify how the theoretical preferred orientations are realized in those cases in which the crystal structures are well known.

Computational procedure

For our calculations we have employed the B3LYP hybrid method as implemented in the Gaussian94 computer code[18] using a double-ζ basis set for cobalt[19] and a 6-311* basis set for the hydrogen and carbon atoms. All the calculations reported in this paper for a cobaltocene dimer correspond to the spin unrestricted triplet state. We have chosen that state due to the experimental paramagnetic behavior of cobaltocene and to avoid the computational problems associated with the description of open shell singlet states using a single determinant wavefunction. The geometry of an isolated molecule has been optimized, and its structure kept frozen in the bimolecular aggregate. This approximation seems reasonable given the weakness of the intermolecular interactions involved between the cobaltocene molecules. For the larger models, the semiempirical PM3(tm) method was used, with the monomers in the geometry optimized at the B3LYP level, and the intermolecular distances and orientations fixed as discussed in the text. The state with maximum spin multiplicity ($S = 7/2$) was calculated for the heptamolecular model.

Structural database searches of unsubstituted transition metal metallocenes were performed with the aid of the Cambridge Structural Database[20] (version 5.18) for compounds with M···M distances between 6.0 and 8.0 Å. A total of 578 contacts were found, corresponding to 127 crystal structures, for which the three structural parameters (d, ϕ and γ, Fig. 2) were calculated.

Interactions in a bimolecular model

In our study, three structural parameters define the relative position of two neighboring metallocene units in the bimolecular model (Fig. 2): (i) the distance between the two metal atoms, d, (ii) the deviation from a parallel alignment of the fivefold symmetry axes of the two metallocenes, ϕ, and (iii) the position of one metallocene molecule relative to the symmetry axis of the other molecule, γ.

Let us discuss first the results for the bimolecular model with the two cobaltocene molecules aligned ($\gamma = 0°$). Fig. 3 shows the dependence of the calculated B3LYP energy on the Co···Co distance for rotation angles ϕ of 60 and 90°. The results for $\phi = 0°$ (not shown) indicate the existence of a minimum at an intermetallic distance of about 7.5 Å, but 2.5 kcal mol^{-1} higher in energy than those obtained for the other two angles. From these results one can conclude that at short Co···Co distances the dimer prefers a perpendicular geometry ($\phi = 90°$), while at distances larger than 7.3 Å an angular orientation is preferred. For the Co···Co distance corresponding to the lattice parameter of cobaltocene intercalated within SnS_2 (7.24 Å),[21] we found a practically negligible energy difference of 0.1 kcal mol^{-1} between the two rotation angles (ϕ = 60 or 90°), while the arrangement with the two cobaltocenes aligned along their fivefold axes ($\phi = 0°$) is 2.1 kcal mol^{-1} higher in energy. Such small energy difference indicates a rather small contribution of the guest···guest interactions to the barrier of rotation of the metallocene molecules in their intercalation compounds. We note that, the values of the interaction energy are rather small, but full optimization of the geometry and the use of a larger basis set could yield higher values for the calculated interaction energies. In any event, the aim of our work is not to accurately calculate the intermolecular interaction energy, but rather to obtain a good description of the changes in the total energy with the relative orientation of neighboring molecules.

Table 1 Interaction energy (kcal mol^{-1}) between two cobaltocene molecules at a Co···Co distance of 7.24 Å and $\gamma = 0°$ (see Fig. 2) as a function of the rotation angle ϕ, calculated by two different methods

ϕ/°	B3LYP	PM3(tm)
0	2.1	−0.3
60	0.0	−2.6
90	0.1	−2.4

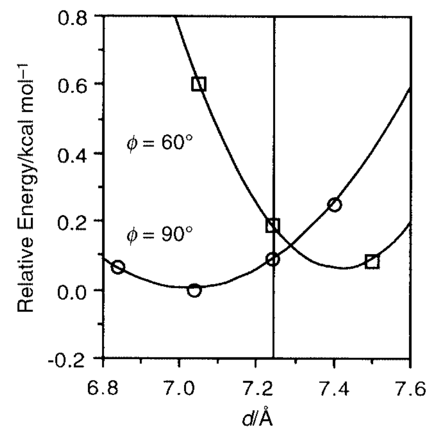

Fig. 3 Relative energy for the $\{CoCp_2\}_2$ dimer calculated with the B3LYP method as a function of the Co···Co distance ($\phi = 90°$, circles; $\phi = 60°$, squares). The vertical line indicates the Co···Co distance corresponding to $CoCp_2$ intercalated in SnS_2.

The calculations of the interaction energy at other relative positions given by different angles γ will be useful to interpret the results for a cluster of seven cobaltocene molecules to be discussed in the next section. To study such large systems, we will need to reduce the accuracy of the computational method. The PM3(tm) method was chosen because it includes a parametrization for transition metals and is also able to treat systems with hydrogen bonds.[22] We have checked the ability of the PM3(tm) method to handle the orientation preference of the cobaltocene molecules by comparison with the above B3LYP results at $\gamma = 0°$ (Table 1). The calculated relative energy values obtained with the two methods differ by only 0.1 kcal mol^{-1}. The PM3(tm) method provides negative interaction energies and the optimized intermolecular distances are slightly shorter than those obtained with the B3LYP method. This result is not unexpected due to the well known behavior of the PM3(tm) method that tends to give too short hydrogen bonds.[22] All in all, it seems reasonable to use the semiempirical PM3(tm) approach to study systems with a larger number of molecules from here on.

The PM3(tm) results at other relative orientations of the bimolecular aggregate are presented in Fig. 4. We note that the interaction energies are little affected by the relative orientation of the neighboring molecules, except for three orientations defined by the pair of coordinates (γ, ϕ): (0°, 0°), (0°, 30°) and (60°, 60°), which appear to be 1.5–3 kcal mol^{-1} less stable. While the higher energy of the former orientation can be attributed to repulsions between the π electrons of the two cobaltocene molecules, in the latter it might be associated with H···H interactions.

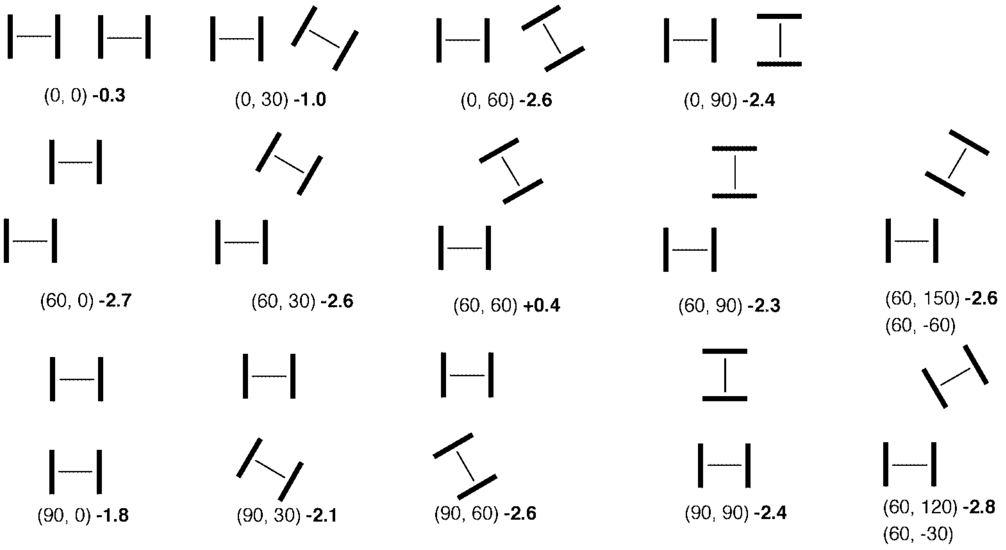

Fig. 4 Interaction energies (in boldface, kcal mol^{-1}) between two cobaltocene molecules at different orientations [PM3(tm) calculations] with a Co···Co distance of 7.24 Å. Each relative orientation is characterized by the two angular parameters (γ, ϕ) defined in Fig. 2.

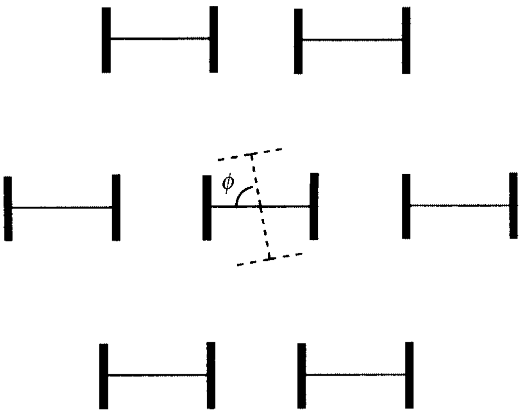

Fig. 5

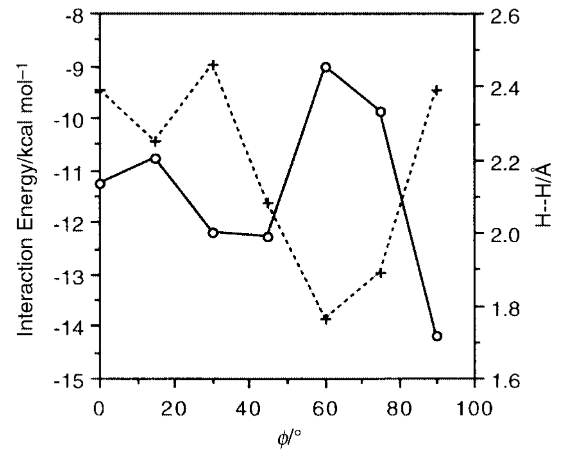

Fig. 6 Relative energy (solid line) for the model with seven cobaltocenes (Fig. 5) calculated with the PM3(tm) method as function of the orientation angle ϕ, and the shortest intermolecular H···H distance for each orientation (dashed line).

Interactions in a heptamolecular model

As a more realistic model we consider a heptamolecular aggregate that includes all nearest neighbors present in the metallocene layer of the intercalation compound, thus adopting the hexagonal arrangement shown in Fig. 5. In such a model we keep the external molecules fixed and study the interaction energy of the central cobaltocene with the surrounding ones as a function of the rotation angle ϕ at a Co···Co distance of 7.24 Å (corresponding to the lattice parameter in the intercalation compound). The result, shown in Fig. 6 (solid line), indicates a preference for the orientation with $\phi = 90°$. For this orientation, there are two contacts with a T conformation for which we calculated an interaction energy of -2.4 kcal mol^{-1} each (see Fig. 4), and four contacts with an L conformation, with a calculated interaction energy of -2.3 kcal mol^{-1}. The sum of the calculated pairwise interaction energies would give a total interaction energy of -14.0 kcal mol^{-1}, in excellent agreement with the calculated value for the heptamolecular model (-14.2 kcal mol^{-1}). For other rotation angles ($\phi = 0$, 30, 60°) the sum of the pairwise interaction energies in Fig. 4 and the calculated energy for the heptamolecular model differ by at most 0.6 kcal mol^{-1}.

Our calculations indicate a barrier for the rotation of one cobaltocene in the frozen matrix of the six surrounding molecules of about 5 kcal mol^{-1}, corresponding to the energy of the rotation angle $\phi = 60°$. According to the results for pairwise interaction energies (Fig. 4), that energy difference can be attributed to the substitution of two (0°, 90°) by two (60°, 60°) interactions. The interaction energy profile is clearly connected to the steric hindrance associated with short intermolecular H···H distances, as seen in Fig. 6, where the dashed line represents the shortest H···H distance for each orientation angle: the interaction energy becomes more negative as the shortest H···H distance increases. Calculations at a longer Co···Co distance (7.56 Å) give smoother variation of the energy with ϕ, with the minimum again at $\phi = 90°$. These results seem consistent with the conclusions of the recent study of the temperature-dependence of the ^{2}H-NMR lineshapes of cobaltocenium intercalated in a layer silicate.[23] In such a study, the NMR spectra could be interpreted in the range 220–300 K by rapid rotation around a C_2 axis of the cobaltocenium cation over a restricted angular range.

Relationship with experimental structural data

Since the metallocene···metallocene interactions are likely to determine the packing in the crystal structures of metallocenes, one should expect to find similar orientation preferences in those structures. In the first place, we have found above that the M···M distance is expected to be shorter for a rotation angle ϕ of 90° than for 60 or 0° when $\gamma = 0°$. A structural database analysis of unsubstituted metallocenes with $\gamma < 10°$ (Fig. 7) shows that indeed for *short* M···M distances (between 6.3 and 6.8 Å) the perpendicular orientation ($\phi \approx 90°$) is favored, while for larger distances the most common values of ϕ are

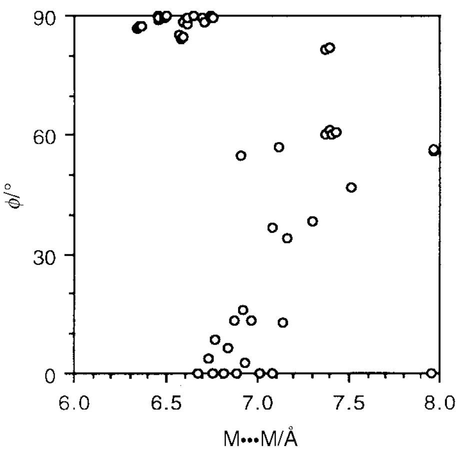

Fig. 7 Values of the orientation angle ϕ as a function of the Co · · · Co distance for unsubstituted transition metal metallocenes, as found in the Cambridge Structural Database.

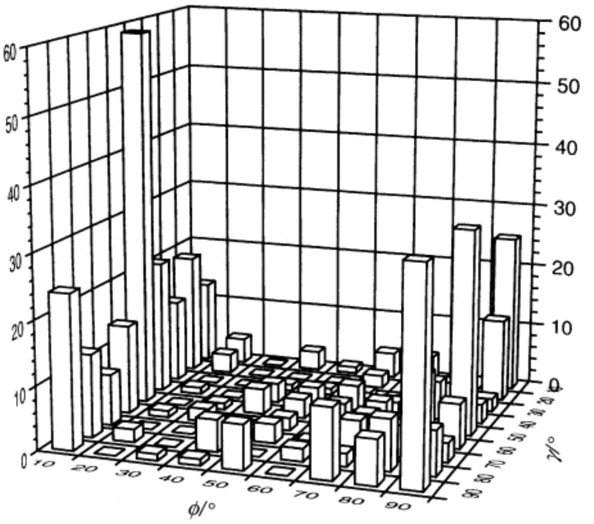

Fig. 8 Number of intermolecular contacts (cutoff M · · · M distance of 8.0 Å) between unsubstituted transition metal metallocene molecules found in the Cambridge Structural Database as a function of the relative orientation given by the angular parameters γ and ϕ (see Fig. 2). The numbers in the x and y axes indicate the highest value of the corresponding parameter for each interval.

around 60 and 0°. Although the experimental structures tend to adopt shorter distances than those obtained from the calculated energy minima, the correlation between intermolecular distance and orientation found in the structural data is in excellent qualitative agreement with our computational conclusions.

The prediction of a preference for contacts with an orientation angle close to 90° is in excellent agreement with the orientation found, *e.g.*, in the monoclinic form of ferrocene,[24] or in related systems such as benzene or dibenzenechromium.[3] To see how general such behavior is, we plot the frequency of structures with each pair of (γ, ϕ) values (Fig. 8). There it can be seen that for $\gamma \approx 0°$ the most frequent orientation corresponds to $\phi \approx 90°$, as predicted by the calculations. Another feature of that distribution is the large frequency of contacts defined by angles close to (50°, 90°), in fair agreement with the expected stability of the (60°, 90°) orientation according to the pairwise interaction energies (Fig. 4). In general, the most common orientations (*i.e.*, those with the highest frequencies) correspond to angle pairs that are expected to be stable enough. Nevertheless, the overall distribution pattern for such a variety of metallocenes cannot be accounted for by the present calculations with two cobaltocene molecules, even if clear orientation preferences are apparent in the structural data.

The topology of the Cp · · · Cp interactions in the preferred orientation, defined by the angles (0°, 90°) is similar to the Ph · · · Ph herringbone interactions known to be a major driving force in the organization of crystal structures of phenyl-substituted compounds.[25] The greater stability of the perpendicular orientation can be interpreted in terms of the Hunter–Sanders rules[26] as a preference for the σ–π interaction at short distances. These kinds of intermolecular σ–π contacts can be described as CH/π interactions[27] where the C–H bonds act as σ acceptors toward the π system of a neighboring molecule. The presence of substituents in the Cp ring can control the strength of the intermolecular interaction, as previously reported for benzene derivatives.[28] Thus, the σ and π donor/acceptor abilities of a substituted aromatic ring can be associated with the inductive and resonant components of the empirical Hammett parameter, providing a simple way to fine tune the strength of such interactions.

Conclusions

For a bimolecular model $[Co(\eta^5\text{-}Cp)_2]_2$, the relative energies of three different orientations calculated with a DFT or the semi-empirical PM3(tm) method differ by only 0.1 kcal mol^{-1}. The PM3(tm) interaction energies for such bimolecular aggregates have been evaluated at different orientations defined by the pair of angular coordinates (γ, ϕ) at a fixed Co · · · Co distance. The pairwise interaction energies seem to be little affected by the orientation of the two molecules, except for three of the studied geometries, corresponding to the angular coordinates (0°, 0°), (0°, 30°) and (60°, 60°), which appear to be between 1.5 and 3 kcal mol^{-1} higher.

The orientation was found to depend also on the intermolecular distance. Hence, at short Co · · · Co distances the dimer prefers a perpendicular geometry ($\phi = 90°$), while at distances larger than 7.3 Å an angular orientation is preferred.

In a heptamolecular model, the orientation of a cobaltocene molecule (defined by the rotation angle) has been studied in a frozen matrix of the six surrounding cobaltocenes. The orientation with $\phi = 90°$ is predicted to be the most stable one, and that with $\phi = 60°$ the most unstable one, some 5 kcal mol^{-1} above the minimum. The calculated interaction energies at different rotation angles for such a model are seen to be well predicted by the sum of the pairwise interaction energies.

A structural database analysis of the unsubstituted metallocenes of transition metals supports the main conclusions of our theoretical study on cobaltocene aggregates. For *short* M · · · M distances, the perpendicular orientation is favored ($\phi \approx 90°$), while for larger distances the values of ϕ cluster around 60 and 0°. Also the experimental distribution of the angular parameters ϕ and γ shows that the most common orientations of neighboring metallocene molecules are predicted by the calculations to be low energy ones. However, understanding the fine details of the experimental angular distribution of contacts between metallocenes requires a more detailed study in which other factors, such as the nature of the metal atom or the counterions present in the structure, are taken into account.

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