Inorganic Chemistry

Article

pubs.acs.org/IC

Simple Ligand-Field Theory of d^4 and d^6 Transition Metal Complexes with a C_3 Symmetry Axis

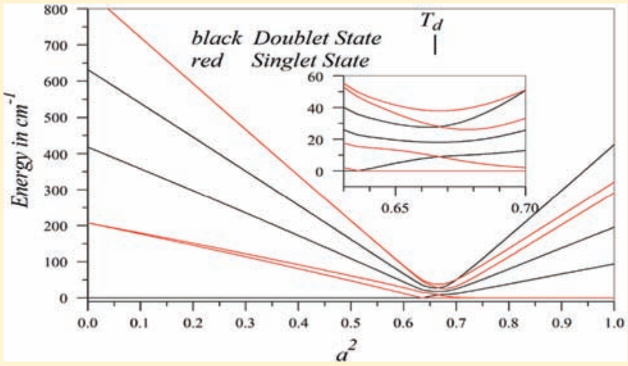
Bruce R. McGarvey

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9A 3P4 Canada

Joshua Telser*

Department of Biological, Chemical and Physical Sciences, Roosevelt University, Chicago, Illinois 60605, United States

Ⓢ *Supporting Information*



ABSTRACT: There have been a number of recent studies reporting high-spin $d^{4,6}$ complexes with three- and four-coordinate geometry, which exhibit roughly trigonal symmetry. These include complexes of Fe(II) with general formula L_3FeX, where L = thioether or dialkylphosphine donors of a tripodal chelating ligand and X is a monodentate ligand on the C_3 axis. In these systems, there is unquenched orbital angular momentum, which has significant consequences on the electronic/magnetic properties of the complexes, including magnetic susceptibility, EPR spectra, and magnetic Mössbauer spectra. We describe here a simple model using a description of the *d* orbitals with trigonal symmetry that along with the application of the spin−orbit interaction successfully explains the magnetic properties of such systems. These *d* orbitals with 3-fold symmetry are complex orbitals with a parameter, *a*, that is determined by the bond angle, *α*, of LFeX. We demonstrate that the *E* symmetry states in such systems with $S > 1/2$ cannot be properly "simulated by" or be "represented by" the Zeeman and second-order zero-field spin Hamiltonian alone because by definition the parameters *D* and *E* are second-order terms. One must include the first-order spin−orbit interaction. We also find these systems to be very anisotropic in all their magnetic properties. For example, the perpendicular values of *g* and the hyperfine interaction parameter are essentially zero for the ground-state doublet. For illustrative purposes, the discussion focuses primarily on two specific Fe(II) complexes: one with the bond angle *α* greater than tetrahedral and another with the bond angle *α* less than tetrahedral. The nature of the EPR spectra and hyperfine interaction of ^{57}Fe are discussed.

■ INTRODUCTION

This work was initiated by the authors' concern about the spin Hamiltonian (eq 1) used by many investigators to represent the ground state of high-spin d^6 complexes (primarily of Fe(II)), and high-spin d^7 complexes (such as of Co(II)), which contain a C_3 symmetry axis.

$$\begin{aligned}\mathcal{H} &= \beta_e S\cdot\mathbf{g}\cdot B + S\cdot\mathbf{D}\cdot S\\ &= \beta_e[g_zB_zS_z + g_xB_xS_x + g_yB_yS_y] + D\left[S_z^2 - \frac{1}{3}S(S+1)\right]\\ &\quad + E[S_x^2 - S_y^2]\end{aligned} \tag{1}$$

The first term is the electronic Zeeman term, and the remaining terms are called a zero field splitting (zfs) interaction for such multispin ($S > 1/2$) systems. Equation 1 was obtained under the assumption that the ground state was free of angular momentum.[1,2] In eq 1, the *g* factor is determined by a second-order (spin−orbit × angular momentum) interaction and *D* and *E* are also determined primarily by a second-order (spin−orbit × spin−orbit) interaction. If $S \geq 2$, then fourth-order contributions involving S^4 terms will also be possible.[1,3] As will become apparent later, it must carefully be noted that in the EPR community, since the days of Abragam and Bleaney,[1] the letters *D* and *E* are reserved for the second-order term in eq 1. The second-order nature of *D* means that it is proportional to $(\lambda^2/\Delta E)$ and thus its magnitude is on the order of 1−10 cm^{-1} because the multielectron spin−orbit coupling constant is $\lambda \approx -100$ cm^{-1} for Fe^{2+}, and for orbitally nondegenerate systems the energy splitting between the ground state and relevant excited states is $\Delta E \approx 10000-1000$ cm^{-1}.

If there is unquenched angular momentum, then eq 1 will require an additional term from the first-order spin−orbit interaction. When a C_3 axis is present, this is the case for both d^6 and d^7 systems. If, however, eq 1 is used to interpret such cases then the *D* values reported in the literature will include the first-order term. This is why *D* values have been reported

Received: June 2, 2011
Published: May 14, 2012

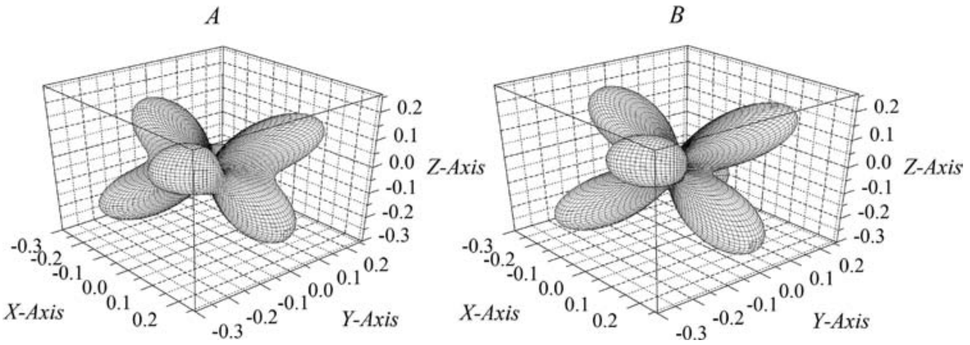


Figure 1. Plots of $E^*_{a1}E_{a1}$. (A) For a^2 = 2/3 (tetrahedral). (B) For a^2 = 0.3786 (specific case discussed here).

with a magnitude of tens of wave numbers, approaching the order of magnitude of λ, which is not what would be expected for a second-order term.

We therefore set out to calculate the effect of including the first-order spin−orbit interaction. In this work, the calculation will be for d^6 systems, namely coordination complexes of Fe(II). We chose this system, not only because of the importance of Fe(II) but because the calculation is simpler than for d^7 (only one magnetic quintet state: ^5D) and Fe complexes can be studied by magnetic Mössbauer spectroscopy, as well as by EPR.

The chemical basis for our study being so topical is the recent development of a number of synthetically very beautiful and versatile tridentate ligands, such as with thioether (S3) donors,[4,5] phosphine (P3) donors,[6−9] carbene (C3) donors,[10−12] and the continued extensive application of the N3 donor scorpionate ligands.[13,14] Other multidentate N donor ligands, such as trispyridylamine and its analogues[15,16] and tris(pyrrolyl-α-methyl)amines,[17−19] have also been extensively employed. These ligands impose trigonal geometry on the transition metal ion which they chelate. As a result, in most cases, the ion has unquenched angular momentum.

Recent interest in high-oxidation state iron complexes has led to the synthesis and characterization of four- and five-coordinate Fe(IV) imido[20] and oxo complexes,[16,21] including one very recently with the pyrrolide ligand.[22] These d^4 complexes all have roughly trigonal symmetry that requires much the same treatment as for the d^6 systems. Another, related synthetic direction has been the preparation of three-coordinate complexes of Fe(II), with approximate trigonal planar symmetry[23] by use of the β-ketiminate "nacnac" ligand framework (N2 donor).[24]

Last, single molecule magnets (SMMs) have engendered great interest in recent years and some of the complexes referred to above have been studied for this property.[17,18,25,26] The prominent SMM $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$[27] has 8 Mn(III), d^4, ions in octahedral sites, which has the same ground state as d^6 in tetrahedral sites.

Four papers on trigonal Fe(II) complexes have recently appeared that included relevant theory, with all orders of the spin−orbit interaction. A crystal field-based equation for spin Hamiltonian parameters (i.e., eq 1) was reported by Popescu et al.[4,28] A second paper by Palii, et al.,[25] did a proper ligand field theory (LFT) calculation for a trigonal-pyramidal Fe(II) complex of a tris(pyrrolyl-α-methyl)amine ligand (FeN4) including the spin−orbit interaction and applied it to magnetic susceptibility data. They reported that the ^{5}E ground state was split into three doublet and four singlet states, which showed that the spin Hamiltonian approach was problematic because this would give four doublets and two singlets (i.e., two sets each of one singlet and two doublets). They, however, did not emphasize that eq 1 was not sufficient. The third paper, by Atanasov, et al.[26] computed the value of D for the same type of FeN4 complex, and the fourth paper, by Neese and Pantazis[27] also computed D for several such FeN4 complexes. These latter two papers gave the second-order equation for D and E, but they calculated the complete spin−orbit interaction including the S^2 and S^4 terms and the first-order term. They assigned the complete spin−orbit interaction, including the first-order term, to D. This is unfortunate because the second-order terms produce a geometric anisotropy in the Zeeman interaction while the first-order term does not. The paper by Atanasov, et al.[26] did point out that the reason for the very large anisotropy in the Zeeman interaction of these complexes is from the anisotropy in the **g** tensor. None of the four papers dealt with interpretation of the EPR or magnetic Mössbauer experiments that have been done on such trigonal systems.

To understand the effect of introducing the first-order spin−orbit interaction on the magnetic properties, such as the nature of the spin Hamiltonian to be used to replace eq 1, we have chosen a simpler theory instead of the sophisticated computer models used by others.[26,27] The reasons are threefold. One, it is sufficient for our purposes, two, our approach offers new insights into the treatment of distorted tetrahedral systems, three, we have no access to large computer clusters nor expertise with the relevant programs. This simpler theory computes quickly and can be used easily to demonstrate the effect of the spin−orbit interaction upon the various ligand field states and predicts energies for the lowest 10 levels of the ^5E ground state to a reasonable accuracy.

■ EXPERIMENTAL SECTION

Computer programs are available from the authors that perform the calculations described herein, providing energy levels, EPR transitions, etc., for the trigonal ^5D or ^2D system described herein. The program Ligfield by Bendix was used for AOM calculations.[29]

■ RESULTS AND DISCUSSION

General Comments on Theoretical Treatment. Our calculation is a perturbation calculation using $|LM_LSM_S\rangle$ functions expressed as Slater determinants. Our calculations are greatly simplified by creating Slater determinants from d orbitals that have a C_3 axis rather than the real functions used in octahedral symmetry. We consider this approach accurate enough because we are interested only in the change of magnetic properties with the introduction of the first-order spin−orbit interaction. Thus we are interested in the spin−orbit splitting of the ^{5}E ground state only. For both EPR and

Table 1. Identification and Numbering of Wave Functions for ^5D System in Trigonal Symmetry

1	$A(+2)$	6	$E_{a1}(+2)$	11	E_{a2} $(+2)$	16	$E_{b1}(+2)$	21	$E_{b2}(+2)$
2	$A(+1)$	7	$E_{a1}(+1)$	12	$E_{a2}(+1)$	17	$E_{b1}(+1)$	22	$E_{b2}(+1)$
3	$A(0)$	8	$E_{a1}(0)$	13	E_{a2} (0)	18	$E_{b1}(0)$	23	$E_{b2}(0)$
4	$A(-1)$	9	$E_{a1}(-1)$	14	$E_{a2}(-1)$	19	$E_{b1}(-1)$	24	$E_{b2}(-1)$
5	$A(-2)$	10	$E_{a1}(-2)$	15	$E_{a2}(-2)$	20	E_{b1} (-2)	25	$E_{b2}(-2)$

magnetic Mössbauer studies, even the excited states within ^{5}E are relatively unimportant, except for the higher temperature magnetic Mössbauer studies. Moreover, we are not really interested in the actual MOs (the large computer programs excel for this), so we represent the effect of covalency by a reduction parameter k and the bond angles, which are strongly affected by the nature of the bonds.

The C_3 *d* Orbitals. In C_3 symmetry the five d_{ml} orbitals classify into the A and E representation.[30]

$$A = d_0 \tag{2a}$$

$$E_{a1} = ad_{+2} - bd_{-1}\text{: } E_{a2} = ad_{-2} + bd_{+1} \tag{2b}$$

$$E_{b1} = bd_{+2} + ad_{-1}\text{: } E_{b2} = bd_{-2} - ad_{+1} \tag{2c}$$

In tetrahedral or octahedral systems, $a = (2/3)^{1/2}$ ($b = (1/3^{1/2})$) and E_a and A become the $t_{2(g)}$ orbital set (E_b is the $e_{(g)}$ orbital set). In tetrahedral and octahedral systems, only E_a has angular momentum, but in a distorted system E_b also has angular momentum. These orbitals seem to be little known, probably because they are complex in nature and have no simple pictures that can be inserted into textbooks. In tetrahedral coordination, the t_2 orbitals are σ orbitals, while in octahedral coordination they are π in character. The functions $E_a^*E_a$ and $E_b^*E_b$ are, however, real and can be pictured. $E_{a1}^*E_{a1}$ is shown in Figure 1 for $a^2 = 2/3$ and 0.3786. The lower right lobe is in the xz plane. The $E_{a2}^*E_{a2}$ function gives the same picture but differs in the direction of rotation about the z axis. The function $E_b^*E_b$ also looks the same but is rotated 60° about z. Notice the change in shape with the change in a^2. This will be discussed below. In tetrahedral symmetry, the E_a functions are σ bonding as the three lobes below the xy plane point to three "basal" atoms and the A function points to the "apical" atom on the C_3, z axis.

The C_3 symmetry is obvious for the E_a and E_b orbitals, but this type of plot is not equivalent to plotting the wave function because the function is positive everywhere. Also, despite the appearance of Figure 1, the direction of the lobes is *not* in the tetrahedral directions (i.e., ($3\cos^2\theta - 1$)). The angle between the maximum of the lobe in the xz plane and the z axis is given instead by eq 3 (a, b as in eq 2):

$$\tan(2\theta) = \frac{2b}{a} \tag{3}$$

This gives $\theta = 117.37°$ for $a^2 = 2/3$, for example. If, however, we do a coordinate transformation by rotating the z axis by α degrees in the xz plane to the bond axis direction, we find that E_{a1} in eq 2b becomes:

$$E_{a1} = \left[\frac{a}{2}\sqrt{3/2}\,\sin^2\alpha - b\sqrt{3/2}\,\sin\alpha\cos\alpha\right]d_0 + ---- \tag{4}$$

where d_0 has the new z axis in the bond direction. If we maximize the d_0 coefficient by varying the parameter a, we obtain:

$$\tan\alpha = -\frac{2a}{b} \tag{5a}$$

which gives the tetrahedral angle of $\alpha = 109.47°$ for $a^2 = 2/3$. Equation 5a can also be given in terms of a^2, which is helpful for its calculation from an α value determined by molecular geometry:

$$a^2 = \frac{\tan^2\alpha}{4 + \tan^2\alpha} \tag{5b}$$

If there is a trigonal distortion of an octahedral complex where the σ bonding orbitals are E_b and the above treatment with E_{b1} is repeated, then eq 5c results:

$$\tan\alpha = \frac{2b}{a} \tag{5c}$$

There should be a null surface which includes the bond axis for the π orbitals, E_b, for a tetrahedral molecule. If one sets $E_{b1} = 0$, then eq 5a results, except the polar angle θ has replaced the angle α. This means that the null surface of E_{b1} is a cone with angle α and includes all four metal–ligand bonds. Thus E_{b1} is a true π orbital. The same applies for E_{a1} for trigonal distorted octahedral complexes. Thus, a in our starting d orbitals (eqs 2) is determined geometrically.

All of the above pertains to a single electron orbital, but since because d^4 and d^6 conformations have a ^5D ground state, it is obvious we should start our calculations with the following wave functions, D_{ml}, which behave the same way as d_{ml} orbitals:

$$^5A = {}^5D_0; \tag{6a}$$

$$^5E_{a1} = a^5D_{+2} - b^5D_{-1};\ {}^5E_{a2} = a^5D_{-2} + b^5D_{+1}; \tag{6b}$$

$$^5E_{b1} = b^5D_{+2} + a^5D_{-1};\ {}^5E_{b2} = b^5D_{-2} - a^5D_{+1} \tag{6c}$$

These 25 Slater spin–orbital determinant functions will be the starting point of the calculation. For completeness, we also include in the Supporting Information the 10 spin–orbital functions for the ^2D ground state of the d^1 and d^9 electronic configurations. The ^2D case will not be discussed further, however.

Calculation of Spin–Orbit and Zeeman Interactions. In this calculation, we will assume that we have determined the energy of the five symmetry defined states (eqs 6) before application of the spin–orbit and Zeeman interactions. This could be done by spectroscopic interpretations, AOM calculations, or DFT or ab initio calculations. These will be input values for the program found in the diagonal terms of the 25 × 25 energy matrix and will be labeled as: $E(A)$, $E(E_a)$, and $E(E_b)$. We have made this simplification because we are primarily interested in the energies of the ten components of the ^5E_b state, which determine the magnetic properties. It will be shown later that the energies of these 10 lowest states is very little affected by the values of $E(A)$, $E(E_a)$. For reasons that will become apparent later, we will do first only the largest term, the spin–orbit interaction. This interaction is generally of the form:

$$\mathcal{H}_{LS} = \lambda\hat{L}\cdot\hat{S} \tag{7}$$

The spin−orbit parameter λ is positive for $d^{4,3}$ and negative for $d^{6,7}$ configurations.

We will label the 25 functions as: $A(M_S)$, $E_{a1}(M_S)$, $E_{a2}(M_S)$, $E_{b1}(M_S)$, and $E_{b2}(M_S)$, where M_S is the spin number (−2, −1, 0, +1, +2). We now label the 25 wave functions as shown in Table 1.

Application of $\mathcal{H}_{LS}$ leads to a 25 × 25 matrix which, upon close inspection, can be broken down into two 8 × 8 matrices and one 9 × 9 matrix. These three matrices are given respectively in eqs S1, S2, and S3 (Supporting Information). The first two matrices are identical except for some changes in the sign of off-diagonal elements. This means both matrices when diagonalized will give the same set of eight energies. Examining the above three matrices tells us that the spin−orbit interaction splits the ^5A states into two doublet levels and one singlet level, while the ^5E_a and ^5E_b states are each split into three doublet levels and four singlet levels.

We next consider the application of an external magnetic field. The electronic Zeeman interaction operator is:

$$\mathcal{H}_Z = \beta_e(g_e\hat{S} + k\hat{L})\hat{B} \tag{8}$$

where β_e is the Bohr magneton, g_e is the free electron g value (2.0023), and k is the orbital reduction factor used to crudely estimate molecular orbital effects. The major orbital effects are handled by proper choice of the parameter a as discussed above. Because we have axial symmetry in C_3 point group symmetry, we use for the magnetic field the two vectors: $B_z = B_0 \cos\theta$ and $B_x = B_0 \sin\theta$. The B_z component makes the first and second matrices nonequivalent and splits the eight doublet states. The B_x component produces off diagonal matrix elements outside the three matrices described above (that are given in Supporting Information), which makes it necessary to diagonalize the total 25 × 25 matrix.

We will find later that in order to understand the EPR and magnetic Mössbauer spectra at low temperatures, it is necessary to distort the molecule slightly from strict C_3 symmetry if there is degeneracy in the ground state. The Jahn−Teller effect is sufficient, or there may be slight structural deviations from trigonal symmetry due to crystal packing, etc. To allow for small distortions from C_3 symmetry, we have assumed, for convenience, a distortion to planar symmetry with the xz plane as the reflection plane. This leads to two new, rhombic distortion parameters, V_n (n = 1, 2):

$$V_2 = E_{x^2-y^2} - E_{xy};\ V_1 = E_{xz} - E_{yz} \tag{9}$$

Because $d_{\pm1}$ is an equal mixture of d_{xz} and d_{yz}, V_1 splits $d_{\pm1}$, and V_2 does the same for $d_{\pm2}$. Values of V_n much greater than the spin−orbit parameter λ quench the angular momentum, and the two functions become the two real orbitals. This quenching is complete only when V_1 and V_2 are both are much larger than 1000 cm^{-1}. The matrix elements this interaction leads to are given in Supporting Information.[31] The introduction of these terms makes the y direction different and for magnetic resonance calculations would require the introduction of magnetic Zeeman terms involving the polar azimuthal angle ϕ, resulting in a matrix with complex numbers. We have not done this because the distortions are small. It should be pointed out that a simple change in the sign of the parameter V_1 will give the solution for yz plane. We have used this to calculate differences for the magnetic field in the x and y directions and find no significant differences in the results for the distortion values used in this work.

The Ground State of Fe(II) in a Tetrahedrally Coordinated Complex with a Trigonal Distortion. For our first use of this program, we will calculate the effect of the parameter a upon the 10 components of ^5E_b. This is the ground state for the Fe(II) ion in a tetrahedrally coordinated complex with a trigonal distortion, as in FeL$_3$X complexes, where L$_3$ represents a tripodal thioether ligand, such as in [PhTt^{tBu}]Fe(Me),[4] or a tripodal trialkylphosphine ligand, such as in [PhBP$^{iPr}{}_3$]FeCl.[8] Before we use the complete program, it will be useful to examine only the first-order perturbation calculation. For the ^5E_b ground state there are no off-diagonal spin−orbit interaction components among the 10 ^5E_b functions and, therefore, a first-order perturbation calculation gives the following energies (in ascending/descending order, depending on the sign of λ). The left column gives the energy and the right column gives the symmetry of the orbitals and their spin.

$$\begin{aligned}
&E(5) = 2(2 - 3a^2)\lambda && E_{b2}(+2);\ E_{b1}(-2)\\
&E(4) = (2 - 3a^2)\lambda && E_{b2}(+1);\ E_{b1}(-1)\\
&E(3) = 0 && E_{b2}(0);\ E_{b1}(0)\\
&E(2) = -(2 - 3a^2)\lambda && E_{b2}(-1);\ E_{b1}(+1)\\
&E(1) = 2(2 - 3a^2)\lambda && E_{b2}(-2);\ E_{b1}(+2)
\end{aligned} \tag{10}$$

The first-order spin−orbit interaction gives five equally split doublet states with the highest and lowest energy levels being $M_S = \pm2$ spin states. Note that the ground state is always an $M_S = \pm2$ doublet, no matter the sign of λ or whether a^2 is greater or less than 2/3. The inclusion of the second-order terms will remove the even spacing in the energy levels and converts two of the doublets into four singlets. Also, the energy spacing is in no way similar to that predicted by eq 1. Note also that the actual ground state is different for elongated ($a^2 < 2/3$) and compressed ($a^2 > 2/3$) complexes even though both are doublet $M_S = \pm2$ states.

We now will calculate the energy levels of these ten states as a function of a^2 from the complete program. For this calculation, we use $E(A) = E(E_a)$ = 7000 cm^{-1} and λ = −107 cm^{-1}. This spin−orbit coupling constant for ^5D is that definitively determined by Bendix et al. for free-ion Fe^{2+} (ζ = 427 cm^{-1} = $2S\lambda$).[29] A plot of these energies is shown in Figure 2.

In Figure 2, there are no labels as to the composition of the wave functions for each line because this composition changes dramatically with the value of a^2. To show these changes, consider the ground state. At a^2 = 0, the energies are given by eq 10, with the ground state being $E(5)$ and the first excited state being $E(4)$. At a^2 = 1, the energies are again given by eq 10 but the ground state is now $E(1)$ and the first excited state is $E(2)$. Thus from eqs 6, for a^2 = 0, the $D_{ml}(M_S)$ ground state is $D_{-2}(+2)$; $D_{+2}(-2)$, and for a^2 = 1, the ground state is $-D_{-1}(-2)$; $D_{+1}(+2)$. When a^2 = 2/3, the 10 states are all zero to first order, but are split by second-order interactions which produce states that are a mixture of spin functions. It is therefore not possible to use simple symmetry and spin labels to represent the various energy states across the range of a^2.

The energy separation between the ^5E_a and ^5E_b states is reasonable for illustrative purposes and is comparable to that obtained from DFT studies of a trigonal Fe(II) complex.[4] In principle, the energies of the ^5E_a and ^5A states would be

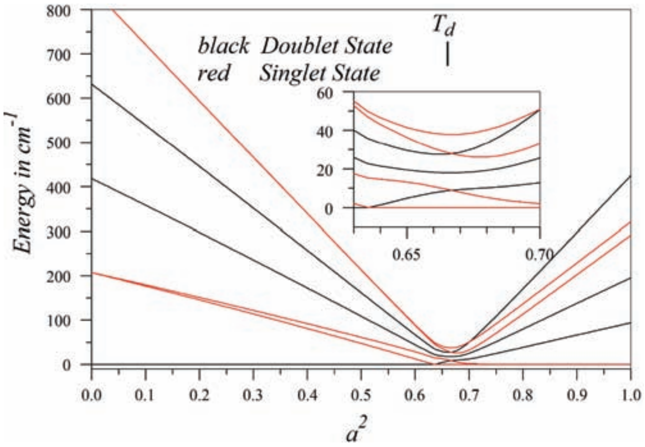


Figure 2. Plot of the 10 energy levels of the ^5E_b ground state for tetrahedral d^6 as a function of trigonal distortion, given by the parameter a^2 ($a^2 = 2/3 \approx 0.67$ corresponds to ideal tetrahedral geometry; the inset shows an expansion of this region). Other parameters are given in the text. The four singlet states (which are in two nearly degenerate pairs, as is most easily seen in the inset) are each shown with a red line; the three doublet states (one of which is the ground state for $a^2 \lesssim 0.64$) are each shown with a black line.

dependent on the distortions from T_d symmetry, as well as bonding parameters. However, we have found that the general features shown in Figure 2 will be preserved, regardless of the ^5E_a and ^5A states' energies because the first-order spin−orbit coupling determines the behavior within the E_b ground state. Thus, in Figure 2, the five doublet energy pattern (i.e., the first-order result from eq 10) is present over almost all values of a^2, except two of the doublets are slightly split into two pairs of singlets (red lines in Figure 2). These splittings into singlets are due to second- and fourth-order terms in the spin−orbit interaction, which are at least an order of magnitude smaller than the first-order terms.

Note that in the region of T_d symmetry (Figure 2, inset), the ^5E_b state is still split into five levels, but the degeneracy of these levels is 1:3:2:3:1. The ground state will be a singlet and is therefore not a magnetic state. There will be no EPR, ENDOR, or magnetic Mössbauer detected from this ground state. The doubly and triply degenerate excited states are also relatively unaffected by the magnetic field, but magnetic susceptibility will be found because other excited states contribute to that property. The spread of energies for the 10 levels is minimized for $a^2 = 2/3$ because for T_d symmetry there is no angular momentum in the ^5E_b state. As a result, splitting of the ^5E_b levels results only from higher-order spin−orbit interactions, which can still be significant due to the small size of 10Dq in tetrahedral complexes.

When a^2 is less than 0.635, there will be magnetic doublet states split by a magnetic field, which will allow for detection of EPR, ENDOR, or magnetic Mössbauer spectra. In this case, the doublet ground state consists mainly of the two wave functions:

$$\psi_+ = E_{b1}(+2) \text{ and}$$
$$\psi_- = E_{b2}(-2)$$

which will be split by the magnetic field into $M_S = \pm 2$ states.

Above $a^2 \sim 0.70$, we have a different situation because the two singlet states are not degenerate in zero-field; they become degenerate only when $a^2 = 1.0$. These two states approach each other closely enough to allow for detection of EPR, ENDOR, or magnetic Mössbauer, e.g., for $a^2 = 0.80$, the separation is 0.125 cm^{-1}. This doublet consists mainly of two wave functions:

$$\psi_+ = 0.7038E_{b1}(-2) + 0.7029E_{b2}(+2) \text{ and } \psi_-$$
$$= -0.7038E_{b1}(-2) + 0.7030E_{b2}(+2)$$

Note that the two states have their spin quenched (i.e., each has nearly equal contributions of opposite spins, in this case ±2) due to the zero field interaction. We will see below that when a magnetic field is applied, this quenching will be removed.

Effect of the Magnetic Field on the Doublet States and the EPR Spectrum. Because there are two different magnetic ground states depending on the value of a^2, we will first discuss an example from the literature for $a^2 < 2/3$.

Case of Elongation along the C_3 Axis. For the case of $a^2 <$ 0.635, we will use the tripodal thioether Fe(II) complex reported by Popescu et al.,[4] [phenyltris((*tert*-butylthio)-methyl)borate]-methyliron(II), [PhTt^{tBu}]Fe(Me). From the average C−Fe−S bond angle of 122.6° and eq 5b we obtain $a^2 = 0.3786$. In our calculations, we have used values of 5000 cm^{-1} and 8000 cm^{-1}, respectively, for the energy differences $E(E_a) - E(E_b)$ and $E(A) - E(E_b)$. These were obtained from our AOM (see Supporting Information, Figure S1 and Table S4) and are sufficient for illustrative purposes. We have chosen to adjust the V_2 value in eq 9 and have found the splitting of the ground state doublet in zero magnetic field to be approximately 10^{-4} that of V_2. We have chosen a value of 140 cm^{-1} for V_2 because it gives a value for the zero-field splitting of 0.0263 cm^{-1}, which is close to the 0.03 cm^{-1} estimated from Mössbauer spectra.[4] We use a value of the covalency reduction parameter $k = 0.8$, as is reasonable for a covalent complex. In Table 2 are given the energies for the 10 levels of the ^5E ground state. The second column is calculated as outlined above. The third column gives energies calculated by the program Ligfield, which includes all 210 d^6 microstates (the AOM and other input parameters are given in Figure S1 and Table S4, Supporting Information). The fourth column is calculated from our program but with the $E(E_a) - E(E_b)$ and $E(A) - E(E_b)$ values interchanged to test the sensitivity of the calculation to

Table 2. Energies of Lowest 10 Energy Levels (in cm^{-1}) of [PhTt^{tBu}]Fe(Me) Calculated by Our Method Compared to That by the Ligfield Program

level no.	calcd in cm^{-1}[a]	calcd by Ligfield[b]	calcd with inverted excited states[c]
1	0	0	0
2	0.0263	0.0048	0.0346
3	85.72	83.42	84.57
4	94.01	100.39	98.88
5	149.12	179.90	167.51
6	235.58	180.69	204.58
7	291.95	263.35	279.78
8	292.21	264.41	279.85
9	373.67	342.24	370.67
10	373.83	343.18	370.77

[a] Calculation using ^5D model with $a^2 = 0.3786$ and (in cm^{-1}): $E(E_a) - E(E_b) = 5000$, $E(A) - E(E_b) = 8000$, $V_2 = 140$, $\lambda = -107$. [b] Calculation using full d^6 basis set with parameters given in Table S4 (Supporting Information). [c] Calculation as in (a), except (in cm^{-1}): $E(E_a) - E(E_b) = 8000$, $E(A) - E(E_b) = 5000$.

these energies. We can see that our simple method is successful and that the details of the AOM for this complex, for which there are no electronic spectroscopic data available to determine energy levels,[4] are not critically important.

Why is our rather simplistic model so successful in calculating these energies? The answer is due to three factors: (1) The energies of the 10 levels in ^5E_b is due to the spin−orbit interaction, (2) the spin−orbit interaction is almost completely due to the d orbital component of the nonbonding MOs containing unpaired electrons, (3) the magnitude of the spin−orbit interaction is due to the nature of the hybridization coefficient a, which, in turn, is determined by the bond directions. The bond directions are determined by the covalent interactions, of course.

Our calculations show that the two wave functions for the doublet are basically $[\psi_+ = E_{b1}(+2), \psi_- = E_{b2}(-2)]$, and with the magnetic field in the z direction the doublet is split into two states with energies of

$$E = g\beta_e BM_S = \pm 2g\beta_e B \tag{11}$$

Note that we will use eq 11 as our definition of g. Much of the literature treats the two energy levels as pseudo spin 1/2 systems with an effective $g_{\mathrm{eff}} = 4g$.

The problem here is that these wave functions would not give a detectable EPR signal because the intensity would be zero. Popescu et al.[4] and others studying analogous complexes,[8] assumed that they could model the ground state doublet as the $M_S = \pm 2$ states of an $S = 2$ zero-field spin Hamiltonian (eq 1) but ran into this same problem. They solved it by assuming there was a distortion from C_3 symmetry, which in their model meant that they gave a nonzero value to the E parameter. This produced a small admixture of other spin states, which in turn allowed for a small intensity in the $\Delta M_S = 4$ transition. We will have to do the same thing using V_2. This is also accomplished by use of the real geometry in the AOM, which is not perfectly trigonal (Figure S1, Supporting Information).

A plot of the energy of the lowest four states as a function of the magnetic field applied along the z and x axes for V_2 = 140 cm^{-1} is given in Figure 3.

Popescu et al.[4] performed magnetic Mössbauer measurements at various temperatures to obtain the energy of the lowest excited state and obtained a range of 90−102 cm^{-1}. They analyzed their results in terms of eq 1, so that this value was assigned to the energy of $M_S = \pm 1$, which should be equal to $3D$, so $D \approx 30$ cm^{-1}. As seen in Figure 3, our calculated average energy of $M_S = \pm 1$ (upper red lines; these have a zero-field splitting of ~8 cm^{-1}) above the ground state is 90.1 cm^{-1}, the same value as reported. Most of this energy comes from the first-order spin−orbit interaction.

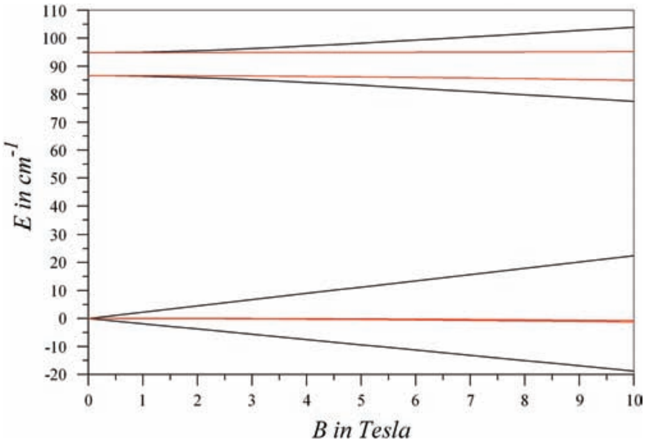


Figure 3. Plot of lowest four states energies versus magnetic field for case of a^2 = 0.3786 and V_2 = 140 cm^{-1} when the magnetic field is in the z (∥, black lines) and x (⊥, red lines) directions.

The g_z value for the $M_S = -2$ state (from the slope of the lowest energy black line at higher fields in Figure 3 and eq 11) is 2.014. The g_x value is 0.2. No EPR transition could be seen with B_x < 1.5 T. The g_z value for the $M_S = +2$ state (from the slope of the second lowest energy black line at higher fields) is 2.404. Popescu et al.[4] reported g_z = 2.5 from their Mössbauer studies. An EPR measurement of the transition $M_S = -2$ to $+2$ would give an average of the two g values (2.21).

To understand the shape of the resulting EPR spectrum, we need to examine how the wave functions behave as the magnetic field changes. What is important for low temperature EPR is the ground state doublet wave function, $\psi_\pm$, which can be written as follows:

$$\begin{aligned}\psi_\pm &= c_{\pm 1}E_{b1}(+2) + c_{\pm 2}E_{b2}(+2) + c_{\pm 3}E_{b2}(-2)\\ &\quad + c_{\pm 4}E_{b1}(-2)\\ &\quad + \text{other terms with } c < 0.1\end{aligned} \tag{12}$$

In Table 3 are given the coefficients of $\psi_\pm$ as a function of the magnetic field.

Table 3. Wave Function Coefficients of the Ground State Doublet, ψ_n, $n = \pm$, for a^2 = 0.3758

B (T)	n	c_1	c_2	c_3	c_4	$\sum_{i=1}^{4} c_i^2$
0	+	−0.6095	−0.3412	0.6097	−0.3412	0.9761
	−	0.6095	0.3412	0.6097	0.3421	0.9761
0.05	+	0.8479	0.4650	−0.1555	0.1315	0.9767
	−	0.1558	−0.1303	0.8479	0.4653	0.9768
0.10	+	0.8583	0.4779	−0.0807	0.0720	0.9768
	−	0.0810	−0.0707	0.8583	0.4779	0.9766
0.15	+	0.8603	0.4808	−0.0541	0.0491	0.9766
	−	0.0544	−0.0478	0.8604	0.4807	0.9767
0.20	+	0.8610	0.4820	−0.0407	0.0372	0.9767
	−	0.0410	−0.0359	0.8611	0.4817	0.9765
0.80	+	0.8617	0.4839	−0.0101	0.0099	0.9769
	−	0.0104	−0.0086	0.8622	0.4826	0.9765
8.0	+	0.8919	0.3701	−0.0007	0.0003	0.9325
	−	−0.0011	−0.0005	0.9028	0.3527	0.9394

The smaller value for the sum of coefficients squared, $\sum_{i=1}^{4} c_i^2$, for 8 T is due to sizable contributions from the excited $M_S = \pm 1$ states. The small rhombic distortion gives rise to a dramatic change in the ground state doublet's wave functions. At zero magnetic field, they change from $M_S = \pm 2$ spin functions to a quenched mixture of the two spin states. This quenching is completely removed only at magnetic fields much larger than the zero field splitting of the doublet. This is what allows detection of EPR and magnetic Mössbauer spectra. Also, at all field values, the $E_{b2}(+2)$ and $E_{b1}(-2)$ functions now make a significant contribution. We now consider the actual EPR spectrum resulting from this doublet, which is easiest for a spectrometer with the oscillating field, B_1, parallel to the main field, B_0. Such a configuration is indeed fruitfully employed to study such systems by EPR.[8,32,33]

The intensity of an EPR transition for $B_{0,1}$ along the z axis will be proportional to:

$$
\begin{aligned}
&|\langle\psi_+|S_z|\psi_-\rangle|^2\\
&\quad = [4(c_{+1}c_{-1} + c_{+2}c_{-2} - c_{+3}c_{-3} - c_{+4}c_{-4})\\
&\qquad + (2 - 3a^2)(c_{+1}c_{-1} - c_{+2}c_{-2} - c_{+3}c_{-3} + c_{+4}c_{-4})]^2
\end{aligned}
$$

When the magnetic field is at angle θ to the z axis the intensity, I, is

$$I = \cos^2\theta|\langle\psi_+|S_z|\psi_-\rangle|^2$$

because the intensity components in the x and y directions are zero. As the angle θ becomes larger, the magnetic field for the transition becomes rapidly larger in magnitude, but the intensity drops off rapidly as well. In a powder sample, the chance of the molecule's orientation being at a given θ becomes larger as well, which partly compensates for the lower intensity. Thus we would expect a peak in the absorption spectrum near $g_{\text{eff}} = 4g_z$. In Figure 4 is a simulated EPR spectrum for our $a^2 = 0.3786$ system, presented in first derivative mode, as in conventional EPR.

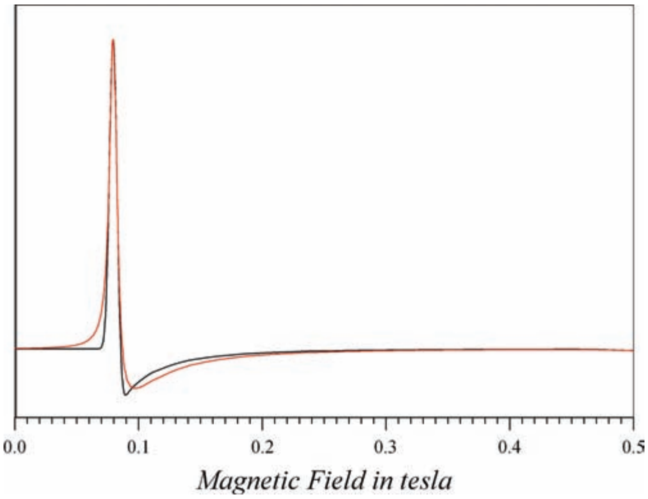


Figure 4. Simulated EPR spectrum for distorted tetrahedral d^6 with $a^2 = 0.3786$ with B_1 parallel to z (B_0). Red line is for Gaussian broadening and black for Lorentzian broadening. Line width is 300 G in each case.

The EPR simulation program was necessary because most simulation programs require a spin Hamiltonian, and we are in the process of demonstrating that eq 1 is not a proper one for the system considered here. We used our theory to calculate the intensity at a large number of orientations of the magnetic field in an organized pattern and convert the results to create our simulation. This is what all simulation programs do. We will propose a suitable spin Hamiltonian later that could be used with other simulation programs.

The above simulation appears to differ from the EPR spectrum for B_1 parallel with the main field reported by Popescu et al.,[4] but that is due to a 180° difference in the spectrometer's phase. The spectrum of Hendrich et al.[8] is similar to Figure 4. The EPR spectra reported for other trigonal Fe(II) complexes[18,23] are also similar to Figure 4. We recommend taking all EPR spectra for these systems with B_1 parallel to the main field because this detection mode will always lead to greater signal intensity.

We will show below that the best application of EPR in these systems is to estimate the magnitude of the zero-field splitting of the ground state. In Figure 4, the peak of the first derivative is about 100 G (10 mT) above the field that marks the appearance of the EPR spectrum.

The most important outcome of the above calculations is the absence of any Zeeman interaction when the magnetic field is perpendicular to the symmetry axis. This tells us to expect large anisotropies in magnetic properties, such as Zeeman interactions, hyperfine coupling interactions, magnetic susceptibility, magnetic Mössbauer, or ENDOR spectroscopy.

Many researchers have attempted to simulate the ground state doublet for a trigonally distorted tetrahedral d^6 complex using eq 1 and $S = 2$ with a negative D value and assumed a significant rhombic splitting (nonzero E parameter) to make the $M_S = \pm 2$ levels split at zero field. We have shown here that it is possible to generate such an EPR spectrum, enhanced in parallel mode detection, without any *significant* rhombic distortion.

Case of Compression along the C_3 Axis. In this case, the ground state changes (see Figure 2) and the ground state doublet is not degenerate even when there is a C_3 axis. We chose for this case the trigonal pyramidal iron(II) trispyrrolylamine complexes, $[\text{Fe(tpa}^{\text{R}})]^-$.[17,18] These have the Fe(II) ion nearly in the plane of three pyrrolide nitrogen atoms of the ligand (N(pyrrolide$_{\text{eq}}$)) and have an axial amine nitrogen (N(amine$_{\text{ax}}$)). For this arrangement, a^2 will be nearly unity. This makes the ground state $^5D_{\pm 1}$. The two wave functions are:

$$\psi_\pm = c_{\pm 2}E_{b2}(+2) + c_{\pm 4}E_{b1}(-2) + \text{other very small terms}$$

We chose this system because it has been treated theoretically by Atanasov et al.,[26] and we can compare our results to theirs. The first comparison is the ground state. Atanasov et al.[26] report the ground state to be a mixture of d_{xz} and d_{yz}, which is our $d_{\pm 1}$. We will use their N-electron valence perturbation theory (NEVPT2) calculations for $[\text{Fe(tpa}^{t\text{-Bu}})]^-$ (tpa$^{t\text{-Bu}}$ = tris(5-*tert*-butyl-1*H*-pyrrol-2-ylmethyl)amine trianion). From their calculation we use $E(E_a) = 8760$ cm^{-1} and $E(A) = 7400$ cm^{-1}. The N(amine$_{\text{ax}}$)−Fe-N(pyrrolide$_{\text{eq}}$) bond angle of 82.55°[17,26] gives $a^2 = 0.9360$ (eq 5b). We use $V_1 = 0$ because we need no distortion to produce a separation in the ground doublet. The energies for the 10 levels of the ^5E_b ground state are listed in Table 4 along with the values calculated by Atanasov et al.[26]

For comparison, as was the case above with [PhTt$^{t\text{Bu}}$]Fe(Me), we also applied the AOM to $[\text{Fe(tpa}^{t\text{-Bu}})]^-$ using the complete d^6 basis set. In this case, however, the parameters are well determined, as Atanasov et al. performed extensive correlations between their ab initio calculations and LFT.[26] Table 4 presents the lowest 10 energy levels calculated using their parameters and a geometrical model, which to the best of our knowledge, corresponds exactly to theirs. Considering the simplicity of our theory, the differences from both LFT and ab initio calculations are small, reaching only 10% in the higher levels.

We have demonstrated that the first-order spin−orbit interaction is the largest term in the spin−orbit interaction and it is improper to assign the symbol D to the total spin−orbit interaction. Thus, eq 1 is not a good representation of the ground state. It is unfortunate that many workers came to assume that the spin−orbit interaction has no zero-order term when the big computer programs were calculating it. We are

Table 4. Energies of the 10 Lowest Energy Levels (in cm^{-1}) of ^5E_b for $[\mathrm{Fe(tpa}^{t\text{-Bu}})]^-$

level no. (symmetry label in D_3*)[a]	energy from our ^{5}D-based calculation[b]	energy from ab initio (NEVPT2) calculation[c]	energy from LFT calculation based on NEVPT2 calculation[d]
1, 2 (A_1, A_2)	0	0	0
	0.006	0.001	0.078
3, 4 (E)	77.4	83.4	80.1
	77.4	83.5	80.1
5, 6 (E)	159.8	168.2	171.2
	159.8	183.2	171.2
7 (A_1)	235.7	259.2	247.1
8 (A_2)	261.7	300.1	308.2
9, 10 (E)	342.7	389.1	390.0
	342.7	389.2	390.0

[a] Symmetry label in D_3* given to provide correspondence with Atanasov et al.[26] [b] Calculation using ^{5}D model with $a^2 = 0.9360$ and (in cm^{-1}): $E(E_a) - E(E_b) = 8760$, $E(A) - E(E_b) = 7430$, $V_2 = 0$, $\lambda = -107$. [c] Calculation done by Atanasov et al.[26] [d] Calculation done here using the Ligfield program with LFT (AOM) parameters determined by Atanasov et al.[26] as corresponding to (derived from) their ab initio (NEVPT2) calculation. The parameters (in cm^{-1}) are as follows (see their Table 6b[26]): $\zeta = 494$, $B = 1213$, $C = 3372$, $e_\sigma^{\mathrm{eq}} = 7540$ (σ-bonding to three equivalent, equatorial pyrrolide N donors: $\mathrm{N^{eq}} \equiv$ N1, N1E, N1K), $e_\sigma^{\mathrm{ax}} = 2330$ (σ-bonding to the axial amine N donor: $\mathrm{N^{ax}} \equiv$ N2). We used the molecular structure of this complex as reported by Harman et al.[17] (CSD code: OSUBIO), with θ defined for the AOM by $\angle\mathrm{N^{ax}{-}Fe{-}N^{eq}} = 82.55°$ and ϕ set equal to 0° (N1), 120° (N1E), and 240° (N1K), as the molecule has crystallographically imposed 3-fold symmetry (space group $P2_13$); inclusion of $\psi \neq 0$ had no effect in our model. This calculation gives (in cm^{-1}) $E(A) = 7640$ and $E(E_a) = 8510 - 9400$ (mean energy 8970), however, with $\zeta = 0$, one obtains $E(A) = 7429.0$ and $E(E_a) = 8760.5$; values identical to those given in Table 4 of Atanasov et al.,[26] which suggests that our AOM is equivalent to theirs. The complete LFT results are given in Table S5 (Supporting Information).

gratified that our simple theoretical approach was better than we expected.

We now go on to use it to learn more about the nature of the EPR spectrum and the electron–nuclear hyperfine interactions in these systems.

Spin Hamiltonian for the Ground State. A spin-Hamiltonian that represents the ground state doublet has been proposed:[23,34]

$$\mathcal{H} = g\beta_e BS_z + \frac{\Delta}{48}(S_+^4 + S_-^4) \tag{13}$$

with the spin functions $|M_S = \pm 2\rangle$. The first term is the Zeeman interaction that has no x and y terms, as has been found experimentally in these systems. The second term is just the zero-field splitting of the ground state doublet. It would seem that one could represent it by the term $(1/4)\Delta S_z$, but this would not give the quenched spin states that are predicted by our theory when the Zeeman interaction is less than Δ. Equation 13 is valid only when the first-order spin–orbit interaction is much larger than the second-order contributions, which is true for the systems considered here. If the first-order spin–orbit interaction is small, then eq 1 prevails.

The solution for eq 13 is in the Supporting Information, which gives the following equation for the energy difference in the doublet:

$$\Delta E = \sqrt{\Delta^2 + 16g^2\beta_e^2B^2\cos^2\theta} = h\nu_0 \tag{14}$$

where θ is the angle between B and the z axis and ν_0 is the EPR frequency. If Δ is greater than $h\nu_0$, no EPR can be seen until B is large enough to make $(\Delta^2 + 16_g^2\beta_e^2B_{\mathrm{start}}^2)^{1/2} > h\nu_0$, where B_{start} is the minimum field value to allow onset of an EPR signal. In our earlier discussion of the spin state, we found that the highest intensity of the EPR signal occurs at fields only slightly larger than B_{start}. Thus as Δ increases, the absorption peak moves to lower fields. This means we can determine Δ from the position of the field. If B_{start} can be estimated, then eq 14 can be solved for Δ:

$$\Delta^2 = (h\nu_0)^2 - 16g^2\beta_e^2B_{\mathrm{start}}^2 \tag{15}$$

In the few simulations we have done, we find a reasonable value for B_{start} to be about 150 G (15 mT) below the first derivative peak in the EPR spectrum. The best method is to create a simulation program from eq 14. Of course, one has to know the g value. This can be done by recording EPR spectra at multiple frequencies so that different B_{start} values are determined.

As an example of using the above equations, we will use EPR spectra given by Andres et al. for (nacnac)FeX, where X = Cl, $\mathrm{CH_3}$.[23] The planar, three-coordinate (nacnac)FeX complexes do not have C_3 symmetry, but it is obvious from the observed large energy separation of the ground state doublet and the first excited state that they have a large first-order spin–orbit interaction. Thus eq 13 will apply. We estimate that $B_{\mathrm{start}} = 145$ G for (nacnac)Fe–Cl and 450 G for (nacnac)$\mathrm{FeCH_3}$. Equation 15 yields $\Delta = 0.30$ cm^{-1} for (nacnac)FeCl and 0.23 cm^{-1} for (nacnac)$\mathrm{FeCH_3}$. Andres et al. used eq 13 and g_{eff} to estimate Δ and obtained $\Delta = 0.255{-}0.284$ cm^{-1} for (nacnac)FeCl and 0.03 cm^{-1} for (nacnac)$\mathrm{FeCH_3}$.[23] Unfortunately, their method broke down for $\mathrm{CH_3}$.

The Nuclear Spin-Electron Spin Hyperfine Interaction. The electron–nuclear hyperfine interaction in these types of Fe(II) complexes has been detected in magnetic Mössbauer studies only by measurement of the "internal field". The interpretation of the magnetic Mössbauer spectra was based on a theory that assumed the ground state could be modeled using only a second-order zero-field spin Hamiltonian. This works reasonably well for low to moderate magnetic fields and very low temperatures but should fail when excited states contribute, which occurs for Mössbauer measurements at high magnetic fields and/or higher temperatures than liquid He.

We will not attempt to fully analyze the Mössbauer results because we have neither the data nor the expertise to do so, but we will comment on published results not only for the tripodal thioether complex[4] but also on the planar three-coordinate complex of Andres et al. because they also reported magnetic Mössbauer data.[23]

We will begin by calculating the hyperfine interaction relevant for these C_3 systems. This interaction in general consists of three terms which are commonly represented by the operator:[35]

$$\begin{aligned}\mathcal{H}_{\mathrm{IS}} = {} & -\kappa P\sum_i s_i\cdot I \\ & - g_e g_N\beta_N\beta_e\sum_i [r_i^2(s_i\cdot I) - 3(s_i\cdot r_i)(I\cdot r_i)]r_i^{-3} \\ & + P(L\cdot I)\end{aligned} \tag{16a}$$

where

$$P = g_e g_N \beta_N \beta_e \langle r^{-3} \rangle_{\mathrm{av}} \tag{16b}$$

The first term is the Fermi contact interaction between electronic and nuclear spins and κ is a parameter for its magnitude. The second term is the dipolar interaction between the electronic and nuclear spins. The third term is the nuclear spin−orbit term, which is of secondary importance in systems with a ground state with no angular momentum ("quenched") but is a dominant term when the ground state possesses angular momentum ("unquenched"). When there is a well separated doublet ground state in a system that really has $S > 1/2$, it is common to treat it as an effective $S' = 1/2$ system with an effective g_{eff} value. Thus for the two cases we are considering, the g_{eff} value is 8−10. For an $S = 1/2$ system, the two hyperfine parameters are calculated from the two equations.

$$\begin{aligned} A_{\parallel} &= -2\langle \psi_- | (\mathcal{H}'_{\mathrm{IS}})_z | \psi_- \rangle, \\ A_{\perp} &= +2\langle \psi_+ | (\mathcal{H}'_{\mathrm{IS}})_x | \psi_- \rangle \end{aligned} \tag{17}$$

in which the $\mathcal{H}'_{\mathrm{IS}}$ operator is the $\mathcal{H}_{\mathrm{LS}}$ operator with the loss of the appropriate I_z or I_x operator. Thus, for $A_{\parallel}$ we use the operator:

$$\begin{aligned} (\mathcal{H}'_{\mathrm{IS}})_z &= -\kappa P S_z - (g_e g_N \beta_N \beta_e) \sum_i (1 - 3\cos^2\theta) r_i^{-3} s_{zi} \\ &\quad + PL_z \end{aligned} \tag{18}$$

to give the following equation for $A_{\parallel}$:

$$\begin{aligned} A_{\parallel} &= -2\langle \psi_- | (\mathcal{H}'_{\mathrm{IS}})_z | \psi_- \rangle \\ &= 2\kappa \langle \psi_- | S_z | \psi_- \rangle P + \langle \psi_- | DP(\text{orbital}) S_z | \psi_- \rangle P \\ &\quad - 2\langle \psi_- | L_z | \psi_- \rangle P \end{aligned} \tag{19}$$

where,

$$\begin{aligned} DP(A) &= \frac{2}{7} \\ DP(E_{a1}) = DP(E_{a2}) &= -\frac{(3a^2 - 1)}{7} \\ DP(E_{b1}) = DP(E_{b2}) &= -\frac{(2 - 3a^2)}{7} \end{aligned} \tag{20}$$

Examination of the coefficients in Table 3 shows that at low magnetic fields, each state in the ground state doublet, $\Psi_{\pm}$, has equal amounts of ±2 spin giving no net spin and therefore $A_{\parallel}$ is also zero. However, $A_{\parallel}$ rapidly becomes larger in magnitude as the field becomes larger than the zero-field splitting of the doublet. Because $A_{\parallel}$ depends on the magnetic field, we have used our program to calculate it at 8.0 T, which is the external magnetic field at which the Mössbauer studies were done.[4] For $a^2 = 1.0$ and $B = 8.0$ T, eq 19 becomes

$$\begin{aligned} A_{\parallel} &= -3.9900\kappa P - 0.2846P + 1.8043P \\ &= -3.9900\kappa P + 1.5595P \end{aligned} \tag{21}$$

and for $a^2 = 0.3786$

$$\begin{aligned} A_{\parallel} &= -3.9882\kappa P + 0.2456P + 1.4295P \\ &= -3.9882\kappa P + 1.6751P \end{aligned} \tag{22}$$

Popescu et al. reported a value of 24.6 T for $A_{\parallel}$ in their elongated complex and used the value of $P = 68$ MHz or 49 T for their analysis.[4] Equation 22 thus yields $\kappa = -0.126$. Andres et al.[23] reported an $A_{\parallel} = 41$ T for their planar triangular complex for which eq 21 yields $\kappa = 0.181$.[23] These κ values are comparable to values found in other first row transition metal complexes.[35] The theory presented here easily explains why Andres et al.[23] found much larger internal fields in their complexes than did Popescu et al.[4] It is due to the large nuclear spin−orbit term for the planar three-coordinate complex.

Our theory finds that for magnetic field values below 1 T, there is no Zeeman splitting when the magnetic field is in the x or y direction and the spin states are mixed as they are at zero field. It follows, therefore, that there is no hyperfine interaction and $A_{\perp}$ is zero. For the case of $a^2 = 1.0$ this continues even up to 10 T and explains why Andres et al. found no evidence of any internal field in the x direction even at an external field of 8 T.[23] However, for $a^2 = 0.3786$, a weak Zeeman interaction is seen due to admixture of the $M_S = \pm 1$ states from the first excited doublet states, which explains why Popescu et al. were able to detect small internal fields at 8 T applied in the x direction.[4]

There are two points to be noted here about the value of $A_{\parallel}$: (1) the largest magnitude component is the angular momentum term which is positive for both the elongated complex and the compressed complex, (2) the dipolar term is negative for compressed complexes and positive for elongated complexes. The contact term is basically $-4\kappa P$ due to the doublet state being an $M_S = \pm 2$ state (a true $S = 1/2$ state would have a contact term of $-\kappa P$). The problem of earlier analyses of the magnetic Mössbauer spectra of these complexes resulted from their assumption that the ground doublet was the result of zero field interaction, which could be treated as an effective $S' = 1/2$ system with g_x values different from zero. They further assumed that the hyperfine Hamiltonian terms were identical in behavior to those found in true $S = 1/2$ systems. That is, they would not change in value with B, the contact term would be isotropic, the dipolar term would average to zero, and the angular momentum contribution would be second-order in magnitude. None of this simple behavior was the case here, where all interactions contribute only to the z hyperfine term.

Analogously to the situation here, an anisotropic Fermi contact term has been detected in NMR studies of uranocene ($[(\mathrm{cot})_2\mathrm{U}]$, U(IV), $5f^2$),[36] which has even higher symmetry than the complexes studied here, namely an 8-fold symmetry axis. Uranocene has a $^3H_4$ ground term and the ground state is a doublet state with $M_J = \pm 4$, which is thus similar to the ^5D systems considered here. It also has a magnetic moment only in the z direction.

■ CONCLUSIONS

We started this work because we were concerned that the $S = 2$ spin Hamiltonian (eq 1) is not appropriate for d^6 tetrahedral systems with a C_3 symmetry axis and a large angular momentum in the ground state, despite its popularity. This equation becomes inappropriate when the separation between the ground state doublet and the first excited state is of the same order of magnitude as the spin−orbit interaction constants. We have also shown that the habit of many investigators in the field to assign the total spin−orbit interaction to the D term of the zero field Hamiltonian is wrong and contrary to the definition of the parameters D and E. For Fe(II), this applies to systems when the first excited state is greater than 20 cm^{-1}. We expected the source of the high energy for the first excited state to be due to the first-order spin−orbit interaction, which appears to have been ignored by most investigators of these complexes. The work above demonstrates that we were correct in our assumptions.

The simple model we developed starting with the ^5D free-ion ground state for high-spin $3d^6$ Fe(II) (and $3d^4$ Fe(IV)) turned out to be very good in predicting the energies of the 10 levels in the ^5E ground state. At least the results were close to the values given by two more comprehensive computer programs. The success of our simple theory is primarily due to our decision to start our calculation with Slater wave functions made from atomic d orbitals that already have C_3 symmetry. The shapes of these orbitals depend on the parameter a, which is determined by the bond angles. Thus the magnitude of the first-order spin−orbit interaction is dependent on the bond angles, which are due to the nature of the bonds. The angle between the bond along the z (C_3) axis and the three other bonds must be between 99° and 118° to have a first-order spin−orbit interaction less than 30 cm^{-1}, at which point the second-order terms become important. Outside 99−118°, the first-order spin−orbit interaction becomes dominant.

The Zeeman splitting from an applied magnetic field is also included. Two representative cases are considered: a four-coordinate complex of type L_3FeX (L_3 = tridentate ligand, X = CH_3) with nearly ideal C_{3v} symmetry and a complex of type L_4Fe (L_4 = tetradentate ligand) of C_3 symmetry where the Fe(II) atom is close to the plane of three equatorial N atoms of L_4. The method used here reproduces the EPR spectra reported for these complexes and the magnetic Mössbauer results for the L_3FeX and planar L_2FeX (L_2 = bidentate ligand) complexes

We extended our theoretical calculations to the nature of the EPR spectrum and the hyperfine interaction. The EPR spectrum had previously been simulated using only eq 1, while the hyperfine interaction was assumed to be the same as found for systems with no first-order angular momentum.

In light of our success in using the C_3 d orbitals in the D ground state, we believe it would also be useful to re-examine Jesson's work on systems with the F ground state,[37] such as d^7 of Co(II), using these orbitals. Many researchers have also ignored the first-order spin−orbit interaction in these systems and assumed a zero-field spin Hamiltonian instead.

■ ASSOCIATED CONTENT

Supporting Information

Complete matrix elements for trigonal $d^{4,6}$ and $d^{1,9}$ cases; three tables of AOM calculation results; proper spin Hamiltonian for $S = 2$ ground state doublet. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jtelser@roosevelt.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Jesper Bendix (Copenhagenn University, Denmark) for the program Ligfield and a reviewer for extensive, constructive criticism.

■ REFERENCES

(1) Abragam, A.; Bleaney, B., *Electron Paramagnetic Resonance of Transition Ions*; Dover Publications, Inc.: Mineola, NY, 1986.

(2) McGarvey, B. R., Electron Spin Resonance of Transition Metal Complexes. In *Transition Metal Chemistry*; Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; pp 89−201.

(3) McGavin, D. G.; Tennant, W. C.; Weil, J. A. *J. Magn. Reson.* **1990**, *87*, 92−109.

(4) Popescu, C. V.; Mock, M. T.; Stoian, S. A.; Dougherty, W. G.; Yap, G. P. A.; Riordan, C. G. *Inorg. Chem.* **2009**, *48*, 8317−8324.

(5) Riordan, C. G. *Coord. Chem. Rev.* **2010**, *254*, 1815−1825.

(6) MacBeth, C. E.; Thomas, J. C.; Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2004**, *43*, 4645−4662.

(7) Mehn, M. P.; Brown, S. D.; Paine, T. K.; Brennessel, W. W.; Cramer, C. J.; Peters, J. C.; Que, L., Jr. *Dalton Trans.* **2006**, 1347−1351.

(8) Hendrich, M. P.; Gunderson, W.; Behan, R. K.; Green, M. T.; Mehn, M. P.; Betley, T. A.; Lu, C. C.; Peters, J. C. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17107−17112.

(9) Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074−5084.

(10) Nieto, I.; Cervantes-Lee, F.; Smith, J. M. *Chem. Commun.* **2005**, 3811−3813.

(11) Cowley, R. E.; Bontchev, R. P.; Duesler, E. N.; Smith, J. M. *Inorg. Chem.* **2006**, *45*, 9771−9779.

(12) Smith, J. M. *Comments Inorg. Chem.* **2008**, *29*, 189−233.

(13) Trofimenko, S. *Polyhedron* **2004**, *23*, 197−203.

(14) Trofimenko, S.; Rheingold, A. L.; Liable Sands, L. M. *Inorg. Chem.* **2002**, *41*, 1889−1896.

(15) Lim, M. H.; Rohde, J.-U.; Stubna, A.; Bukowski, M. R.; Costas, M.; Ho, R. Y. N.; Münck, E.; Nam, W.; Que, L., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3665−3670.

(16) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev.* **2004**, *104*, 939−986.

(17) Harman, W. H.; Harris, T. D.; Freedman, D. E.; Fong, H.; Chang, A.; Rinehart, J. D.; Ozarowski, A.; Sougrati, M. T.; Grandjean, F.; Long, G. J.; Long, J. R.; Chang, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 18115−18126.

(18) Freedman, D. E.; Harman, W. H.; Harris, T. D.; Long, G. J.; Chang, C. J.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 1224−1225.

(19) Chang and co-workers[17,18] used the abbreviation tpa for their trispyrrolylamine-based ligands; this should not be confused with the use of tpa for trispyridylamine-based ligands; here we are concerned only with trispyrrolylamine complexes and use the ligand abbreviations of Chang and co-workers.

(20) Nieto, I.; Ding, F.; Bontchev, R. P.; Wang, H.; Smith, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 2716−2717.

(21) Que, L., Jr. *Acc. Chem. Res.* **2007**, *40*, 493−500.

(22) Bigi, J. P.; Harman, W. H.; Lassalle-Kaiser, B.; Robles, D. M.; Stich, T. A.; Yano, J.; Britt, R. D.; Chang, C. J. *J. Am. Chem. Soc.* **2012**, *134*, 1536−1542.

(23) Andres, H.; Bominaar, E. L.; Smith, J. M.; Eckert, N. A.; Holland, P. L.; Münck, E. *J. Am. Chem. Soc.* **2002**, *124*, 3012−3025.

(24) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066.

(25) Palii, A. V.; Clemente-Juan, J. M.; Coronado, E.; Klokishner, S. I.; Ostrovsky, S. M.; Reu, O. S. *Inorg. Chem.* **2010**, *49*, 8073−8077.

(26) Atanasov, M.; Ganyushin, D.; Pantazis, D. A.; Sivalingam, K.; Neese, F. *Inorg. Chem.* **2011**, *50*, 7460−7477.

(27) Neese, F.; Pantazis, D. A. *Faraday Discuss.* **2011**, *148*, 229−238.

(28) They give: $D_{zz} = (-4)\lambda^2/\Delta$, $D_{xx} = D_{yy} = -\lambda^2/\Delta_2$ ($\Delta_2 \approx 10Dq$), and $g_{z,\mathrm{eff}} = [2.0 + 2(-4)\lambda]/\Delta$.

(29) Bendix, J.; Brorson, M.; Schäffer, C. E. *Inorg. Chem.* **1993**, *32*, 2838−2849.

(30) McGarvey, B. R. *J. Chem. Phys.* **1963**, *38*, 388−392.

(31) The rhombic terms provided are not comprehensive but are sufficient to produce a small splitting of two orbital doublet states. We are interested only the effect of a small splitting of the ground state. The addition of multiple parameters that could be fitted would be counterproductive at this point.

(32) Britt, R. D.; Peloquin, J. M.; Campbell, K. A. *Annu. Rev. Biophys. Biomol. Struct.* **2000**, *29*, 463−495.
(33) Campbell, K. A.; Lashley, M. R.; Wyatt, J. K.; Nantz, M. H.; Britt, R. D. *J. Am. Chem. Soc.* **2001**, *123*, 5710−5719.
(34) Surerus, K. K.; Hendrich, M. P.; Christie, P. D.; Rottgardt, D.; Orme-Johnson, W. H.; Münck, E. *J. Am. Chem. Soc.* **1992**, *114*, 8579−8590.
(35) McGarvey, B. R. *J. Phys. Chem.* **1967**, *71*, 51−66.
(36) McGarvey, B. R.; Nagy, S. *Inorg. Chem.* **1987**, *26*, 4198−4203.
(37) Jesson, J. P. *J. Chem. Phys.* **1966**, *45*, 1049−1057.