Quantum Chemical Study of Three Polymorphs of the Mononuclear Spin-Transition Complex [Fe(DPPA)(NCS)$_2$]

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The calculations of the high spin (HS) and low spin (LS) states of the [Fe^{II}(DPPA)(NCS)$_2$] complex have been performed at three experimentally observed geometries corresponding to three synthesized polymorphs with different spin-transition behavior. The structure optimization leads to a single molecular structure, suggesting that the existence of three geometries is not an intrinsic phenomenon but is induced by the crystal lattice. The structural difference between three forms can be reproduced by introducing the Madelung field of the crystal lattice. However, the calculations show that the differences in magnetic behavior of the three polymorphs cannot be attributed only to variations of the energy gap between two spin states.

Introduction

The studies of the thermal spin transition in transition metal complexes have developed considerably in the last fifteen years.[1] These studies mainly concern compounds of iron (II) and to a lesser extent iron (III), cobalt (II), and, in a few cases, other metals. The synthesis of new spin-transition systems and the accumulation of new experimental data provided a deeper insight into the microscopic mechanism of this fundamentally interesting phenomenon that is potentially valuable for applications. At the molecular scale, the spin transition results from the excitation of two electrons from the t_{2g} orbitals that are completely filled in the low-spin (LS) state into empty e_g states leading to the high-spin quintet state. The prerequisite for such excitation is the closeness of the ligand field strength and the interelectronic interaction. The efforts of synthetic chemists are concentrated on the design of molecular structures satisfying this condition.

However, the characteristics of spin transition are not only defined at the molecular level. The excitation of two electrons to an antibonding orbital is accompanied by the breathing of the metal ion coordination sphere, which in the case of iron (II) complexes can go up to 0.2 Å. Thus, the information about the spin transition is transferred to neighboring molecules through intermolecular interactions, such as van der Waals contacts, hydrogen bonds, and π-stacking. These interactions are responsible for the cooperative character of the spin transition, which can vary from a continuous (extended over rather large temperature range) to a very abrupt transition, sometimes with a hysteresis. Although, several phenomenological models,[2] featuring elastic interactions, have been proposed to describe the nature of the spin transition in a crystal, the microscopic mechanism of the collective phenomena is far from being fully understood.

The special place in the analysis of the spin transition shaping by crystal packing effects is occupied by polymorphic systems. Several examples are described in the literature,[3−8] when the same molecular system crystallizes in different structures and the manifestation of the spin transition in these structures is different. A striking example of such an effect is given by the recently synthesized mononuclear complex [Fe^{II}(DPPA)(NCS)$_2$] (DPPA = (3-aminopropyl)bis(2-pyridylmethyl)amine].[6] This complex forms three polymorphs at room temperature, named A, B, and C. Polymorph A crystallizes in the $P1$ triclinic space group, whereas the B and C polymorphs crystallize in the $P2_1/c$ monoclinic and the $Pbca$ orthorhombic space groups, respectively. The magnetic and Mössbauer measurements revealed that polymorph A undergoes a rather gradual spin transition at 176 K. Polymorph B remains in the HS state in the whole 4.5−295 K temperature range. And finally, polymorph C exhibits a very abrupt spin transition with hysteresis at 112 and 120 K in the cooling and warming modes, respectively. The X-ray crystallographic studies at room temperature have shown that the structure of the asymmetric unit in the three polymorphs is almost identical with the same configuration and conformation. However, the small differences in the coordination spheres of the [Fe(DPPA)(NCS)$_2$] complex in the three polymorphs were analyzed in ref 6 within the ligand−field model to explain the different magnetic behavior.

In the present paper, we describe the results of quantum chemical DFT (Density Functional Theory) calculations of the [Fe(DPPA)(NCS)$_2$] compound. Of course, periodic calculations of this compound at three different crystallographic structures should give important information about the origin of their different magnetic behavior. However, such calculations involve difficult methodological problems, and the development of corresponding theoretical approaches presents a challenge for future studies. Instead, we perform calculations of the [Fe(DPPA)(NCS)$_2$] complex, simulating in some cases the crystal environment. The examples of such molecular calculations of spin-transition systems are also rather scarce, and no generally accepted methodology exists for such calculations. In particular, different exchange correlation functionals have been suggested to correctly reproduce the energy gap between the LS and HS states.[9−12] Studies of *the same* molecular system at different geometries have an important advantage. Even if the calculations do not give exact values of the energy gap, one can hope to describe a tendency in the behavior of this important parameter. Recently, we demonstrated the usefulness of quantum chemical DFT approaches in the analysis of the order−disorder phenomena in the coordination sphere of spin-transition complexes,

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when the electronic structure of the same complex is considered at different geometries.[13,14]

Computational Method

DFT calculations of the [Fe(DPPA)(NCS)$_2$] complex have been carried out with the *Gaussian 98* package.[15] The restricted Kohn−Sham calculations have been performed for molecules with singlet states and unrestricted DFT calculations for the HS quintet states. Two hybrid DFT methods have been used: The standard B3LYP[16] was used as implemented in *Gaussian 98* and the reparametrized version B3LYP*,[11] differing from B3LYP by the coefficient for the Hartree−Fock exchange. The B3LYP* functional has been proposed especially for spin-transition systems, as it has been shown to give the correct order of spin states at optimized geometries, with the LS state lying lower than the HS state. The LANL2DZ basis set, including the double-ζ basis set with the Los Alamos effective core potential for Fe and the Dunning−Huzinaga all-electron double-ζ basis set with polarization functions for the H, C, and N atoms,[17,18] has been used. The spin eigenvalue $\langle S^2\rangle$ for the HS state varied in the range 6.03−6.04, confirming good quality of the obtained wave functions. The incertitude of the energy value after electronic relaxation was less then 10^{-6} au. The MOLEKEL software[19] was used for all molecular visualization.

Results and Discussion

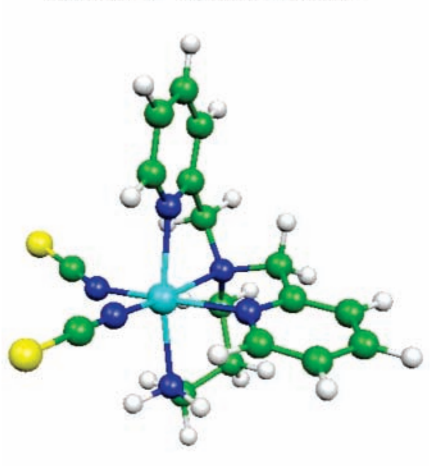
At the first step, single-point calculations for experimental structures[6] of the [Fe(DPPA)(NCS)$_2$] complex in three polymorphs at room temperature have been performed in the HS state. Surprisingly, the total energy difference was found to be very large (about 500 kJ/mol), which does not agree with the coexistence of all polymorphs. As such difference may be due to the positions of hydrogen atoms, which correspond to their involvement in hydrogen bonding in the crystal, we performed the optimization of all hydrogen atom positions in all structures. After such optimization, the total energy differences become lower than 10 kJ/mol, which seems far more reasonable. Then, the LS states were calculated for the three obtained structures, and in all cases, they lie higher than the HS states. The energy gaps, calculated with the B3LYP* functional, have been found equal to 68.6, 70.1, and 68.9 kJ/mol, for the A, B, and C polymorphs, respectively. The order of the three values qualitatively agrees with the experimental observations, indicating that at high temperature the structure most distant from the spin transition is polymorph B (no transition at all), followed by polymorphs C (with $T_c\uparrow = 120$ K and $T_c\downarrow = 112$ K) and A ($T_c = 176$ K). However, the calculated difference between energy gaps is too small and lies within the precision of the calculation method.

At the next step, we performed a total optimization of the molecular geometry. The experimental geometries of the complex in the three polymorphs were taken as departure points. For all three polymorphs, the unit cell contain pairs of enantiomeric *fac*-[Fe(DPPA)(NCS)$_2$] (one, two, and four for polymorphs A, B, and C, respectively).[6] The experimental data given in ref 6 correspond to enantiomer Δ in polymorph A and to enantiomer Λ in polymorphs B and C. The calculations taking as the departure point structures B and C converged to the same optimized structure, whereas the calculations starting from structure A converged to its mirror image. These results show that the existence of three polymorphs does not arise from the existence of several minima on the potential energy surface, corresponding to quasi-equienergetic isomers of the complex. It means that the difference in magnetic behavior must be looked for entirely in the crystal packing effects. The optimized structure was also calculated for the LS state. The calculations with the geometry optimization have been performed with both B3LYP and B3LYP* functionals. We must note that, as in previously documented cases,[11,20] only the B3LYP* functional gives a correct order of spin levels with the optimized LS state lying lower than the optimized HS state. Therefore, only the results obtained with this functional will be presented further on. The energy gap between the LS and HS states was found equal to 15.6 kJ/mol. This value is higher than the 6.8 kJ/mol obtained from the fitting of the experimental Mössbauer data with the mean field equation of the two-level Ising-like model.[6] This difference can be attributed to the fact that a simple molecular approach does not reproduce all the energetics of the spin crossover. The neglect of zero-point vibrations also can be responsible for the overestimation of the energy gap.

To study the influence of the vibrational zero-point energy (ZPE) on the LS−HS energy gap, we performed calculations of vibrational frequencies in the HS and LS states. The modified energy gap $\Delta E^\circ = \Delta E^{\mathrm{el}} + \Delta^{\mathrm{ZPE}}$ becomes equal to 4.1 kJ/mol, which is closer to the estimated Ising model parameter. It is very difficult to make a complete assignment of observed vibrational modes to calculated ones because of the important number of observed lines. The comparison of vibrational frequencies in two spin states is also complicated by the different composition of normal vibrations resulting from the difference in the force field. To perform such an analysis, we proposed to project vibrational modes of one spin state on those from another state and consider the pairs giving a maximal projection coefficient.[21] The analysis is most straightforward for characteristic vibrations such as stretching vibrations of NCS ligands. As the [Fe(DPPA)(NCS)$_2$] contains two NCS ligands, in the vibrational spectrum, the symmetric and antisymmetric combinations of corresponding vibrations are present. The projection coefficients between the HS and LS states for these vibrations are close to 1. We obtain for the vibrational frequencies 2042 and 2060 cm^{-1} in the HS state and 2096 and 2109 cm^{-1} in the LS state. The calculated values are in a good agreement with the experimentally observed frequencies at room temperature (2065 and 2079 cm^{-1} for polymorph A and 2053 and 2071 cm^{-1} for polymorph B).

Although the optimized structure in the HS state reproduces rather well the geometric parameters of the first coordination sphere, the visual comparison of optimized and experimental structures clearly evidences some differences (Figure 1). Until now, we completely ignored the effects of the crystal environment on the studied complex. Different methods of cluster embedding for bulk solids or surfaces were described recently in the literature,[22,23] but to our knowledge, only once was the Madelung field included in calculations of the LS−HS gap.[24] To take into account the crystal effects, we surrounded the complex studied quantum mechanically by point charges representing all atoms of complexes with metal atoms separated from the central Fe atom by distances less than 15 Å for a given crystal structure. This approach resulted in the model presented in Figure 2. The point charges representing the environment were calculated as natural charges of the complex at the experimental geometry. First, we again calculated the energy of the central complex in the HS and LS states at experimental geometry, but now in the presence of point charges. The energy gap between the ground HS and excited LS states were found equal to 80.5, 51.0, and 59.3 kJ/mol for polymorphs A, B, and C, respectively. It can be seen that polymorph B, which in reality remains in the HS state, is energetically closer to the spin

Polymorph C – experimental structure



Polymorphs A, B, and C – optimized structure

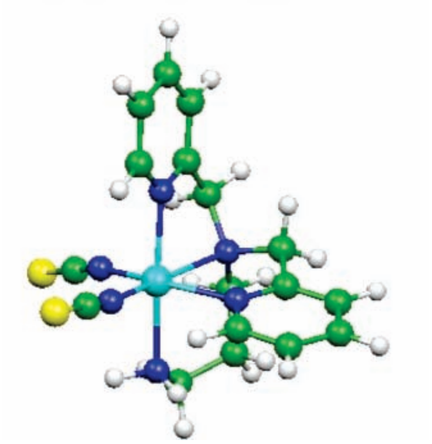


Figure 1. Ball-and-stick representations of the experimental (polymorph C) and optimized structures of the [Fe(DPPA)(NCS)$_2$] complex.

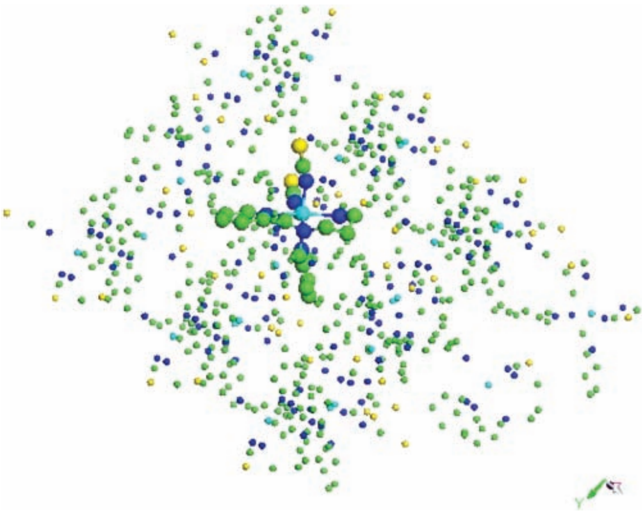
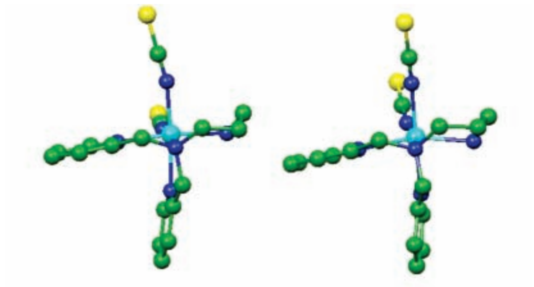
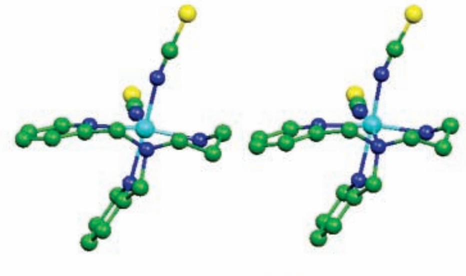


Figure 2. Schematic representation of the [Fe(DPPA)(NCS)$_2$] complex surrounded by point charges modeling the crystal environment.

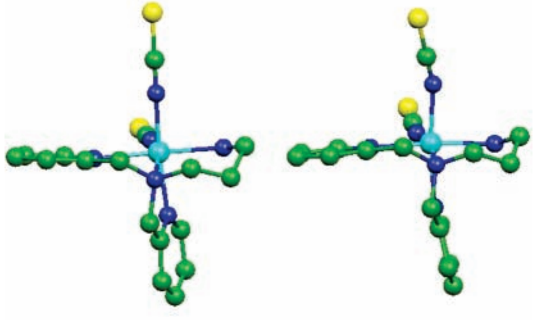
transition than polymorphs A and C. However, our model does not take into account the modification of the Madelung field, which should accompany such a transition. In fact, our results suggest that the transition of a complex to the LS state is more advantageous in polymorph B, if the environment remains in the HS state. The account of structural transformations in the crystal lattice seems essential to explain different behavior of three polymorphs.



Polymorph A



Polymorph B



Polymorph C

Figure 3. Ball-and-stick representations of the experimental (left) and optimized in the presence of the Madelung field (right) structures of the [Fe(DPPA)(NCS)$_2$] complex in polymorphs A, B, and C.

We also performed the optimization of the molecular structure in the presence of point charges modeling the crystal environment. The optimization procedure converged to three different structures. Although the calculations overestimate metal–nitrogen distances in the HS state, as has already been observed for the [Fe(phen)$_2$(NCS)$_2$] complex,[11] the general shapes of the optimized structures are very similar to the experimental ones observed in the three polymorphs (Figure 3). In particular, we were able to reproduce a strong reduction of the dihedral angle between the pyridine planes of the ligand, observed for polymorph B. It has been proposed[6] that this reduction can be due to the presence of strained regions in B, which may be responsible for the stabilization of the HS ground state. This result demonstrates that an account of the crystal environment, even within a simple point-charge approach, can lead to the essential improvement in the description of spin-transition systems.

Conclusion

The results of our DFT calculations for the same spin-transition molecule allow one to attribute different magnetic behavior of the three polymorphs not only to the molecular geometry but also to crystal lattice effects. For the first time, we performed DFT calculations of spin-transition systems with inclusion of the crystal environment. Such calculations give a better energetic and structural description of complexes. Further calculations, also exploring low-temperature crystal structures, should be useful. Even in the absence of periodic crystal calculations, this approach can provide important information about microscopic mechanisms of the spin transition.

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References and Notes

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