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Article

A Systematic Density Functional Study of the Zero-Field Splitting in Mn(II) Coordination Compounds

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This work presents a detailed evaluation of the performance of density functional theory (DFT) for the prediction of zero-field splittings (ZFSs) in Mn(II) coordination complexes. Eighteen experimentally well characterized four-, five-, and six-coordinate complexes of the general formula $[Mn(L)_nL'_2]$ with $L' = Cl$, Br, I, NCS, or N_3 ($L =$ an oligodentate ligand) are considered. Several DFT-based approaches for the prediction of the ZFSs are compared. For the estimation of the spin–orbit coupling (SOC) part of the ZFS, it was found that the Pederson–Khanna (PK) approach is more successful than the previously proposed quasi-restricted orbitals (QRO)-based method. In either case, accounting for the spin–spin (SS) interaction either with or without the inclusion of the spin-polarization effects improves the results. This argues for the physical necessity of accounting for this important contribution to the ZFS. On average, the SS contribution represents ∼30% of the axial D parameters. In addition to the SS part, the SOC contributions of d–d spin flip ($\alpha\beta$) and ligand-to-metal charge transfer excited states ($\beta\beta$) were found to dominate the SOC part of the D parameter; the observed near cancellation between the $\alpha\alpha$ and $\beta\alpha$ parts is discussed in the framework of the PK model. The calculations systematically (correlation coefficient ∼0.99) overestimate the experimental D values by ∼60%. Comparison of the signs of calculated and measured D values shows that the signs of the calculated axial ZFS parameters are unreliable once $E/D > 0.2$. Finally, we find that the calculated D and E/D values are highly sensitive to small structural changes. It is observed that the use of theoretically optimized geometries leads to a significant deterioration of the theoretical predictions relative to the experimental geometries derived from X-ray diffraction. The standard deviation of the theoretical predictions for the D values almost doubles from ∼0.1 to ∼0.2 cm^{-1} upon using quantum chemically optimized structures. We do not find any noticeable improvement in considering basis sets larger than standard double- (SVP) or triple-ζ (TZVP) basis sets or using functionals other than the BP functional.

1. Introduction

The existence of open-shell transition-metal ions in metalloenzymes allows their characterization by means of magnetochemical methods.[1] Among other transition-metal elements, manganese ions play a key role in a number of biological reactions.[2] A representative mononuclear metalloenzyme is manganese superoxide dismutase (MnSOD) that disproportionates superoxide to dioxygen and hydrogen peroxide.[3] A dinuclear manganese active site is found in the active site of manganese catalase, which catalyzes the disproportionation of H_2O_2.[4] An important biological function

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is performed by the tetranuclear manganese cluster, which catalyzes the oxidation of water to dioxygen, in photosystem II.[5]

Electron paramagnetic resonance (EPR) techniques provide information about the oxidation and spin states as well as the coordination geometry and the ligands around the magnetic transition-metal ions.[6] When EPR is applied to high-spin Mn(II) coordination compounds, an important piece of information that can be extracted from the analysis of EPR spectra is the splitting of the six magnetic sublevels of the ground state $S = {}^5/_2$ level in zero-magnetic field (zero-field splitting, ZFS). The splitting is parametrized by a term in the phenomenological spin-Hamiltonian (SH) that is biquadratic in the electron spin (**D** tensor; for reviews see refs 7 and 8). If the frame of reference is the principal axis system of the **D** tensor, only two parameters serve to completely characterize the biquadratic ZFS. These parameters are termed D and E; in a "proper"[9] coordinate system they obey $0 \leq E/D \leq {}^1/_3$. Typical values for $|D|$ in Mn(II) complexes fall in the range of 0−1.3 cm^{-1}.[10] The interpretation of these rather small D and E values in terms of the detailed coordination environment was found to be challenging since the physical origin of the ZFS tensor is fairly complex, with various contributions resulting from a variety of factors of different physical origins.[11,12] In this situation. quantum chemistry might play an essential role by (a) aiding in the interpretation and rationalization of the observed EPR spectra, (b) determining if a given proposed structure is in accord with the measured **D** tensor, and (c) elucidating in detail the physical factors that contribute to the observed ZFSs.

Theoretical studies of ZFS parameters on the basis of modern quantum chemical methods are still scarce.[7,10,13−17] From fundamental considerations, it is well-known that two physical factors contribute to the bilinear term in the ZFS: the direct dipole−dipole interaction of unpaired electrons (SS) and the spin−orbit coupling (SOC) of excited states into the ground state.[11] While the SS contribution has been largely discarded for the interpretation of the ZFS in transition-metal complexes, recent evidence suggests that this is not justified, at least not if $|D|$ is on the order of a few wavenumbers.[10,11] In fact, detailed calculations have been successfully applied for the prediction of the SS contribution to the ZFS in a variety of systems.[18−21] A recent calibration study[22] (DFT treatment) showed that the restricted open-shell Kohn−Sham (ROKS) approach led to better agreement with the experiment for the estimation of the SS contribution to ZFS in organic radicals compared with the unrestricted KS (UKS) approach. The physical origin of this effect was found to be subtle and was studied in comparison with high-level ab initio calculations.[22]

The interpretation of the SOC contribution to the ZFS has been extensively pursued on the basis of ligand field theory (LFT) in the literature.[23−29] LFT arguments were often used to give a qualitative scheme of the involved interactions, but failed at the quantitative level. In addition, frequently used ligand field equations that assume a proportionality between the **D** tensor and the g shift lack a solid theoretical foundation.[7,30,31] The general second-order perturbation of the ZFS tensor in terms of many-electron states has been known for quite a while.[30] It is, however, unsuitable to be directly applied in the context of DFT. Rather simple arguments have been brought forward in this context by Pederson and Khanna (PK).[14] Another equally simple treatment that seeks a connection to the many-electron treatment is the previously proposed quasi-restricted orbitals (QRO) method.[11] These perturbational methods have been successfully applied to large high-spin systems and will be considered in this paper together with the SS methods, cited above. Two component relativistic calculations of the SOC contribution to the ZFS have been considered for a few cases.[32] At the present level of development they appear to provide predictions that are similar to the computationally much

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cheaper perturbation-theory-based methods unless the SOC effects become very large.[32]

The main aim of the present paper is to determine how accurately the ZFS can be predicted for Mn(II) complexes. This complements our earlier works on the enolase active site[16] and the interpretation of the ZFS for Mn(II)−dihalide complexes.[10] The work presented here is an important prerequisite for future application studies since by applying the same methods to a sufficiently large set of Mn(II) complexes (18 compounds) with known structure and accurately determined (through high-field EPR) spectroscopic parameters the reliability and the systematic errors of the theoretical methodology are determined. Such errors are still significant if the calculations are based on present day DFT, and one hopes to correct for systematic deficiencies by calibration studies such as the one presented here. Finally, in addition to studying the importance of the functional and basis set as well as the relative contributions of the SS and SOC parts, some considerations of a qualitative nature are presented.

2. Theory

Orbital nondegenerate magnetic compounds with a total ground state spin $S > {}^1/_2$ are subject to zero-field splitting (ZFS) which describes the lifting of the degeneracy of the $2S + 1$ magnetic sublevels $M_S = S, S - 1, ..., -S$ even in the absence of an external magnetic field.[7,8] Perturbation theory has shown that the ZFS arises from two contributions:[7,9] (a) the direct spin−spin coupling (SS), originating from the dipole−dipole interactions of open-shell electron spins (to first order in perturbation theory) and (b) the spin−orbit coupling (SOC, to second order in perturbation theory).[7,11] Phenomenologically, these effects can be collected in a SH of the general form[8,23]

$$\hat{H}_{\mathrm{ZFS}} = \hat{S}\mathbf{D}\hat{S} \tag{1}$$

In a coordinate system that diagonalizes the **D** tensor, the ZFS Hamiltonian can be written as

$$\hat{H}_{\mathrm{ZFS}} = D\left(\hat{S}_z^2 - \frac{1}{3}\langle\hat{S}^2\rangle\right) + E(\hat{S}_x^2 - \hat{S}_y^2) \tag{2}$$

where D and E are the axial and rhombic ZFS parameters, respectively:

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}) \tag{3}$$

and

$$E = \frac{1}{2}(D_{xx} - D_{yy}) \tag{4}$$

2.1. Quasi-Restricted DFT Orbitals Approach (SOC-QRO). In this paper, the SOC operator is assumed to be an effective reduced one-electron operator ($h_{\mathrm{p}}^{\mathrm{SO}}(i)$) treated by the spin−orbit mean-field (SOMF) approximation.[33−35] In the case where the SOC operator is an effective one-electron operator, the general treatment shows that for a system with ground-state spin S to the second-order-only excited states with total spin $\Delta S = S' - S = 0, \pm 1$ contribute to the **D** tensor. Excited states with $\Delta S = 0$ are same-spin excited states and those with $\Delta S = \pm 1$ are referred to as spin-flip excited states.[30] We have previously outlined a simple treatment to construct approximate spin-eigenfunctions from a spin-unrestricted DFT wavefunction.[11,17] The result has been termed QRO treatment since it is based on a set of "quasi-restricted" orbitals that are constructed from the spin-unrestricted natural orbitals.[17,36,37] They nearly coincide with the ROKS orbitals.[22,38] The SOC part of the ZFS may then be expressed conveniently as follows:

$$D_{pq}^{(\mathrm{SOC})} = D_{pq}^{\alpha\alpha} + D_{pq}^{\beta\beta} + D_{pq}^{\alpha\beta} + D_{pq}^{\beta\alpha} = -\frac{1}{4S^2}\sum_{ta} M_{ta}^{pq;\alpha\alpha} - \frac{1}{4S^2}\sum_{it} M_{it}^{pq;\beta\beta} + \frac{1}{2}\frac{1}{S(2S-1)}\sum_{t\neq u} M_{tu}^{pq;\alpha\beta} + \frac{1}{2}\frac{1}{(S+1)(2S+1)}\sum_{ia} M_{ia}^{pq;\beta\alpha} \tag{5}$$

With

$$M_{rs}^{pq;\sigma\sigma'} = \frac{\langle\psi_r|h_p^{\mathrm{SOC}}|\psi_s\rangle\langle\psi_s|h_q^{\mathrm{SOC}}|\psi_r\rangle}{\epsilon_s^{\sigma'} - \epsilon_r^{\sigma}} \tag{6}$$

$p,q = x,y,z$, i,j = doubly occupied QROs, t,u = singly occupied QROs, and a,b = virtual QROs. As may be justified from the lowest orders of DFT perturbation theory,[39−41] orbital energy differences are zeroth-order approximations to state energy differences in DFT as long as no nonlocal potentials, such as the Hartree−Fock exchange, are present. The first two terms in eq 5 account for the contribution of the same spin excited states (sextets in this paper) and the $D^{\alpha\beta}$ term accounts for the spin-flips in the singly occupied molecular orbitals (SOMOs) (quartets), while $D^{\beta\alpha}$ is constructed to account for octet states that arise from shell-opening excitations.[11]

2.2. PK Approach (SOC-PK). Pederson and Khanna (PK) used uncoupled perturbation theory to suggest an equation for the SOC contribution to the ZFS based on UKS treatments.[14] Their equation is

$$D_{pq}^{(\mathrm{SOC})} = D_{pq}^{\alpha\alpha} + D_{pq}^{\beta\beta} + D_{pq}^{\alpha\beta} + D_{pq}^{\beta\alpha} = \frac{1}{4S^2}\left(-\sum_{i_\alpha a_\alpha} M'^{pq}_{i_\alpha a_\alpha} - \sum_{i_\beta a_\beta} M'^{pq}_{i_\beta a_\beta} + \sum_{i_\alpha a_\beta} M'^{pq}_{i_\alpha a_\beta} + \sum_{i_\beta a_\alpha} M'^{pq}_{i_\beta a_\alpha}\right) \tag{7}$$

with

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$$M'^{pq}_{r_\sigma s_{\sigma'}} = \frac{\langle \psi_r^\sigma | h_p^{\mathrm{SOC}} | \psi_s^{\sigma'} \rangle \langle \psi_s^{\sigma'} | h_q^{\mathrm{SOC}} | \psi_r^\sigma \rangle}{\epsilon_s^{\sigma'} - \epsilon_r^\sigma} \qquad (8)$$

The differences in the physical contents of the PK and QRO equations are discussed elsewhere.[11]

2.3. Spin−Spin Contribution (SS). On the basis of the ground-state Slater determinant, the SS part of the **D** tensor can be estimated according to the following formula:[42]

$$D_{kl}^{(\mathrm{SS})} = -\frac{g_e^2}{16}\frac{\alpha^2}{S(2S-1)} \times \sum_{\mu\nu}\sum_{\kappa\tau}\{\mathbf{P}^{\alpha-\beta}_{\mu n}\mathbf{P}^{\alpha-\beta}_{\kappa\tau} - \mathbf{P}^{\alpha-\beta}_{\mu\kappa}\mathbf{P}^{\alpha-\beta}_{\nu\tau}\}\langle\mu\nu|r_{12}^{-5}\{3r_{12,k}r_{12,l} - \delta_{kl}r_{12}^2\}|\kappa\tau\rangle \qquad (9)$$

where $\mathbf{P}^{\alpha-\beta} = \mathbf{P}^{\alpha}-\mathbf{P}^{\beta}$ (P capital letter) is the spin density matrix with $P^\sigma_{\mu n} = \sum_{p\sigma} c^\sigma_{\mu p} c^\sigma_{\nu p}$ and c^σ are the MO coefficient matrix of spin σ; α is the fine structure constant ($\sim{}^1/_{137}$ in atomic units); and μ,ν,κ,τ are the atomic basis functions.[42] The performance of this equation in a DFT framework was recently evaluated for organic triplets and diradicals where the SS contribution represents the main source of ZFS.[22] It was shown that the use of the ROKS approach resulted, in favor of UKS results, in important improvements in comparison to experiment and highly correlated ab initio calculations. The ROKS result, on the other hand, was very closely approximated by the unrestricted natural orbitals (UNO) determinant. Hence, the SS part of the ZFS from UNO and UKS will be considered in this paper for comparison. They will be designated as SS-UNO and SS-DIRECT, respectively. The advantage of the UNO treatment relative to the ROKS determinant is that the SS-UNO contribution to the ZFS can be conveniently diagonalized together with the contributions from any other method used for the calculation of the SOC (e.g., SOC-QRO or SOC-PK) contribution.

3. Test Set

A total number of 18 experimentally characterized systems (high-field EPR and X-ray crystallography) have been considered for the study of the ZFS in mononuclear Mn(II) complexes. This set of compounds covers tetra-, penta-, and hexacoordinated manganese ions, with N, O, and different halides in the first coordination sphere. Table 1 summarizes the experimental data.

Table 1. Experimental Data of the Studied Mn(II) Compounds[a]

complex[b]	coord sphere	D (cm^{-1})	E/D	no.
[Mn(OPPh$_3$)$_2$Cl$_2$][43,44]	O$_2$Cl$_2$	0.165	0.027	**1**
[Mn(terpy)Cl$_2$][45]	N$_3$Cl$_2$	−0.260	0.290	**2**
[Mn(tpa)Cl$_2$][10]	N$_4$Cl$_2$	+0.118	0.200	**3**
[Mn(OPPh$_3$)$_2$Br$_2$][43,46]	O$_2$Br$_2$	0.507	0.264	**4**
[Mn(terpy)Br$_2$][45]	N$_3$Br$_2$	+0.605	0.260	**5**
[Mn(tpa)Br$_2$][10]	N$_4$Br$_2$	−0.355	0.190	**6**
[Mn(OPPh$_3$)$_2$I$_2$][43,47,48]	O$_2$I$_2$	0.906	0.246	**7**
[Mn(terpy)I$_2$][45]	N$_3$I$_2$	+1.000	0.190	**8**
[Mn(tpa)I$_2$][10]	N$_4$I$_2$	−0.602	0.160	**9**
[Mn(dpya)Cl$_2$][45]	N$_3$Cl$_2$	−0.315	0.222	**10**
[Mn(Br-terpy)Cl$_2$][49]	N$_3$Cl$_2$	−0.273	0.311	**11**
[Mn(Me$_2$N-terpy)Cl$_2$][49]	N$_3$Cl$_2$	+0.270	0.222	**12**
[Mn(phenyl-terpy)Cl$_2$][49]	N$_3$Cl$_2$	−0.319	0.223	**13**
[Mn(mesityl-terpy)Cl$_2$][49]	N$_3$Cl$_2$	−0.295	0.271	**14**
[Mn(tolyl-terpy)Cl$_2$][49]	N$_3$Cl$_2$	−0.250	0.320	**15**
[Mn(EtO-terpy)Cl$_2$][49]	N$_3$Cl$_2$	−0.295	0.322	**16**
[Mn(terpy)(NCS)$_2$][45]	N$_5$	−0.300	0.170	**17**
[Mn(*t*Bu-terpy) (N$_3$)$_2$][50]	N$_5$	−0.315	0.254	**18**

[a] When experimentally available, the sign of D is indicated. [b] OPPh$_3$ = triphenylphosphine oxide, terpy = 2,2′:6″,2″-terpyridine, tpa = tris-2-picolylamine, dpya = dipyrido[4,3-*b*;5,6-*b*]acridine, Br-terpy = 4′-bromo-terpy, Me$_2$N-terpy = 4′-(*N*,*N*-dimethylamino)-terpy, *t*Bu-terpy = 4,4′,4″-tri-*tert*-butyl-terpy, tolyl-terpy = 4′-(4-methylphenyl)-terpy, mesityl-terpy = 4′-mesityl-terpy, and EtO-terpy = 4′-ethoxy-terpy.

The structures of all considered complexes are shown in Figure 1.

4. Computational Details

All calculations have been performed with the *ORCA* package.[51] ZFS parameters have been calculated on X-ray as well as optimized structures. Geometry relaxations have been optimized using the BP[52,53] functional and the TZVP[54] basis set.

In preliminary work, we tested the effects of the basis set size (SV(P),[55] SVP, TZV, TZVPP[54] for all atoms, and CP(PPP)[56] for the metal together with the TZVP for the ligands) and the nature of the density functional (LSD,[57] BP, BLYP,[58] OLYP,[59] PBE,[60] and RPBE[61]) on the quality of the calculated parameters. As shown in Figures S.I. 1 and S.I. 2 (Supporting Information), there is no noticeable difference between any of the cited basis sets or functionals. To be on the safe side, we have used relatively large TZVP basis set for all atoms, together with the standard BP functional. The wave functions were to within $\Delta E < 10^{-7}\ E_\mathrm{h}$.

Since we previously found that accounting for scalar relativistic effects improves the results—in particular if heavier ligands are

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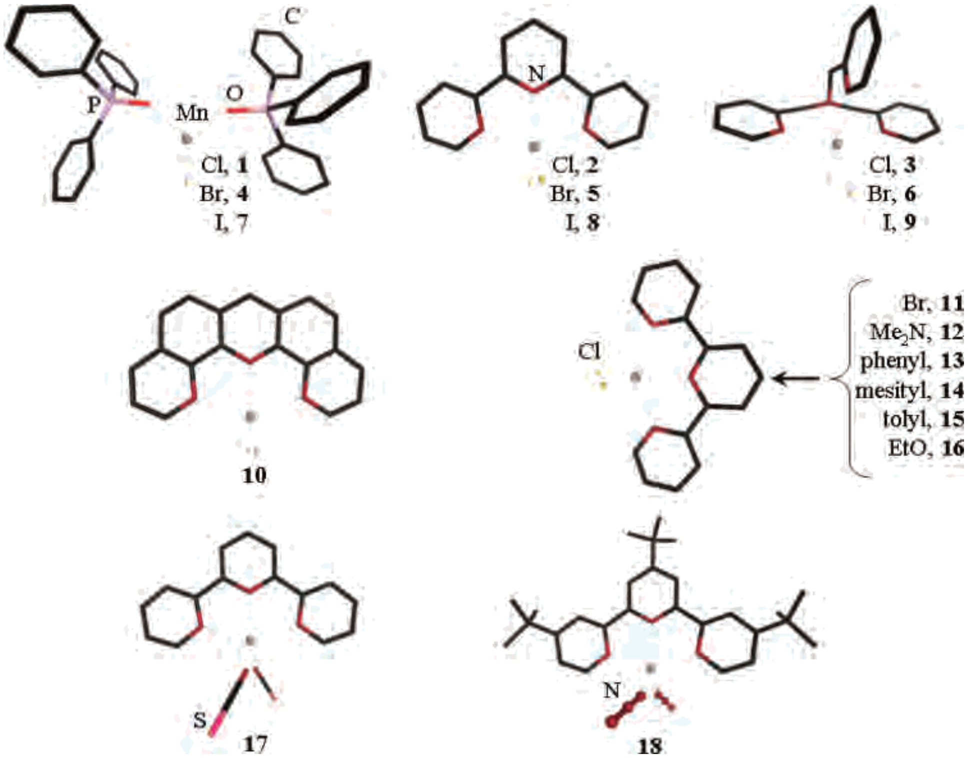

Figure 1. Molecular structures of the 18 studied Mn(II) complexes (see Table 1).

involved[10]—the zeroth-order regular approximation[62] (ZORA) approximation has been included in our calculations. Our implementation follows the model potential idea of van Wüllen.[63]

The QROs have been drawn with the *MOLEKEL* software.[64]

5. Results

5.1. Studies Based on X-ray Structures: SOC versus SS Contributions to the ZFS. Six sets of calculations have been performed on the entire test set: (1−3) using the PK approach for the SOC part and either no SS treatment, SS-DIRECT, and SS-UNO and (4−6) similar but with the QRO-SOC method substituting for PK-SOC. The quality of the theoretical result is best judged from the standard error of the linear regression analysis since this parameter directly documents the predictive power of the theoretical method. Of course, ideally, the slope of the correlation line as well as the correlation coefficient would be unity. Deviations from these ideal values indicate systematic errors of the theoretical method for the particular test set. In the linear regression, the intercept was forced to zero since both calculated and experimental D and E are equal to zero in cubic symmetry. The results of the analysis are presented in Table 2, while the individual calculated values can be found in the Supporting Information (Table S.I. 3).

The following conclusions may be drawn from this data: (1) The inclusion of the SS term does improve the predictive power of the calculations since the correlation coefficients improve with its inclusion. (2) There is practically no difference between SS-UNO and SS-DIRECT for the test set. (3) All calculations overestimate the absolute value of D. (4) The QRO method is inferior to PK for the prediction of D in Mn(II) complexes. (5) In the best case, the ZFS can be predicted to an accuracy of ∼0.1 cm^{-1} in Mn(II) complexes with present day DFT methods. (6) The correlation coefficient of ∼0.99 indicates that the errors of the calculations are highly systematic. And (7) Our experience with similar calculations indicates that these conclusions are specific to the difficult case of Mn(II) and are not transferable to the general case of transition-metal complexes or main-group high-spin systems.

Table 2. Comparison of Computational Methods Performance for the Estimation of the D Parameter

		correlation coefficient	slope	standard error (cm^{-1})
SOC-PK	no SS	0.978	1.336	0.134
	SS-DIRECT	0.987	1.532	0.124
	SS−UNO	0.984	1.547	0.132
SOC-QRO	no SS	0.865	1.714	0.471
	SS-DIRECT	0.891	1.887	0.457
	SS−UNO	0.892	1.901	0.457

As fully documented in the Supporting Information and evident from Figure 3, the calculations do not, unfortunately, lead to accurate values for E/D, with the SOC-PK + SS direct approach giving the least poor agreement with experimental data.

5.2. Ground- and Excited-States Contributions to the ZFS. As explained above, the calculation of the SS contribution to the ZFS involves only the ground-state wavefunction (approximated here by the Kohn−Sham determinant) whereas the SOC contribution originates from same-spin and spin-flip excited states interactions with the ground state.

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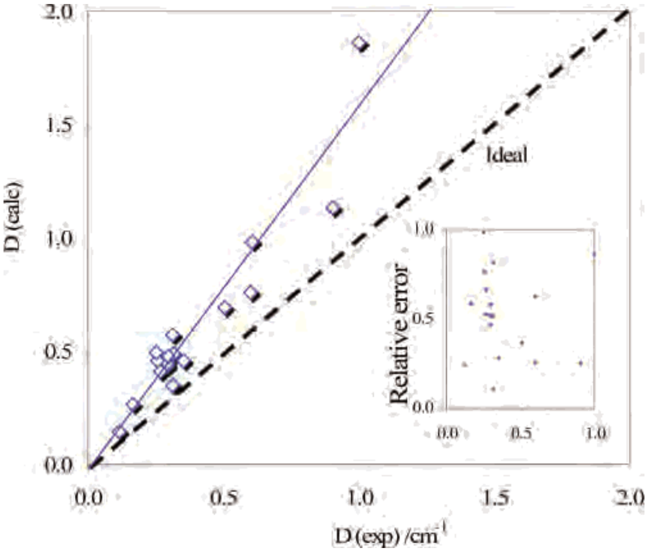


Figure 2. Correlation between calculated and measured D parameters, from SOC-PK + SS-DIRECT method, documented in the text. The absolute values of the relative errors defined as $|D(\text{exp}) - D(\text{calc})/D(\text{exp})|$ as a function of D(exp) are included in the figure; this plot shows that the error of the employed method does not depend on the magnitude of the calculated quantity.

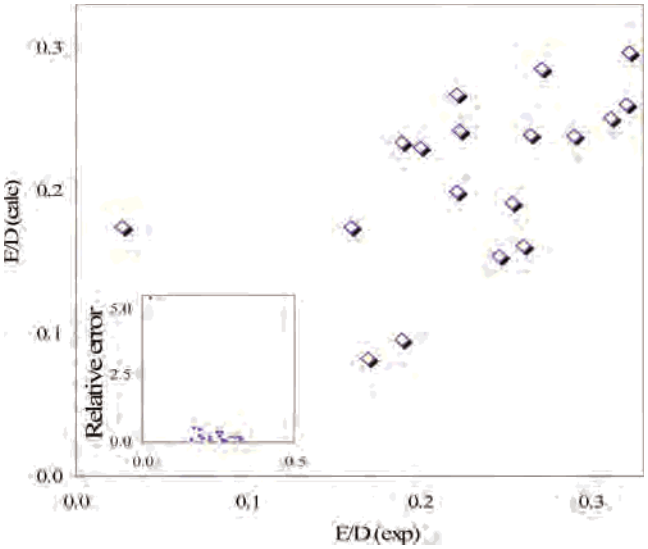


Figure 3. Correlation between calculated and measured E/D parameters, from SOC-PK + SS-DIRECT method.

In order to obtain more insight into the ZFS variations observed in the studied compounds, we have investigated the sign and the magnitude of the various contributions to the ZFS in the test set (sorted in Figure 4 by the increasing importance of the SS contribution).

Figure 4 shows that the SS contribution to the D parameter varies from 2 to 42%. In most of the compounds the SS term accounts for around ~30% of $|D|$, which is far from being negligible. We observe that the SS contribution is always of the same sign as the final D value. The first four compounds in Figure 4 (counting from the left) contain iodide or bromide in the first coordination sphere. As discussed elsewhere, the interference terms between the metal and ligand SOC dominate the D values for these cases.[10] However, for the remaining complexes, the SS part contributes significantly to the final D value.

Concerning the SOC part, the $D^{\alpha\alpha}$ and $D^{\beta\alpha}$ contributions cancel each other nearly perfectly for all studied Mn(II) complexes. If these two contributions were omitted from the actual treatment, one would obtain linear regression coefficients similar to the ones presented above. Chemically speaking, this result indicates that the D parameter of Mn(II) complexes is largely determined by the subtle balance between the d−d spin-flip excitations (dominating $D^{\alpha\beta}$), the ligand-to-metal charge transfer (LMCT) contributions (dominating $D^{\beta\beta}$), and the SS interaction. This is, of course, specific for the case of Mn(II), and other metals and oxidation states must be subjected to detailed calibration studies in order to determine the prevailing contributions to the **D** tensor. Within the PK method the observed cancellation is readily understood: the $\alpha\alpha$ contribution involves excitations from occupied spin-α orbitals to virtual spin-α MOs while the $\alpha\beta$ contribution features occupied spin-β and virtual spin-α MOs. In the absence of significant spin-polarization, the occupied spin orbitals may be ordered into pairs of nearly identical shape except for the "excess" spin-up orbitals that are to be identified with the SOMOs of the system. Assuming perfect pairing of the remaining occupied MO pairs, it is clear from eq 7 that the $D^{\alpha\alpha}$ and $D^{\beta\alpha}$ contributions must cancel, since they enter with different signs. The remaining $\alpha\alpha$ contributions correspond to spin-conserving excitations out of the SOMOs into virtual MOs. They are best identified with metal-to-ligand charge transfer (MLCT) states in the case of Mn(II). The fact that the $D^{\alpha\alpha}$ and $D^{\beta\alpha}$ contributions nearly cancel then indicates that the MLCT excitations only play a minor role for the ZFS of Mn(II) complexes—at least to the extent that the present test set is representative of this class of compounds. Note that this systematic and near-perfect cancellation is specific to the PK model that features a prefactor of $\pm 1/(4S^2)$ for all four terms. As will be argued elsewhere, this is not fully justified. A calibration study for a recently developed linear response theory for the SOC contribution to the **D** tensor will be published separately in conjunction with ab initio calculations of the ZFS in Mn(II) complexes. Here, we stick to the more conventional PK treatment since it is presently the most used DFT approach to the ZFS.

A discussion about the orientations of the ZFS principal axes (Figure S.I. 3) of the studied compounds can be found in the Supporting Information.

5.3. Results Based on Optimized Structures. So far all calibrations and analysis were made on experimental structures. Under usual circumstances, high-quality experimental structures are not available and one has to rely on theoretically calculated structures. There are actually good reasons why theoreticians often prefer theoretical structures over experimental ones even when the latter are available: (a) The theoretical structures represent well-defined points on the potential energy surfaces; (b) they do not suffer from inaccuracies in the experimental structures, in particular concerning the positions of hydrogen atoms; and (c) they are of a uniform and usual quite acceptable quality. However, in the case of Mn(II), even minor errors in the computed structures may translate into significant errors in the predicted

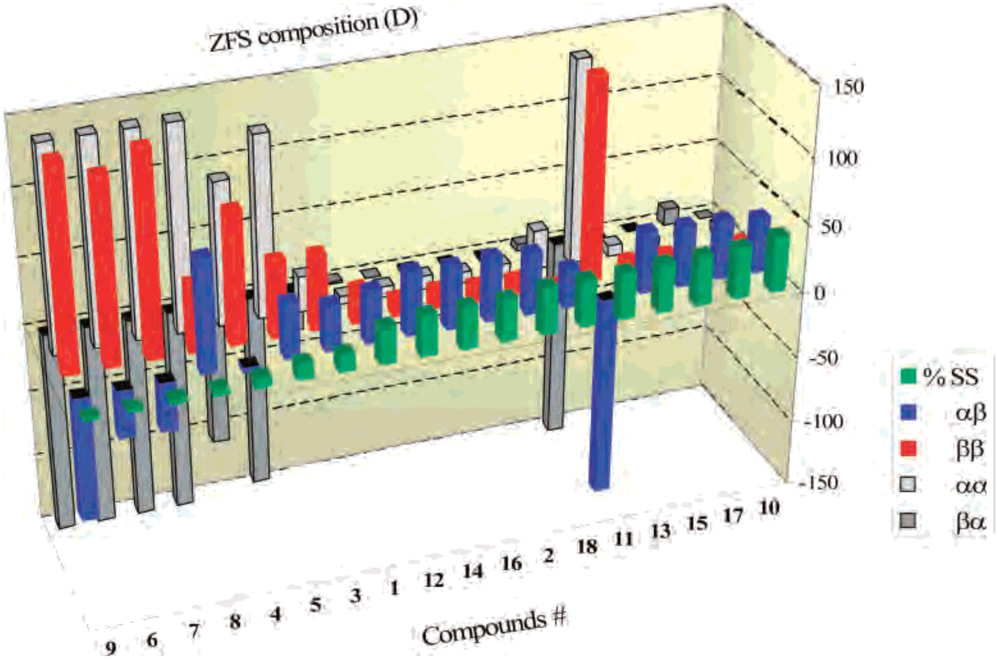
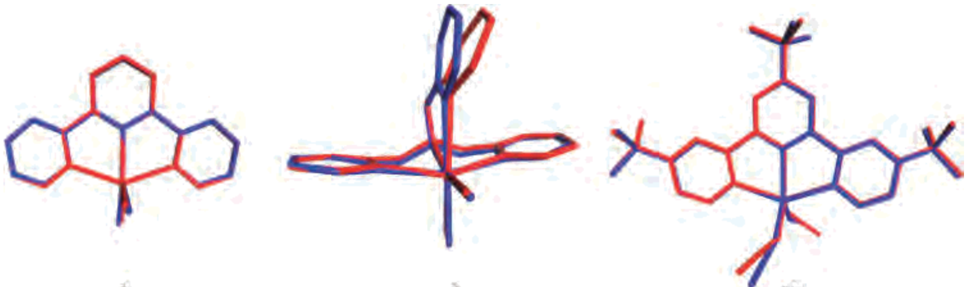


Figure 4. Decomposition of the calculated *D* values in the test series into the five individual contributions evident from eqs 7−9. Only percentages between −150 and +150% are included (for individual contributions see Table S.I. 5, Supporting Information). The compounds are ordered by increasing importance of the direct spin−spin term.



2 **3** **18**

Figure 5. Experimental (blue) versus optimized structures (red) of compounds **2**, **3**, and **18**; hydrogen atoms were omitted for clarity.

ZFS owing to the subtle interplay of factors that contribute to the ZFS.[10,17] We have therefore repeated the calculations based on quantum chemically optimized structures where all optimizations were started from the respective X-ray structures.

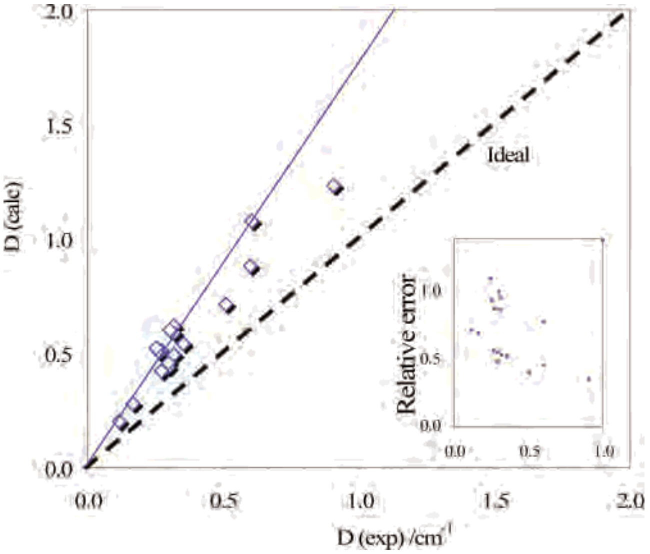


Figure 6. Correlation between calculated and measured *D* parameters, from SOC-PK + SS-DIRECT method on optimized structures (regression coefficient, 0.975; slope, 1.786; standard error, 0.194).

Geometry optimization, in general, leads to minor changes in the geometry of the first coordination sphere but some significant deviations in the position of the atoms in the second and third coordination spheres. Figure 5 illustrates the situation for the cases of [Mn(terpy)Cl_2], [Mn(tpa)Cl_2], and [Mn(*t*Bu-terpy)$(N_3)_2$] complexes. The optimized structures are collected in the Supporting Information.

Metal−ligand bonds slightly change (∼4−9 pm) in the optimized structures relative to the experimental ones. Also, in structure **3**, the plane of the apical pyridine ring is significantly bent after the optimization. In structure **18**, the N−N−N angles in the N_3 ligands are much farther from linearity in the optimized structure. Perhaps less importantly, small rotations of the *tert*-butyl groups in the optimized geometry of complex **18** relative to the X-ray structure were observed. Such limited deviations between theory and experiment are expected and are attributed to the intrinsic limitations of DFT, the basis sets used, and the neglect of the crystal environment and solvent in the calculations. It is, however, noteworthy that the quality of the predicted ZFS

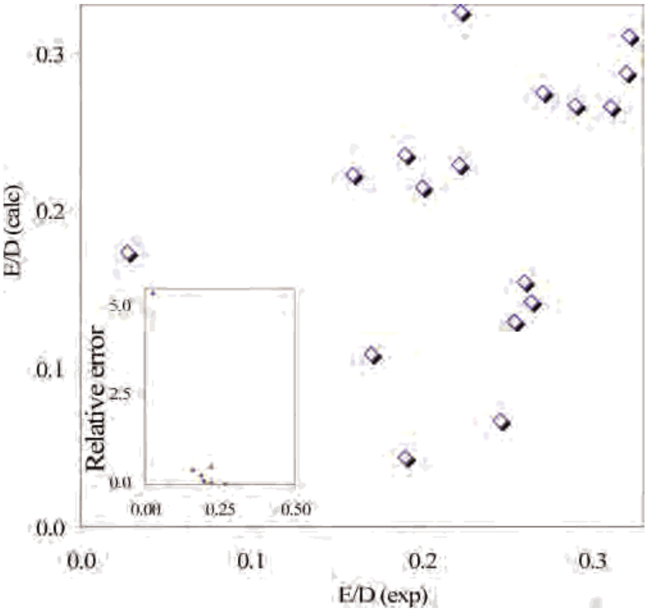


Figure 7. Correlation between calculated and measured E/D parameters, from the SOC-PK + SS-DIRECT method on optimized structures.

parameters decreases markedly for the optimized structures (Figures 6 and 7 and Table S.I. 7, Supporting Information). In fact, the standard error increases by almost a factor of 2 compared with the calculations that were based on the X-ray structures. This demonstrates once more the difficulties that theory is facing in trying to predict the ZFS parameters of high-spin d^5 complexes. Owing to the smallness of the target quantity and the complexity of the individual contributions, the predicted D and E/D values react very sensitively to almost every aspect of the calculation.

Individual calculated values can be found in table S.I. 6 in the Supporting Information.

5.4. The Sign of *D*. It is well-known that the sign of the D parameter becomes more difficult to determine upon approaching the rhombic limit, where finally, for $E/D = {}^1/_3$, it becomes irrelevant.[1] In Section 4.1 we compared absolute experimental and calculated D values in order to avoid this problem. Now the question of the limit of the calculated E/D ratio at which the sign of the calculated axial parameter can be trusted may be addressed. Figure 8 shows the calculated and experimental D values of the studied complexes ordered by increasing E/D ratio. It is observed that the calculated sign of D has been found to be correct in all cases as long as $E/D < 0.2$. Thus, at the presently available sophistication of DFT, we can state that the sign of calculated D will be unreliable for $E/D > 0.2$ in the case of Mn(II). This is an important criterion for future predictions of ZFS parameters, based on similar methods.

6. Discussion

The aim of the present study is the assessment of theoretical methods for the estimation of ZFS parameters in Mn(II) complexes and the analysis of its different components, in comparison with experiment. Concerning the basis set size and different GGA density functionals, we do not find any noticeable improvement in considering basis sets larger than those of the standard double- (SVP) or triple-ζ (TZVP) basis sets or using functionals other than the standard BP functional. Perhaps future implementations of hybrid functionals for the estimation of ZFS parameters may lead to some improvements, as is the case for the calculation of exchange parameters[65−67] or g tensors.[65,68] This work will be reported in due course.[69]

For the estimation of the SOC part of the ZFS in Mn(II) complexes, it was found here that the PK approach is superior to the QRO method. In any case, taking care of the spin−spin interaction either with or without the inclusion of the (very limited) spin-polarization effects definitely improves the results and clearly argues for the physical necessity of accounting for this important contribution to the ZFS. In fact, for Mn(II) complexes the SS contribution represents ~30% of the axial D parameter, on average. In addition to the SS part, the SOC contributions of d−d spin flip ($\alpha\beta$) and LMCT excited states ($\beta\beta$) were found to dominate the SOC part of the D parameter while the $\alpha\alpha$ and $\beta\alpha$ contributions very nearly and systematically cancel each other. This is specific to the PK model. The comparison of the signs of calculated and measured D values shows that the sign of the calculated axial ZFS parameters is unreliable for $E/D > 0.2$.

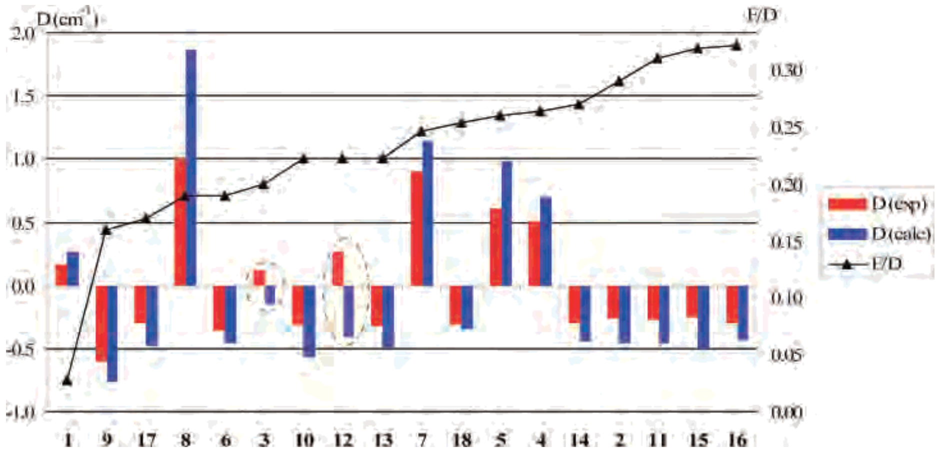


Figure 8. SOC-PK + SS-DIRECT vs experimental D values for increasing E/D(exp) ratio. Only compounds with known X-ray structures were included. Highlighted circles show two cases of discordance between experimental and calculated signs of D. This occurs for $E/D > 0.2$.

Another significant result of the present study is the sensitivity of the results to the employed structures. Despite the fact that optimized structures using DFT methods match fairly well the first coordination spheres of the metal sites, they lead to a significant deterioration of the ZFS predictions relative to high-quality X-ray structures. This is particularly problematic for studies where the geometric structures of the Mn(II) sites are not precisely known, as is the case for the majority of protein active sites. At present, there seems to be no satisfactory solution to this problem. Thus, one should be aware that **D** tensor predictions for Mn(II) complexes based on optimized or inaccurate experimental structures carry an error bar that is twice as large as would be the case if accurate structures were employed.

The present conclusions are valid for Mn(II) compounds. It is evident that similar systematic studies on other transition-metal compounds and oxidation states are indeed needed in order to come to more general conclusions. Work in this direction is in progress in our research groups.

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Supporting Information Available: Orientations of the main axes of the ZFS tensor and QRO orbitals; tables with the values presented in the figures above; Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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