

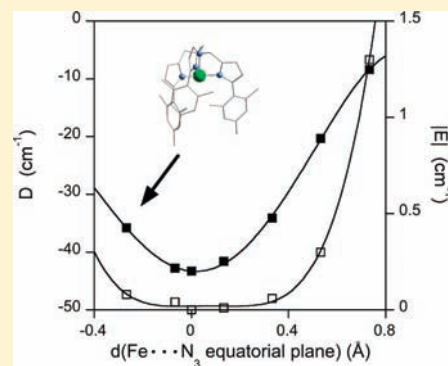
Mononuclear Fe^{II} Single-Molecule Magnets: A Theoretical Approach

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Supporting Information

ABSTRACT: The single-molecule magnet behavior found in mononuclear tetra-coordinate Fe^{II} complexes with trigonal monopyramidal coordination due to large magnetic anisotropy has been analyzed using theoretical methods based on CASSCF-RASSI calculations. We focus our study on the dependence of such magnetic properties on the geometrical parameters of the complexes (asymmetry of the ligands and the out-of-plane shift of the Fe^{II} cation with respect to the three equatorial nitrogen atoms) and the influence of the basicity of the N ligands. Low basicity, larger shifts, and larger distortions of the FeN₄ central framework decrease the *D* value and increase the *E* value. Also, we predict similar magnetic properties for similar pentacoordinate complexes adding an axial ligand that will increase the chemical stability of such systems.



1. INTRODUCTION

Since the discovery in 1993 of the slow relaxation of the magnetization in a Mn₁₂ complex by Gatteschi et al., many researchers have tried to synthesize new polynuclear complexes with a high-spin ground state (*S*) and a large negative magnetic anisotropy (*D*).^{1,2} It is common knowledge that the energy barrier that avoids the spin flip directly relates to the product of $|D| \cdot S^2$, providing a value of approximately 46 cm⁻¹ for the Mn₁₂ complex mentioned above. Despite the large number of research groups engaged in the development of complexes with an upgraded magnetic response (usually pursuing systems with a large number of paramagnetic centers in order to reach a high *S* value), only a couple of years ago, a Mn₆ complex synthesized by Brechin et al. slightly overcame the value of the barrier of the original Mn₁₂ complex.³

More recently, amazing results toward this goal have been obtained with mononuclear species capable of showing slow magnetic relaxations that can be a serious alternative to polynuclear complexes, especially because in principle, they can be easily deposited on surfaces to build up molecular devices. So far, there are only a few examples in the literature, the first two cases were both octacoordinate lanthanide complexes: a phthalocyanine double-decker complex with Tb⁴⁺ or Er^{III} encapsulated in a polyoxometalate framework.⁵ The [TbPc₂] complex exhibits an extremely high barrier; however, relevant tunneling effects make this application difficult for practical purposes.⁶ Also, Jian et al. reported a mononuclear dysprosium complex [Dy(acac)₃(H₂O)₂] featuring single-molecule magnet behavior.⁷ Lately, two new mononuclear complexes with slow magnetic relaxation have been obtained by Long et al., a prismatic trigonal U^{III} complex⁸ and the first 3d mononuclear complex in the literature, containing a tetra-coordinate Fe^{II} center

(A, see Figure 1) with a trigonal monopyramidal coordination.⁹ Harman et al. have expanded this family with related compounds (B, C, and E, see Figure 1).¹⁰ Concerning this matter, the goal of this paper is to analyze the magnetic properties of a variety of Fe^{II} complexes using theoretical methods and to give some insight into the design of systems with improved magnetic properties.

2. COMPUTATIONAL DETAILS

A two-step procedure has been used to calculate the ZFS parameters:¹¹ first, we have done a CASSCF calculation, and second, the energy of these CASSCF states has been mixed up within the SO-RASSI approach (MOLCAS code).¹² We have used an all-electron ANO-RCC basis set: Fe atoms (6s5p4d2f), N and O (4s3p1d), C (3s2p), and H (2s) with an active space considering the six d electrons of the Fe^{II} centers and the five d orbitals (6,5). All quintuplet (5), triplet (45), and singlet (50) states have been considered.

3. RESULTS AND DISCUSSION

Besides these compounds (A, B, C, and E), a search in the CSD database reported two more compounds with similar coordination spheres around the Fe^{II} cations (D and B', see Figure 1).^{10,14} The B' complex corresponds to a previous X-ray structure of complex B, showing different geometrical parameters (see complexes sorted from the least to the most symmetric in Table 1). This way, complexes A–C^{9,10,14} show three different Fe–N_{eq} distances, while complex D¹³ exhibits two equivalent distances out of three, and finally, complexes E and B' display three identical Fe–N_{eq} distances.^{9,10} Nevertheless, despite the high symmetry of the two

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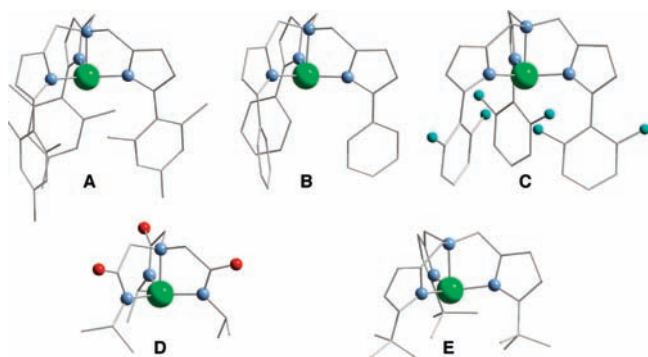


Figure 1. Structure of complexes $[\text{Fe}(\text{tpa}^{\text{Mes}})]^-$ (tpa = tris(pyrrolylmethyl)amine; Mes = mesityl)^{9,10} (A), $[\text{Fe}(\text{tpa}^{\text{Ph}})]^-$ (Ph = phenyl)^{10,14} (B), $[\text{Fe}(\text{tpa}^{\text{DFP}})]^-$ (DFP = 2,6-difluorophenyl)¹⁰ (C), $[\text{Fe}(\text{tcma}^{\text{i-Pr}})]^-$ (tcma = tris(carbamoyl-methyl)amine, *i*-Pr = *N*-isopropyl)¹³ (D), and $[\text{Fe}(\text{tpa}^{\text{t-Bu}})]^-$ (*t*-Bu = *tert*-butyl)¹⁰ (E). Light green, dark green, blue, and red spheres represent iron, fluorine, nitrogen, and oxygen atoms, respectively, while carbon atoms are represented as gray cylinders and hydrogen atoms are omitted for clarity.

Table 1. Calculated Values of D and E (in cm^{-1}) for the Six Fe^{II} Complexes (Sorted by Symmetry)^a

	D_{calc} ($ E_{\text{calc}} ^b$)	D_{exp} (E_{exp})	Fe–N _{eq}	Fe···N _{eq} plane ^c
A	–31.4 (0.6)	–39.6 (–0.4) ^d –44 (6) ^e	2.041 2.024 2.008	–0.265
B	–31.1 (0.6)	–26 (5)	2.019 2.016 2.013	–0.233
C	–16 (2.1)	–6.2 (0.1) $\pm 4.397(0.574)^f$	2.042 2.038 2.036	–0.290
D	–33.0 (0.4)		2.026 2×2.017	–0.233
E	–42.8 (0.001)	–48 (0.4)	3×2.031	–0.263
B'	–42.7 (0.002)		3×2.006	–0.254

^a The structural parameters (in Å) are provided to analyze their influence on the zero-field parameters. ^b The method allows only to estimate the absolute value of E (ref 11). ^c A negative value means the metal is below the equatorial plane (Figure 1). ^d Ref 9. ^e Ref 10. ^f Absolute values obtained from high field EPR measurements.

last compounds (E and B'), one should expect them to be distorted due to the presence of a Jahn–Teller effect, and this fact is discussed later on.¹⁰ A seventh compound has been described by Harman et al.¹⁰ However, it was not possible to obtain a satisfactory resolution of the crystal structure; thus, it will not be studied henceforth.

As Table 1 indicates, the calculated D values are in nice agreement with the experimental ones, corroborating the huge magnetic anisotropy of such systems. At this point, the difficulties in the achievement of proper experimental values should be stressed, because magnetization measurements usually give larger error bars and high field EPR is only applicable for the C complex (small D values will be also discussed later). It is important to keep in mind that the calculated values correspond only to the spin–orbit contribution, while the spin–spin term is not included. An estimation of such spin–spin contribution to

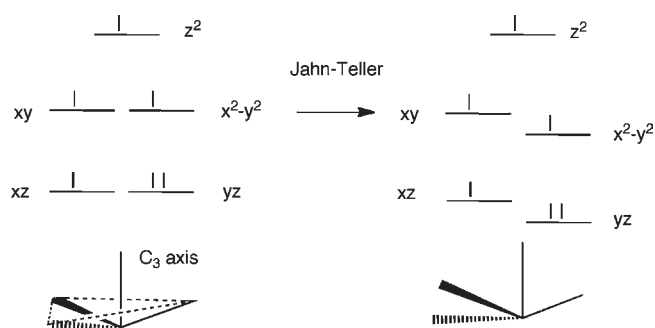


Figure 2. Splitting of the d orbitals for a nondistorted (left) and distorted (right) trigonal bipyramidal coordination.

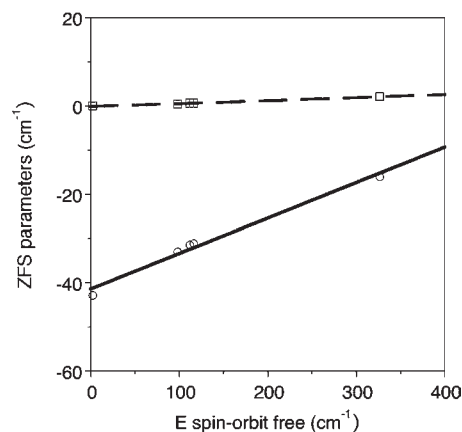


Figure 3. Dependence on the calculated zero-field splitting parameters D and $|E|$ (circles and squares, respectively) for the A–E complexes with the first spin–orbit free excitation energy calculated with the CASSCF method.

the D value was done with the ORCA code¹⁵ for complex A, providing a value of -0.5 cm^{-1} . Therefore, the inclusion of such a term does not modify considerably the calculated D values when there is a large spin–orbit term, which is the case for the trigonal bipyramidal complexes studied in this article.

To understand the reason for such a large anisotropy in these mononuclear Fe^{II} complexes, we have analyzed their electronic structures, where the splitting of the d orbitals is that represented in Figure 2, as pointed out previously by Freedman et al.⁹ In general, for a high spin $d^6 \text{Fe}^{\text{II}}$ complex, the degeneracy of the d_{yz} and d_{xy} orbitals results in a Jahn–Teller effect. Such distortion has been corroborated with the optimization (at DFT level using the B3LYP functional and a triple- ζ basis set, see geometry in the Supporting Information) of the B' compound that leads to three different distances and angles around the Fe^{II} center. For this optimized B' structure, the D value decreases (meanwhile, the E value increases) from -42.7 (0.002) to -32.5 (0.5) cm^{-1} . It is worth noting that the nonbonding character of such orbitals causes a tiny distortion of the symmetry and, consequently, a small deviation of the degeneracy. The main component of D will be D_{zz} , which is inversely proportional to the energy difference between the d_{xz} and d_{yz} orbitals (see eqs 1–4). Hence, the presence of excited states very close in energy is the reason for the very large D values; a linear correlation between the zero-field splitting parameters and the first excitation energy is found (see Figure 3). Regarding the E value and for a hypothetical symmetric

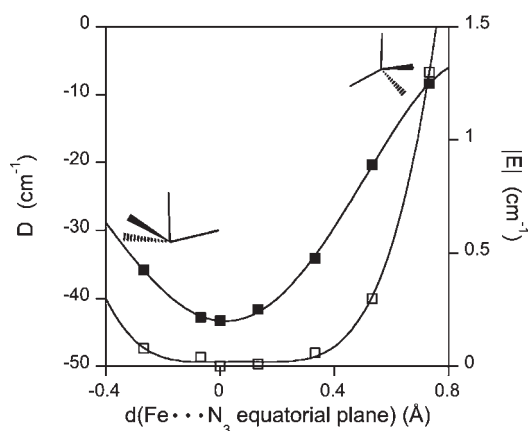


Figure 4. Dependence of the calculated D (black squares) and $|E|$ (white squares) values for a $[\text{Fe}(\text{NH}_3)_4]^{2+}$ model with the distance of the Fe^{II} center to the equatorial plane from a trigonal bipyramidal coordination (left) to a tetrahedral coordination (right).

complex, such a component must be zero. The inclusion of the geometrical distortion due to Jahn–Teller will give a non-negligible E value that is relatively small because the D_{xx} and D_{yy} are very similar (see eqs 1–4). For other metals, for instance, octahedral Mn^{III} centers are the source of magnetic anisotropy in many polynuclear single-molecule magnets, where antibonding d orbitals (e_g for octahedral symmetry) are involved, presenting large structural distortions. Such distortions give a large energy splitting of the degenerated orbitals, resulting in high first excitation energies (in general, around 10^4 cm^{-1} , while for the studied Fe^{II} complexes, they are close to 100 cm^{-1}) and, consequently, relatively small magnetic anisotropy.

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}); E = \frac{1}{2}(D_{xx} - D_{yy}) \quad (1)$$

$$D_{zz} \sim -(E_{yz} - E_{xz})^{-1} \quad (2)$$

$$D_{xx} \sim -(E_{yz} - E_{x^2-y^2})^{-1} \quad (3)$$

$$D_{yy} \sim -(E_{yz} - E_{xy})^{-1} \quad (4)$$

Recently, Palić et al. argued that the first-order orbital degeneracy of these Fe^{II} complexes leads to the strong magnetic anisotropy.¹⁶ However, such degeneracy must strictly appear in nondistorted complexes, which is not the case for the studied systems due to the Jahn–Teller effect. The analysis of the CASSCF-RASSI function indicates the presence around 20% of the orbital component for the studied nonsymmetric Fe^{II} complexes. The calculated D and E values indicate that small structural distortion in the $\text{Fe}-\text{N}$ equatorial distances from the symmetric structure results in large D parameters but also will facilitate the achievement of a negligible E value. This point is crucial because the latter is probably responsible for the presence of a large tunneling effect, as was pointed out by Freedman et al.⁹ Related to this matter, we believe that it would be interesting to consider the possibility of diluting the paramagnetic centers with similar diamagnetic complexes, for instance, with Zn^{II} related systems, as has been done in lanthanide systems, to investigate in more detail the relaxation mechanisms.¹⁷

Here, we have also analyzed the influence on the magnetic properties of the position of the Fe^{II} center with respect to the

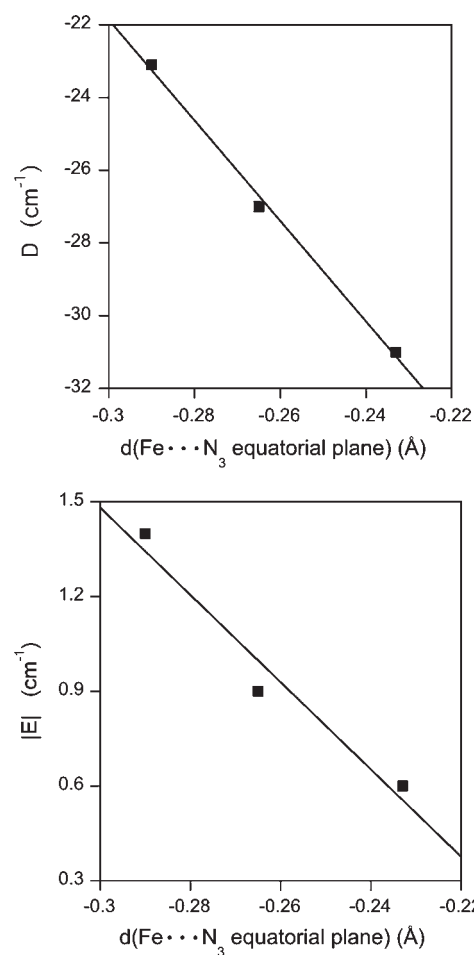


Figure 5. Dependence of the zero-field splitting parameters D (above) and E (below) with the out-of-plane shift of the Fe^{II} cation with respect to the equatorial plane containing the three nitrogen atoms of the ligands for the three nonsymmetric Fe^{II} complexes (A, B, and C) replacing the original substituents of the pyrrol by phenyl groups.

equatorial plane formed by the three nitrogen atoms. Calculated D and E values represented in Figure 4 have allowed us to extract the following conclusions: (i) The calculated D and E values obtained with the $[\text{Fe}(\text{NH}_3)_4]^{2+}$ model are close to those obtained for all of the above complexes (see Table 1). (ii) The largest D value corresponds to the species that present the Fe^{II} metallic center located in the equatorial plane of the three nitrogen atoms of the ligand. (iii) The E values reach a minimum when the Fe^{II} cation is placed in the equatorial plane (almost a negligible $|E|$ value of 0.0005 cm^{-1} was calculated), remaining relatively small for little shifts of the Fe^{II} center around this position.

Previously, Harman et al.¹⁰ linked the rising of the D parameter with the increasing of the ligand's basicity (from the most to the least basic behavior of the ligand: $\text{E}-\text{A}-\text{B}-\text{C}$); such a tendency was also reproduced with the experimental and calculated values here. To check for such a dependence, we have repeated the calculations of the A and C complexes using the substituent of the pyrrolic amine corresponding to the complex B, a phenyl group. The new $D(|E|)$ results for the phenyl-substituted A and C complexes, -27.0 (0.9) and -23.1 (1.4) cm^{-1} , respectively, confirm the role of the ligand basicity (together with the structural distortions of the complex). The decrease in the basicity for the

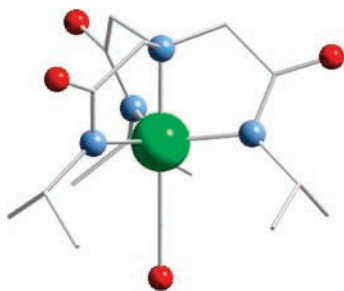


Figure 6. Structure of pentacoordinate TEQQA complex $[\text{Fe}(\text{tcma}^{i\text{-Pr}})(\text{CO})]^-$ (tcma = tris(carbamoyl-methyl)amine, *i*-Pr = N-isopropyl).¹⁸ Green, blue, and red spheres represent iron, nitrogen, and oxygen atoms, respectively, while carbon atoms are represented as gray cylinders and hydrogen atoms are omitted for clarity.

phenyl-substituted **A** complex causes a decrease in the D (E increases) value in comparison with the original one (-31.4 (0.6) cm^{-1}). On the other hand, the relatively low D value of the original **C** complex (D ($|E|$) = -16 (2.1) cm^{-1}) is clearly due to the presence of the least basic ligand containing fluoro groups in the substituent of the pyrrolic amine. A nice linear correlation between D (and E) and the out-of-plane shift of the Fe^{II} cation has been found, considering only the phenyl-substituted nonsymmetric Fe^{II} complexes (**A**, **B**, and **C**, see Figure 5). As expected, small out-of-plane shifts result in larger D values and smaller E values. Thus, our investigations have concluded that the basicity of the ligands and the degree of the structural distortion of the complex (asymmetry of the $\text{Fe}-\text{N}$ equatorial distances and out-of plane shift of the Fe^{II} atom) are the main parameters required to tune the magnetic anisotropy in this family of complexes.

In a practical way and due to the low coordination of the Fe^{II} center, these complexes are relatively unstable, and this aspect is the biggest problem for the application of this type of system. Hence, we have to consider how to increase such stability without a large change in the magnetic properties. One possibility that will not affect severely the electronic structure of the complex is the addition of a fifth ligand in the axial position of the Fe^{II} center. This ligand should basically affect the energy of the highest d_{z^2} orbital (see Figure 2), not being crucially related to zero-field splitting parameters. In the literature, there is a nice example of a complex with such coordination (see Figure 6, CSD refcode TEQQA).¹⁸ This complex presents the same ligand as the **D** complex (see Figure 1) but with a CO axial ligand. The calculated D and $|E|$ values are -29.7 and 1.2 cm^{-1} , while for the same complex without the CO ligand, they are -35.3 and 0.2 cm^{-1} , very close to those found for the **D** complex. These results present the TEQQA complex as a very attractive synthetic target due to the high anisotropy and larger stability compared to those of the tetracoordinate Fe^{II} complex.

4. CONCLUDING REMARKS

The origin of the large magnetic anisotropy of a family of mononuclear tetracoordinate Fe^{II} complexes with trigonal monopyramidal coordination due to large magnetic anisotropy has been analyzed using theoretical methods based on CASSCF-RASSI calculations. The existence of a Jahn–Teller distortion in the coordination sphere of the Fe^{II} centers able to break the degeneracy of the nonbonding d_{xz} and d_{yz} orbitals results in the presence of first excited states very close to the ground state in comparison with other metal cations. The zero-field splitting D

parameter is inversely proportional to the first excitation energies, being amazingly large for these Fe^{II} complexes. For instance, in the case of quasi-octahedral Mn^{III} cations, widely used in molecular magnetism to include magnetic anisotropy in polynuclear complexes, the involved e_g orbitals are antibonding. Thus, the geometrical distortion induced by the Jahn–Teller effect causes a large energy splitting of the degenerated orbitals, resulting in high first excitation energies and, consequently, relatively small magnetic anisotropy.

We analyzed the dependence of such magnetic properties on the geometrical parameters of the complexes (asymmetry of the ligands and the out-of-plane shift of the Fe^{II} cation with respect to the three equatorial nitrogen atoms) and also the influence of the basicity of the N ligands. The main dependence appears with the structural parameters; thus, larger shifts and larger distortions of the FeN_4 central framework decrease the D value and increase the E value. The basicity of the ligand also can modulate the magnetic anisotropy; a low basicity of the N ligands also decreases the D values.

Finally, we have explored how to improve the stability of such complexes, for instance, with the addition of a fifth ligand in the axial position of the Fe^{II} center that will not affect severely the electronic structure of the complex, mainly the energy of the highest d_{z^2} orbital. The results for the pentacoordinate TEQQA complex show only a slight reduction of the D value, but we expect a larger stability than the tetracoordinate Fe^{II} complexes.

■ ASSOCIATED CONTENT

S Supporting Information. Atomic coordinates of the calculated complexes and CASSCF energies and those of the optimized structure of complex **B'** at the B3LYP level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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