

Explanation of the site-specific spin crossover in $\text{Fe}(\text{mtz})_6(\text{BF}_4)_2$

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Abstract

The spin crossover behavior of the two $[\text{Fe}(\text{mtz})_6]^{2+}$ complexes occupying different lattice sites in $\text{Fe}(\text{mtz})_6(\text{BF}_4)_2$ is addressed by combining quantum chemical calculations with a careful analysis of the crystal structure. It is first established from the calculations that the energy difference between high spin and low spin states depend on the orientation of the tetrazole ligands; small rotation angles favor the low spin state, while for angles larger than $\sim 20^\circ$ the high spin state is more stable. The crystal structure shows that the two complexes have different average rotation angles of the ligands. It is larger for the site that remains HS down to low temperatures and smaller for the site that shows spin crossover to LS. The origin of the different rotation angles is found to be determined by a subtle interplay amongst steric repulsion between the ligands, $\text{H}\cdots\text{F}$ interactions between the complex and the counterions, and intersite interactions involving $\text{N}\cdots\text{H}$ contacts and $\pi - \pi$ interactions between the $\text{N}=\text{N}$ double bonds of the tetrazole rings.

1. Introduction

The spin crossover (SCO) phenomenon attracted considerable attention because it can lead to materials with a magnetic bistability; two different (meta-) stable phases can be observed under the same external conditions. When such bistability can be realized under normal conditions, and switching between the phases can be done in a fast and controlled manner, the way lies open to interesting technological applications.¹⁻⁷

In many cases, SCO materials are molecular systems with a first-row transition metal (TM) in the center of the complex. SCO is mostly observed for TMs with 3d⁴ to 3d⁷ electronic configurations and the prototype material is based on a Fe(II) ion coordinated by six N atoms in a quasi-octahedral fashion. The occupation of the valence 3d-shell is dictated by the ligand field. An octahedral field splits the d-levels into t_{2g} and e_g subshells. In a strong field all six valence electrons associated to Fe(II) are in the t_{2g} orbitals, leading to complete electron pairing, and hence, a low spin (LS) singlet state. For weaker ligand fields, two electrons are in e_g orbitals and such electron configuration corresponds to the high spin (HS) quintet state. Unlike t_{2g} orbitals, e_g orbitals are pointing in the direction of the ligands, leading to a much stronger anti-bonding character of the e_g orbitals. The electrons in these orbitals push the ligands away from the central Fe(II) ion in the HS state and increase the equilibrium metal-to-ligand distances upon the SCO transition by approximately 0.2 Å. Typical energy differences between the two spin states are in the range of 0 – 2000 cm⁻¹.

Switching between the LS and HS states can be done by varying temperature, applying pressure or light irradiation. In the first and the second case the population of the LS and HS states is fully determined by thermodynamic equilibrium and such transitions are called temperature- and pressure-induced spin crossover transitions.⁸⁻¹² In case of light-induced spin crossover, after initial excitation to d-states or to metal-to-ligand charge transfer states, the system undergoes a complex cascade of intermediate transitions and eventually gets trapped in a non-equilibrium metastable state. The whole process is called light-induced excited spin state trapping (LIESST). The details of LIESST process are still under debate.¹³⁻²⁶

In this work we focus on the thermal SCO and emphasize the importance of the geometrical degrees of freedom in addition to the metal-ligand distance for the process. At thermodynamic equilibrium, the temperature of the system determines the population of the LS and HS states. The transition temperature $T_{1/2}$ is defined as the temperature where the two states are equally populated. This corresponds to the change in the Gibbs free energy (ΔG) between the HS and LS states being equal to zero. At constant pressure, ΔG contains both enthalpy and entropy contributions. The entropy contribution is dominated by the vibrational term and always favors the HS state. The enthalpy contribution, on the other hand can be either negative or positive. It is important to highlight for further discussion that the enthalpy contribution has to be positive in order for the thermal spin crossover to take place. If it is negative the system will remain in the HS state at thermodynamic equilibrium independent of the temperature. Photo-induced spin crossover at such conditions is still possible.

Steric effects and crystal packing influence the molecular geometry and can play crucial role in condensed systems such as porous metal-organic frameworks^{2, 27} and SCO molecular crystals²⁸⁻³⁰. In this work we strive to understand the mechanism of the thermal SCO transition in the $\text{Fe}(\text{mtz})_6(\text{BF}_4)_2$ compound (mtz=5-methyl-1H-tetrazole). From the crystallographic and magnetic susceptibility data it is known that only half of the $[\text{Fe}(\text{mtz})_6]^{2+}$ units is susceptible to thermal spin crossover^{29, 30}. Site A undergoes thermal SCO at 78 K, while site B remains in HS down to 10 K. The reason for the different behavior of the two sites is not fully understood. Examination of the crystal structures reveals that the only substantial geometrical difference between the two sites is the ligand rotation angle of the $[\text{Fe}(\text{mtz})_6]^{2+}$ units, shown in Figure 1, which in site A is 12.5° on average and 21° for site B. These angles are practically independent of the spin state of a given site³⁰. This fact motivated us to scan the potential energy surface in two dimensions. In addition to changing the metal-ligand distance, we also vary the rotation of the methyl-tetrazole groups around the Fe-N bonds. Calculations on different models for the material enable us to unravel the different behavior of site A and B. Steric repulsion between the ligands, H

bonding with the counterions and interunit $\text{N}\cdots\text{H}$ contacts influence the rotation angle, and in this way the relative stability of the HS and LS states of the $[\text{Fe}(\text{mtz})_6]^{2+}$ units.

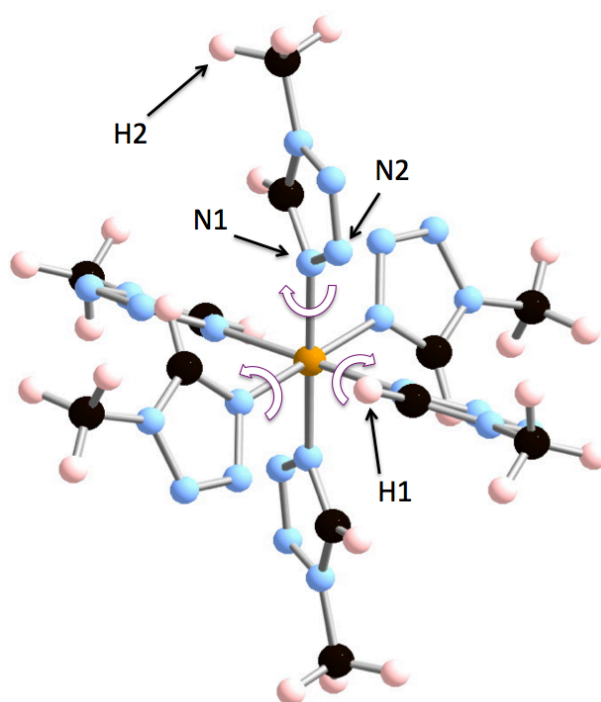


Figure 1. $[\text{Fe}(\text{mtz})_6]^{2+}$ molecular complex. Fe is in the center of the complex (yellow sphere), N atoms in blue, C atoms in black and H in pink. Arrows indicate the ligand rotations.

2. Computational Information

In this work we combine density functional theory (DFT) to optimize geometries and calculate frequencies with accurate wave function based methods to calculate energy differences. DFT is a computationally efficient method for performing geometry optimization with relatively high accuracy, but its performance for describing energy differences between states with different spin in TM based compounds is heavily debated in the literature³¹⁻⁴⁵. On the other hand, multiconfigurational second-order perturbation theory (CASPT2) has amply proven its ability to provide accurate vertical and adiabatic relative energies, while geometry optimizations are only possible for small systems⁴⁶⁻⁵⁹.

DFT calculations with the hybrid PBE0 functional were performed with TurboMole 6.3⁶⁰. The basis set is of valence triplet zeta + polarization quality for all atoms⁶¹ in the calculations on the isolated complex. When counterions are also considered, split-valence + polarization basis sets are applied. The CASPT2 calculations were done with Molcas⁷⁶²⁻⁶⁴ using a generally contracted basis set of the atomic natural orbital type^{65, 66}. This basis set is optimized for electron correlation in the valence shell and also between semi-core and valence electrons. Moreover, it is designed to accurately describe the scalar relativistic effects through the Douglas-Kroll-Hess Hamiltonian⁶⁷. The basis set contractions are as follows: Fe (7s,6p,5d,3f,2g,1h) and N(5s,4p,1d) for the central FeN₆ unit, smaller contractions of valence double zeta quality are used for the remaining atoms.

The scans of the CASPT2 potential energy surfaces were done in the following way. The geometry of an isolated 5-methyl-1H-tetrazole (mtz) molecule was optimized with CASPT2. Subsequently, six mzt ligands were attached to the Fe²⁺ ion in such a way that the whole complex possesses inversion symmetry, the rotation angle θ was initially set to 0° —ligand rings being coplanar with four N atoms of the first coordination sphere. By displacing six ligands equidistantly in Fe-N directions and calculating the CASPT2 energy in each point, potential energy curves for the LS and HS states have been computed. This procedure is repeated for a series of rotation angles to produce the two dimensional potential energy surface.

The CASPT2 energy of each point along the different scans and at the DFT optimized geometries has been calculated with a complete active space self-consistent field (CASSCF) reference wave function. The active space used to construct the CASSCF wave function contains 10 electrons and 12 orbitals. The active orbitals are the five Fe-3d orbitals, a second set of more diffuse Fe-d orbitals to account for the large electron correlation effects in the crowded d-shell, and two ligand orbitals. The presence of the latter orbitals ensures a correct treatment of the interaction between the N lone pairs and the electrons in the Fe-3d(e_g) orbitals. All electrons, except the deep core electrons (Fe-1s², 2s², 2p⁶ and C,N-1s²) are included in the second order perturbative treatment of the electron correlation by CASPT2.

Although the geometries of the calculated complexes are not strictly compatible with the O_h symmetry group, we will refer to the electronic states and the molecular orbitals with the labels of the octahedral symmetry.

3. Results and discussion

3.1 DFT geometry optimization and frequency calculation.

The most basic description of the material is obtained by optimizing the geometry for HS and LS of the isolated $[\text{Fe}(\text{mtz})_6]^{2+}$ complex. DFT/PBE0 gives an Fe-N distance of 2.017 Å for the LS and three slightly different distances for the HS state, ranging between 2.216 and 2.232 Å. This is in good agreement with experimental estimates of 1.991-2.031 Å and 2.178-2.187 Å for LS and HS, respectively. Bond distances and bond angles for the mtz ligand also compare quite well to experimental data. The situation is however dramatically different for the rotation angles of the ligand with respect to the Fe-N bond. Experimentally these angles are between 7 and 25 degrees, but the DFT optimization of the geometry leads to much larger angles of 52 (LS) and 49 (HS) degrees. These large rotation angles can be understood in light of the repulsion between the six ligands, which is smallest for angles near 50°. The fact that the geometry is optimized in vacuum makes that no other interactions counterbalance this stabilization, and hence, the minimum energy is encountered for rotation angles close to 50°.

From the DFT frequency results, the total zero point vibrational energy (ZPVE) change between the HS and LS states is -1042 cm^{-1} . This difference in the ZPVE mainly arises from the change in bonding within the first coordination sphere. Frequency analysis shows that the major contribution, namely 70%, is due to the change in the frequencies of those modes that involve off-center displacements of the Fe ion. The frequencies of the ligand vibrations are similar for HS and LS. These findings are in line with earlier studies on related compounds⁶⁸.

3.2 Potential energy surfaces

The scan of the CASPT2 potential energy curves as function of the Fe-N distance for $\theta = 0^\circ$ leads to slightly shorter optimal Fe-N distances than for the DFT/PBE0 optimization. The minima in the LS and HS curves are located at 1.930 Å and 2.141 Å, respectively. The energy difference between the HS and LS states ΔE_{HL} – calculated as $E_{\text{HS}}(r_{\text{eq}}^{\text{HS}}) - E_{\text{LS}}(r_{\text{eq}}^{\text{LS}})$ – is 1060 cm^{-1} . Since the

experimental data and the DFT geometry optimization indicate that the ligand rotation angle of 0° is not very realistic, it is interesting to investigate how ΔE_{HL} depends on θ . In order to explore the angular dependence of the relative stability, a series of potential energy curves has been computed for the range of ligand rotation angles from 0° to 70° . The results for the angles up to 60° are shown in Figure 2. In the first place, it can be seen that the total energy of both spin states is lowered when θ increases due to a reduction of the steric repulsion between the ligands. The minimum is reached near 50° , for larger angles the energy of both states start to increase again. Furthermore, the graphic shows that the optimal Fe-N distance does almost not depend on the rotation angle.

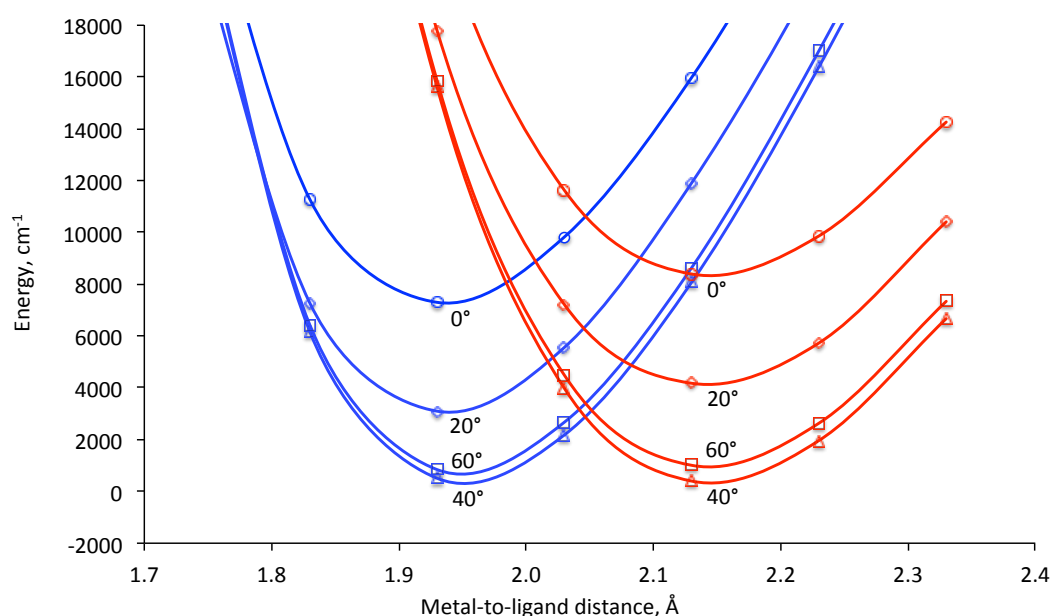


Figure 2. CASPT2 potential energy curves for LS (blue) and HS (red) along symmetric Fe-N stretch mode for different ligand rotation angles θ .

Although it can be seen in Figure 2 that the LS state has a lower energy than the HS state for small angles and that the relative stability is inverted for $\theta = 50^\circ$, the dependence of ΔE_{HL} on θ is better illustrated in Figure 3. The dashed line depicts ΔE_{HL} as function of the rotation angle. For small angles it remains nearly constant with the LS about 1000 cm^{-1} lower than the HS state. Starting at 20° , the energy difference decreases until the energy of the HS state becomes lower at angles around 40° . At $\theta \geq 60^\circ$ the situation is again

inverted. At the global minimum of the 2D scan, $\Delta E_{\text{HL}} = -180 \text{ cm}^{-1}$. Since the ZPVE favors the stability of the HS state, it has to be concluded that $[\text{Fe}(\text{mtz})_6]^{2+}$ behaves as a HS system in vacuum and cannot show thermal SCO on its own.

When considering the experimental average rotation angles, $\theta_{\text{avg}} = 12.5^\circ$ for site A and $\theta_{\text{avg}} = 21^\circ$ for site B, the calculated ΔE_{HL} is practically the same as for $\theta = 0^\circ$, and hence, does not explain the different behavior of the two sites. Furthermore, the relatively large value of ΔE_{HL} is incompatible with the experimental $T_{1/2}$ of 78 K for site A.

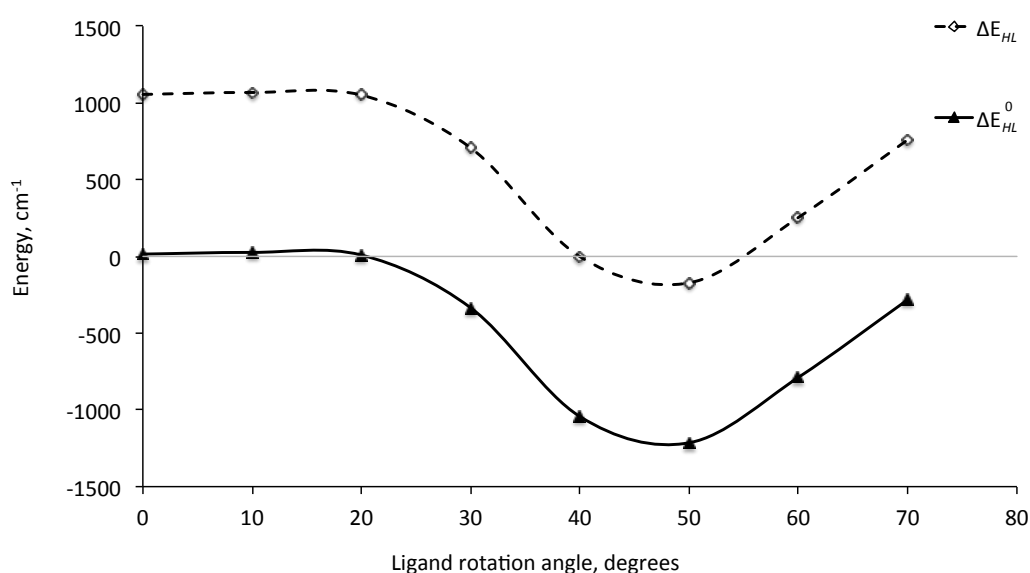


Figure 3. CASPT2 HS-LS energy difference ΔE_{HL} (dashed curve) and HS-LS zero-point energy difference ΔE_{HL}^0 (solid curve) as function of the ligand rotation angle.

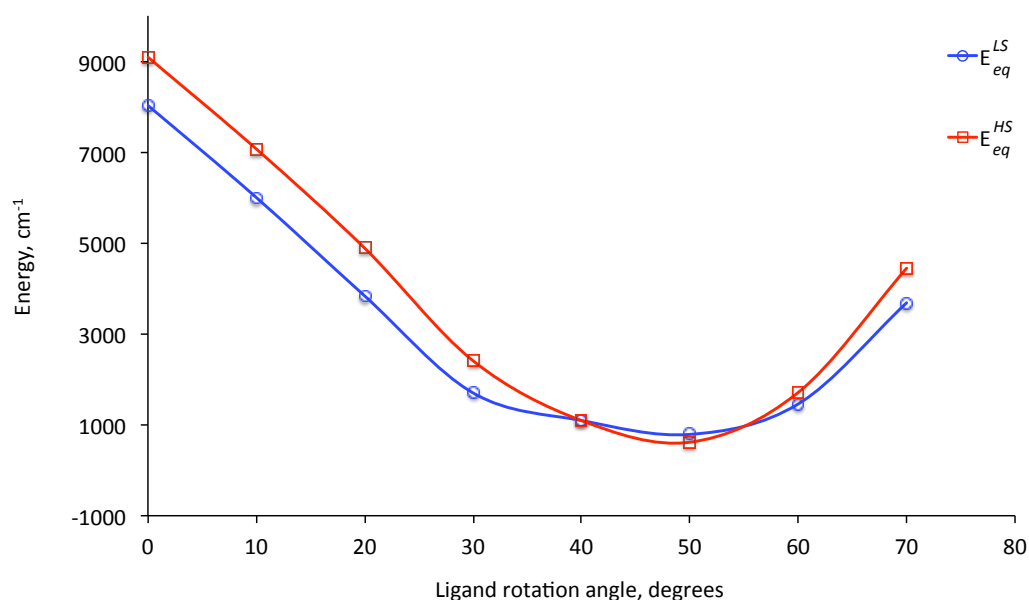


Figure 4. CASPT2 relative energies of LS (blue) and HS (red) along the ligand rotation angle.

However, the electronic energy is not the whole story. To obtain a more realistic picture of the relative stability of the HS and LS state, one has to take into account the zero point vibrational contribution. The continuous curve in Figure 3 was obtained by adding the calculated ZPVE (Sec. 3.1) to the dashed curve, obtaining in this way an estimate of the zero point energy difference ΔE_{HL}^0 as function of θ . Formally speaking, this correction can only be calculated for structures that correspond to minima on the PES and cannot be used to obtain the dependence of ΔE_{HL}^0 on the rotation angle. In order to correct the ΔE_{HL} curve for the zero-point energy, we assume that the correction calculated with DFT is approximately independent on the rotation angle. Actually, this assumption can be justified by looking at the energy curves of HS and LS depicted in Figure 4. These curves represent the energy dependence of the states on the rotation, and hence, the curvature is a measure of the vibrational frequency associated to this motion. Since this curvature is approximately the same for both states, the differential contribution to the ZPVE is small and can safely be neglected. The angle dependence of ΔE_{HL}^0 explains much better the SCO characteristics of the $[\text{Fe}(\text{mtz})_6]^{2+}$ complex than considering only the electronic energy. For small rotation angles up to $\sim 20^\circ$ the LS is slightly more stable than the HS, and for larger angles the situation is inverted. This is exactly in line with the

experimental observation that site A with the smaller θ_{avg} ($\sim 12^\circ$) is susceptible to SCO, while site B –showing larger angles of $\sim 21^\circ$ – is HS down to very low temperatures.

Analyzing the HS and LS structures, we observed two N...H interactions that change significantly with the rotation angle. In the first place there is a N...H interligand electrostatic interaction involving N1 and H1 with increasing distance when the angle increases (see atom labeling in Figure 1). The second N...H contact implies H1 and N2 and these two atoms become closer when θ becomes bigger.

To start with the first interaction, we observe that N1 and H1 accumulate the largest charges of all the ligand atoms; $q(\text{N1}) = -0.25$ (LS), $q(\text{N1}) = -0.31$ (HS) and $q(\text{H1}) = 0.19$, independent of θ . As can be seen in Table 1, the distance N...H is significantly smaller in the LS state compared to the HS, suggesting that this interaction is more important for the LS state. At small angles, the distance does not vary and ΔE_{HL}^0 is not affected, but as soon as the angle becomes 30° or larger, the N...H distance clearly increases, and the interaction weakens. This affects the energy of the LS state, while it only plays a minor role in the HS due to the larger N...H distances.

Table 1. Distances (in Å) between N1 and H1 and the calculated charges ⁶⁹ for the LS and HS states at different rotation angles θ . The labeling of the atoms is given in Figure 1.

θ	LS			HS		
	d(N1...H1)	q(N1)	q(H1)	d(N1...H1)	q(N1)	q(H1)
0°	2.628	-0.245	0.180	2.883	-0.303	0.181
15°	2.667	-0.247	0.188	2.940	-0.318	0.209
30°	2.802	-0.247	0.200	3.093	-0.314	0.199
45°	3.010	-0.250	0.207	3.313	-0.307	0.202

On the other hand, the rotation reduces the distance between N2 and H1. For $\theta = 0^\circ$, the atoms are separated by >3.6 Å and the repulsion between the two is small, both for the LS and the HS state. Upon the increase of the

rotation angle, the distance is decreased to reach a minimum around 50° . There, $d(\text{N2-H1})=2.3 \text{ \AA}$ in the HS state and $2.1 \text{ \AA}$ in the LS state. At these distances, the repulsion between H1 and N2 is significantly larger for the LS than for the HS. Both effects (the $\text{N1}\cdots\text{H1}$ contacts and the $\text{N2}\cdots\text{H1}$ repulsion) destabilize the LS state with respect to the HS state when the rotation increases. Hence, the observed behavior of ΔE_{HL}^0 depicted in Figure 3 can be explained by interligand contacts between N and H. The considered interactions are of course rather weak. Note, however, that ΔE_{HL}^0 is also rather small and the variations as function of θ as well.

In conclusion, the calculations on the complex in vacuum show that ΔE_{HL}^0 varies with the rotation angle and the origin of this dependence lies in interligand $\text{N}\cdots\text{H}$ contacts. The model does not correctly reproduce the experimental angle, since geometry optimizations lead to angles of approximately 45° for both spin states. However, the ΔE_{HL}^0 calculated at the experimental rotation angles is in agreement with the SCO behavior of the compound; site A can change from LS to HS, while site B behaves as a HS molecule at all temperatures. Given the importance of the ligand rotation for the relative stability of the two spin states, it is highly desirable to establish the driving force that leads to different rotation angles for site A and site B. In the next section we address this question by studying the effect of the environment on the site geometries.

3.3 Effect of the environment

Both the DFT geometry optimization and the CASPT2 scan of the energy places the optimal ligand rotation angle around 50° for the HS and LS state of the isolated $[\text{Fe}(\text{mtz})_6]^{2+}$ complex. To study the crystal packing effects on this geometric parameter, we have embedded the $[\text{Fe}(\text{mtz})_6]^{2+}$ unit in six $(\text{BF}_4)^-$ anions as illustrated in Figure 5. These counterions were clamped at the experimental positions³⁰ and the Fe ion was also fixed. This improvement in the representation of the crystal leaves the optimized bond distances and bond angles nearly unchanged but strongly affects the ligand rotation angles. The 'Single complex' entries of Table 2 show that all θ 's are close to zero for

both sites. The orientation of the ligands is ruled by the formation of hydrogen bonds between the negatively charged fluorine atoms of the counterions and the hydrogens of the mtz ligand. For site A, in four of the six ligands the distance between F and the H atom bounded to the carbon of the tetrazole ring (H1 in Figure 1) is smallest (<2.2 Å) when θ is close to zero and in the other two when the angles are around 10° . Formation of such short $\text{CH}\cdots\text{F}$ contacts is reported in literature and is known to have far-reaching effect on the properties of the materials.⁷⁰⁻⁷² For site B, all six $\text{H1}\cdots\text{F}$ distances are smallest for θ close to zero. The hydrogens of the methyl group (H2 in Figure 1) also interact with F, but the nearly free rotation of the CH_3 group makes these hydrogen bonds less determinative with respect to θ .

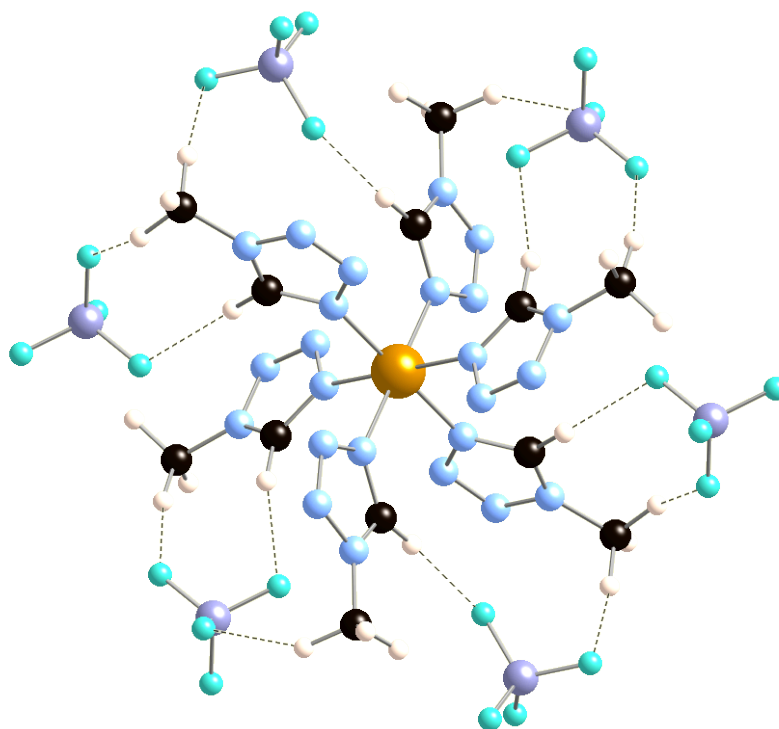


Figure 5. $[\text{Fe}(\text{mtz})_6]^{2+}$ embedded in six $(\text{BF}_4)^-$ counterions. The dashed lines indicate $\text{H}\cdots\text{F}$ contacts shorter than 2.2 Å.

These results confirm the hypothesis that the crystal packing largely affects the rotation angle and therewith plays an important role in the relative stability of the HS and LS states. The interaction with the counterions pushes the rotation angle to smaller values and according to results in Figure 3 both sites would undergo thermal spin crossover. Unlike the vacuum model, the model with inclusion of the nearest neighboring counterions is compatible with the occurrence of thermal SCO, but does not distinguish site A from site B.

Table 2. DFT/PBE0 ligand rotation angles θ (in degrees) obtained in restricted geometry optimizations of the single and double complexes representing site A and B. Numbering of the ligands is in accordance with Figure 6.

Ligand	Site A			Site B		
	Single complex	Double complex	Exp.	Single complex	Double complex	Exp.
1	3.2	17.1	17.1	1.1	17.8	24.8
2	3.3	14.1	13.7	0.6	21.2	17.4
3	12.7	5.5	6.8	1.7	17.8	21.8
4	3.2	1.2	17.1	0.9	0.9	24.9
5	3.3	0.5	13.7	0.3	-16.5	17.4
6	12.7	14.8	6.8	1.9	5.8	21.8
Average	6.4	12.2 ^(a)	12.5	1.1	18.9 ^(a)	21.3

(a): Averaging over ligand 1, 2, and 3.

The next improvement of the material model is to combine the two embedded complexes into one large cluster to treat site A and site B simultaneously. The resulting $\text{Fe}^{\text{A}}(\text{mtz})_6\text{Fe}^{\text{B}}(\text{mtz})_6(\text{BF}_4)_{12}$ model –schematically depicted in Figure 6– not only includes the hydrogen bonds between the TM complex and the counterions but also possible intersite interactions. Again we performed a restricted geometry optimization in which the BF_4 and the Fe ions are fixed at their experimental lattice positions. Ligands 1, 2 and 3 of each complex point in the direction of the other complex, the other three experience a similar environment as in the embedded single site cluster. Hence, it is not unexpected that the optimized rotation angles for the latter three remain practically the same both for site A and site B (with one exception), and that the ligands pointing to the other complex suffer moderate changes, especially for site B. The 'Double complex' entries in Table 2 show that the rotation angles of these ligands become larger and closer to the experimental values. When averaging the three relevant θ 's, we obtain $\theta_{\text{avg}}(\text{A})=12.2^\circ$ and $\theta_{\text{avg}}(\text{B})=18.9^\circ$. These values are in reasonable agreement with the average rotation angles of the crystal structure, but more

importantly, they are distinct for site A and site B. While the rotation angle for site A is still in the region where the LS is the most stable state, allowing for thermal SCO, the angle for site B is close to the borderline where the HS becomes the most stable one, in line with the HS nature of this site down to very low temperatures.

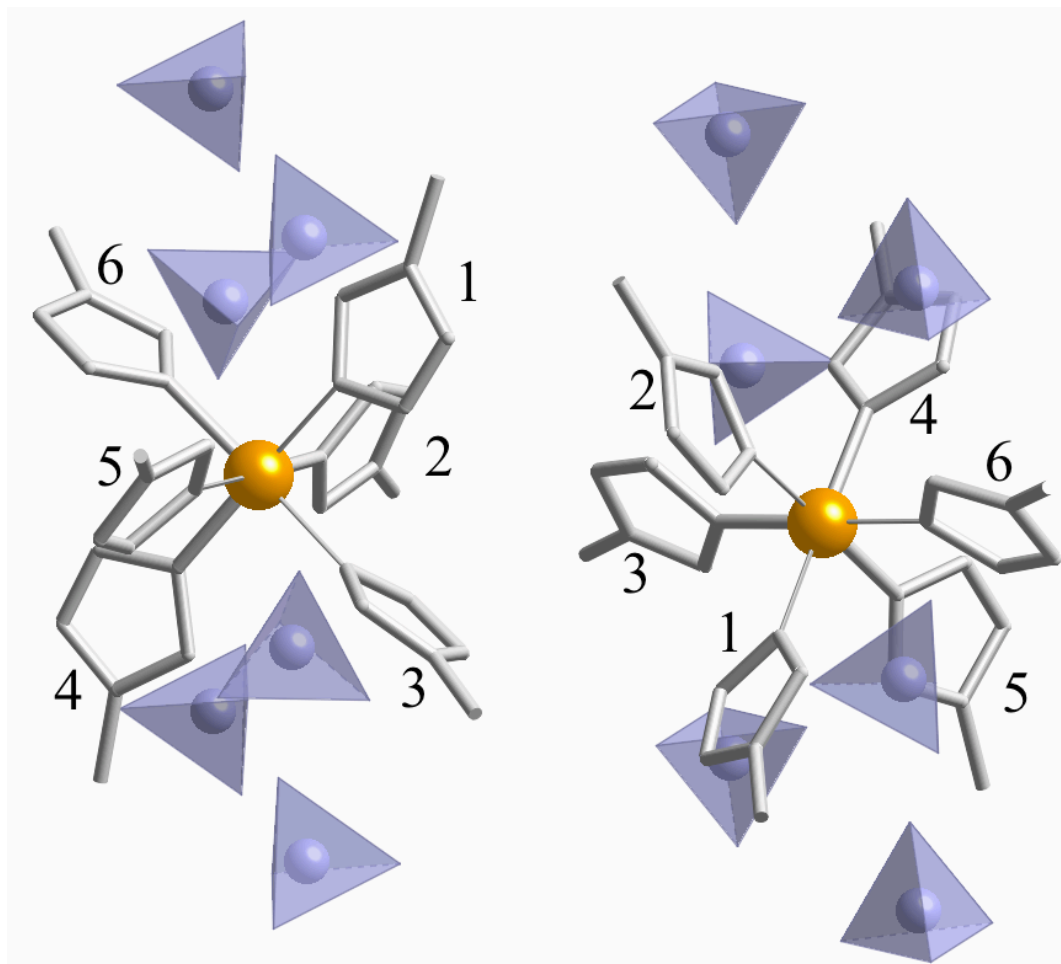


Figure 6. $[\text{Fe}^{\text{A}}(\text{mtz})_6 \text{Fe}^{\text{B}}(\text{mtz})_6]^{4+}$ embedded in twelve $(\text{BF}_4)^-$ counterions. Hydrogen and fluorine atoms are omitted for clarity. The BF_4 anions are represented by the purple tetrahedra and the tetrazole ligands with a stick representation. The numbering is used in Table 2. The complex on the left is site A, the one on the right corresponds to site B.

The most likely source of the changes in the rotation axis with respect to the 'Single complex' results are the presence of weak interunit interactions between the ligands of site A and site B, absent in the single complex treatments. The closest intersite contacts include $\text{N2}\cdots\text{H2}$ interactions over a distance of 2.6 Å, and there is also a possibility of $\pi - \pi$ interactions of the $\text{N}=\text{N}$ double bonds of the tetrazole ligands marked with '3' in Figure 6. These N atoms are separated by approximately 3.4 Å.

4. Conclusions

The two-dimensional potential energy scan shows that the HS-LS energy difference ΔE_{HL} of $\text{Fe}(\text{mtz})_6(\text{BF}_4)_2$ depends on the ligand rotation angle. For small angles the difference is nearly constant, favoring the LS state, but around 20° the difference becomes smaller and at 40° ΔE_{HL} changes sign. When the zero point energy correction is applied this inversion point is shifted to smaller angles, approximately 20° . This suggests two regimes of thermodynamic behavior: 1) in case of large rotation angles, the $[\text{Fe}(\text{mtz})_6]^{2+}$ complex behaves as a HS compound; 2) in case of small rotation angles, it is susceptible to thermal SCO. Such view is in a good agreement with the experimental data, which show that in the crystal the $[\text{Fe}(\text{mtz})_6]^{2+}$ complexes occupy two non-equivalent sites. Complexes on site B behave according to the first regime, site A complexes according to the second.

Crystal packing is the determining factor for the degree of ligand rotation at the different sites. There are three mechanisms that partially counterbalance each other and lead to the observed rotation angles. In the first place, the steric repulsion between the ligands of the same complex tend to put the ligands in between the planes formed by Fe and the N atoms coordinated to it. The geometry optimization of the complexes in vacuum nicely illustrates this tendency leading to rotation angles close to 50° . This reduction of the steric repulsion is hindered by the presence of hydrogen bonds between the H atoms of the tetrazoles and the F atoms of the counterions. The strongest $\text{H}\cdots\text{F}$ interactions are obtained when the ligand rotation angle stays close to zero. Finally, there are indications of intersite interactions that modify the rotation angle. These include $\text{N}\cdots\text{H}$ contacts of $\sim 2.6 \text{ \AA}$ and $\text{N}=\text{N}$ interactions at $\sim 3.4 \text{ \AA}$.

Combining the three effects using a large embedded cluster model containing two neighboring complexes (site A and site B) yields optimized rotation angles that are close to the experimental ones. The angles are on average larger for site B than for site A, which is in line with the possibility for SCO in site A and the HS character of site B even at low temperatures. The conclusions about the angle dependence of ΔE_{HL}^0 and the effects of the crystal

packing on the geometry of the complexes in the crystal can also be used to understand the SCO process in other complexes with monodentate ligands.

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