The Effect of Spin-Orbit Coupling on the Magnetic Properties of H2Ti(μ–H)2TiH2

Simon P. Webb
Iowa State University

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

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Abstract
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Keywords
Spin orbit interactions, Angular momentum, Excited states, Band gap, Charge coupled devices

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The effect of spin-orbit coupling on the magnetic properties of $\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2$

Simon P. Webb and Mark S. Gordon

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Excited states of singlet and triplet $\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2$ have been calculated using multiconfigurational wave functions. The effects of orbital relaxation are determined by optimizing orbitals for all states separately and comparing to state-averaged calculations, and are found to be small. Dynamic electron correlation included through second-order perturbation theory is found to have a considerable effect on excited state relative energies, but not on the ordering of states. Spin-orbit coupling effects are introduced by a one-electron operator which uses an effective nuclear charge to replace two-electron effects. The resulting splittings of the lowest energy triplet state components are 0.027 and 0.199 cm$^{-1}$, respectively. The former is due to the angular momentum operator which acts along the Ti–Ti axis; the latter is due almost entirely to the angular momentum operator which acts in the direction perpendicular to the plane of the Ti–H–Ti bridge. An overall ferromagnetic effect of 0.660 cm$^{-1}$ on the ground state singlet-first excited triplet energy gap is predicted. Orbital interactions responsible for spin-orbit coupling effects are identified. © 1998 American Institute of Physics. [S0021-9606(98)01327-0]

I. INTRODUCTION

Often the magnetic properties of molecular systems are highly dependent on intramolecular interactions. In dinuclear complexes comprising two metal centers each with an unpaired electron, if singlet coupling of the electrons is energetically favored over triplet coupling, the interaction is antiferromagnetic; if triplet coupling is favored over singlet coupling, the interaction is ferromagnetic. There are a number of effects which can contribute to the intramolecular interaction. The magnitude and sign of the singlet-triplet energy gap, where the singlet and triplet are the two lowest energy states, and where effects due to spin-orbit coupling and magnetic dipole–dipole interactions are neglected, is a measure of the isotropic exchange interaction. In a previous study on the isomers of Ti$_2$H$_6$ (Ref. 2) we calculated the isotropic exchange interaction of $D_{2h}$ $\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2$ to be antiferromagnetic with $J = -250$ cm$^{-1}$, where $J$ is defined by $-2J = E(\text{triplet}) - E(\text{singlet})$.

The isotropic exchange interaction usually dominates spin-orbit coupling and magnetic dipole–dipole interaction effects in determining the magnetic properties of dinuclear complexes. However, when the singlet-triplet splitting itself is very small and ferromagnetic, these normally subtle effects can be important, influencing the magnetic properties of the system in the low temperature range. What is more, electron paramagnetic resonance (EPR) experiments are generally able to detect these much smaller effects as they result in the zero-field splitting (ZFS) of the triplet state $M_s$ components. In EPR experiments there are two allowed transitions within the triplet manifold, corresponding to $\Delta M_s = \pm 1$, and a forbidden transition $\Delta M_s = 2$ (between $M_s = +1$ and $M_s = -1$) at half field. In a randomly oriented ensemble of molecules the transitions are only observable when the principal axes of the molecules (see Fig. 1) are parallel or nearly parallel to the $x, y, z$ components of the applied magnetic field; otherwise they contribute only to continuous background. A $\Delta M_s = \pm 1$ spectrum, then, consists of three sets of doublet peaks corresponding to applied magnetic fields in $x, y, z$ directions. Analysis of the spectrum is carried out by use of an effective spin Hamiltonian $H$ associated with the triplet spin quantum number $S = 1^{\pm 1}$.

$$H = \beta H \cdot g \cdot S + S \cdot D \cdot S.$$ (1)

The first term in Eq. (1) accounts for the Zeeman perturbation due to the applied magnetic field $H$; $g$ is the gyromagnetic tensor and $\beta$ is the electronic Bohr magneton. The second term accounts for dipolar and spin-orbit coupling effects and involves the zero-field splitting (ZFS) tensor $D$. The principal values (diagonal elements) of $g$ and $D$ are deduced from a fit to the experimental data; that is a fit to the measured resonance fields of the allowed transitions. The zero-field splitting parameters $D$ and $E$ are then calculated from the principal values of $D$ according to

$$D = 3D_x/2,$$ (2)

$$E = (D_x - D_y)/2.$$ (3)

The principal axes of $D$ (i.e., its orientation) are chosen such that $|D| \geq |E|$. $D$ is known as the axial zero-field splitting parameter; $E$ is the rhombic zero-field splitting parameter. A recent application of EPR spectroscopy and analysis of the resulting spectrum using the method just outlined can be found in a study of $\text{rac} \cdot ([\text{C}_2\text{H}_5(\eta^5\text{tetracyclo}[2.2.2.0^{2,5}]heptadienyl)]_2\text{Ti}(\text{III})(\mu-\text{H})_2)^{\pm 1}$. As mentioned above, the origin of the splitting of the triplet $M_s$ components lies in two types of interactions; the interaction between magnetic dipoles and the interactions due to spin–orbit coupling. The spin–orbit coupling interactions are often referred to as anisotropic ex-
change interactions or pseudodipolar interactions. In this work we consider the spin-orbit coupling part of the problem.

The anisotropic exchange interaction tensor $D_e$ is found in the analysis of experimental data by subtraction of the magnetic dipole-dipole interaction tensor $D_d$ from the total ZFS tensor $D$. The dipole-dipole interaction tensor $D_d$ is calculated according to an expression dependent on $g$ and $\frac{1}{r^3}$, where $r$ is the metal-metal separation; axial and rhombic terms $D_d$ and $E_d$ are calculated by application of Eqs. (2) and (3) to this tensor. The exchange tensor $D_e$ may be found by

$$D_e = D - D_d.$$  

The principal axes of $D_d$ and $D_e$ which ensure that $|D_d| \geq 3E_d$ and $|D_e| \geq 3E_e$, respectively, may or may not coincide depending on the system under study. If they do not coincide then one may either define two different molecular orientations, one for each tensor, or alternatively allow the dominant effect to determine the principal axes for both; i.e., $D$ defines the principal axes. The axial and rhombic exchange interaction parameters for the latter approach, $D_e$ and $E_e$, are then found by simply applying

$$D_e = D - D_d,$$

$$E_e = E - E_d.$$  

Experiment has shown that $D$ in di-titanium systems is dominated by $D_d$ with the $z$ principal axis defined along the metal internuclear axis. Therefore we have defined the Ti–Ti axis in $D_{2h}$ H$_2$Ti($\mu-H$)$_2$TiH$_2$ as the $z$ axis (see Fig. 1).

The approach just outlined is a purely phenomenological one which extracts parameters related to the triplet splitting energies due to certain phenomena from experiment. It does not reveal any information on the mechanisms by which these phenomena occur. To this end the parameters $D_e$ and $E_e$ have been used in expressions based on perturbation theory to calculate singlet-triplet splitting energies of excited states. Two examples are: the study of $[\text{Cp}_2\text{Ti}(\mu-\text{OR})]_2$ by Samuel et al., and the study of $[\text{Cu}_2(\text{t-Bupy})_4(\text{N}_3)_2] \times (\text{ClO}_4)_2$ by Gatteschi et al. The aim is not only to characterize the excited states, but also to also to establish how he singlet versus triplet stability of the excited states affects he spin-orbit coupling related terms $D_e$ and $E_e$. A priori prediction of the sign and magnitude of these anisotropic exchange effects is cited as the ultimate goal.

However, the expressions used are highly dependent on approximations, such as the determination and use of orbital energy differences from only the singly occupied orbitals (the “active orbital approach”). Also, assumptions are made as to which excited state orbitals are included in the spin-orbit coupling scheme. In addition these expressions can only be used when the EPR spectrum is highly resolved, producing reliable values for $D$ and $E$. This is not always the case. To our knowledge ab initio methods have not, until now, been applied directly to this spin-orbit coupling problem. Through ab initio calculations on H$_2$Ti($\mu-H$)$_2$TiH$_2$ using multiconfigurational wave functions, our aim is twofold: to predict excited state energies, and to determine spin-orbit effects at a level of theory which enables clear identification of the orbital or state interactions which cause the exchange effects represented by the parameters $D_e$ and $E_e$. These spin-orbit effects are determined by calculation of the spin-orbit coupling matrix elements between ground and excited states (and between excited states) and diagonalization of the resulting matrix to give energy levels and eigenvectors of spin-mixed states.

The relative simplicity of H$_2$Ti($\mu-H$)$_2$TiH$_2$ makes it an ideal first candidate due both to manageability of calculations and its status as the simplest model for di-titanium (III) systems. Any modification of energy splittings by the presence of more complex ligands may then be identified readily in any future calculations by direct comparison.

II. COMPUTATIONAL DETAILS

A triple $\zeta$ with polarization (14s11p6d/10s8p3d) basis set is used for titanium. This consists of Wachter’s basis set with two additional sets of $p$ functions and a set of diffuse $d$ functions. For hydrogen Dunning’s (5s1p3s1p) basis set was used. Collectively this basis set is referred to as TZVP.

Preliminary calculations on singlet $D_{2h}$ H$_2$Ti($\mu-H$)$_2$TiH$_2$ were carried out at the restricted Hartree–Fock (RHF) level. After convergence of this single determinant wave function, modified virtual orbitals (MVOs) were generated by freezing the occupied orbitals; forming a cation by removal of six electrons and performing one self-consistent field (SCF) iteration. The resulting orbitals were used as a starting point for a two configuration (TCSF) geometry optimization. For the triplet state a geometry optimization at the restricted open-shell Hartree–Fock (ROHF) level of theory was performed.

For the ground state and lowest energy triplet, TCSF and ROHF wave functions have been shown to be qualitatively correct. Excited state calculations require fully optimized reaction space (FORS) multiconfigurational SCF (MCSCF) calculations with an active space that consists of 2 electrons in up to 10 orbitals depending on symmetry.

Dynamic electron correlation effects, when required, are included through single point multiconfigurational quaside-
generate second-order perturbation theory calculations (MCQDPT).\textsuperscript{13}

Spin-orbit coupling effects (SOC) are treated using a one-electron spin-orbit coupling operator.\textsuperscript{14} The operator uses an effective nuclear charge $Z_{\text{eff}}$ to replace two-electron effects. The $Z_{\text{eff}}$ of 9.873 used for titanium was chosen to reproduce the first zero-field splitting energy in neutral atomic $^3\text{F} \text{Ti}$, $J(2 \rightarrow 3) = 170.132$ cm$^{-1}$.\textsuperscript{15} A similar $Z_{\text{eff}}$ is obtained if one chooses to reproduce the doublet splitting in $^2\text{D} \text{Ti}(\text{III})$.

All calculations were done using the electronic structure code GAMESS.\textsuperscript{16}

III. RESULTS AND DISCUSSION

Calculated geometries for the lowest energy singlet and triplet states of $D_{2h}$ $\text{H}_2\text{Ti}(\mu-\text{H})\text{TiH}_2$ at the TCSCF/TZVP and ROHF/TZVP levels, respectively, are shown in Fig. 1. We first consider the excited states of $D_{2h}$ $\text{H}_2\text{Ti}(\mu-\text{H})\text{TiH}_2$, and then examine SOC effects.

A. Excited states

It is necessary to consider 2 electrons in 10 orbitals in order to arrive at correct descriptions of the excited states of $\text{H}_2\text{Ti}(\mu-\text{H})\text{TiH}_2$. These orbitals include Ti–Ti bonding and antibonding interactions of the type $\sigma\sigma^*$, $\pi\pi^*$, and $\delta\delta^*$ with some participation of bridging and terminal hydrogen atomic orbitals (see Fig. 2). Tables I and II show the electronic structures and energies of the first 20 singlet and 20 triplet states of $D_{2h}$ $\text{H}_2\text{Ti}(\mu-\text{H})\text{TiH}_2$.

The singlet energies in Table I are from a state-averaged 2 electron, 10 orbital MCSCF calculation at the TCSCF/ TZVP $^1\text{A}_g$ ground state geometry (see Fig. 1). Starting orbitals were symmetrized ($D_{2h}$) and resemble those shown in Fig. 2. The calculation was carried out with no symmetry constraints, with each of the first 20 states weighted equally. Using this wave function as a starting point and freezing the nonactive orbitals, a 2 electron, 10 orbital MCSCF triplet calculation was carried out at the same geometry using the same procedure to obtain the first 20 triplet states that are detailed in Table I. These are the orbitals used in the SOC calculations described below.

To assess the effects of orbital and geometry relaxation, as well as dynamic electron correlation, a subset of the states shown in Table I was analyzed (see Table II). The singlet energies were calculated at the TCSCF/TZVP $^1\text{A}_g$ ground state geometry; the triplet energies at the ROHF/TZVP $^3\text{B}_{1u}$ geometry (see Fig. 1). Initially, all orbitals allowed by symmetry were included in each MCSCF calculation on each state. Then, any orbitals with negligible occupation were discarded and the reduced space used for reoptimization of the wave function and subsequent perturbation corrections for dynamic electron correlation. When more than one state of a given symmetry was considered (five $^1\text{A}_g$ and five $^3\text{B}_{1u}$ states), the orbital coefficients for each of the roots were optimized separately.

From Tables I and II one can see the effects of orbital and geometry relaxation by comparing the columns headed MCSCF. For the first six states the difference is less than $\sim 0.6$ kcal/mol and for the remaining states it is no greater than $\sim 1.0$ kcal/mol. The MCQDPT results in Table II show that the effects of dynamic correlation are greater, with differences in the range $\sim 0.3$ to $\sim 5.7$ kcal/mol between the MCSCF and MCQDPT methods. However, except for two cases ($S_g$, $S_9$ and $T_9$, $T_{10}$), the MCSCF wave function does order the states correctly.

B. Spin-orbit coupling

The effects of SOC on the ground state singlet $S_0$ and first excited triplet $T_1$ were determined using a one-electron SOC operator which includes two-electron effects through an effective nuclear charge.\textsuperscript{14} Since current codes do not include the effects of dynamic electron correlation as obtained by MCQDPT in the SOC calculation, one does not anticipate...
TABLE II. Excited state energies (kcal/mol) of $D_{3h}$ H$_2$Ti($\mu$-H)H$\bar{H}$. Energies are relative to the ground state $^1A_g$. Singlet energy calculations were obtained at the lowest energy $^2B_{3u}$ geometry. A separate MCSCF/TZVP calculation was done for every excited state allowing the orbitals to be optimized specifically for the state in question. The natural orbitals are those defined in Fig. 2.

<table>
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number of states included in the SOC calculation; ferromagnetic or antiferromagnetic effects can be assigned to the mixing of specific adiabatic states.

Figure 3 is a schematic representation of the effect of SOC when all 20 singlet and triplet states are included in the calculation. For the purposes of the following discussion, both $S_0$ and $T_1$ will be referred to as ground states; $S_1-S_{19}$ and $T_{2}$-$T_{20}$ will be referred to as excited states. The manner in which the energy levels are labeled with their associated principal axes $X, Y, \text{ and } Z$ is discussed below. The relationship between $\Delta E(1)$ and $\Delta E(2)$ in Fig. 3 and $D_e$ and $E_e$ is explained in the Appendix.

From Fig. 3 the effect of SOC on the ground state singlet–triplet gap in $D_{2h}$ $H_2Ti(\mu-H)_2TiH_2$ is predicted to be a ferromagnetic one. This effect, however, is very small compared to the much larger isotropic effect $-204.856 \text{ cm}^{-1}$. The lack of dynamic correlation in the present calculations means that qualitative information, such as identifying which SOC interactions are important, is more reliable than the absolute values of the SOC induced splitting energies of $T_1$. However, the calculated splitting energies, $\Delta E(1)=0.027 \text{ cm}^{-1}$ and $\Delta E(2)=0.199 \text{ cm}^{-1}$, imply values of $D_e$ and $E_e$ (see the Appendix) which lie within the range of experimentally determined exchange parameters for related systems. Gatteschi et al. found $D_e=0.376 \text{ cm}^{-1}$ and $E_e=0.070 \text{ cm}^{-1}$ in their di-copper system; Samuel et al. found $D_e=0.0012 \text{ cm}^{-1}$ and $E_e=-0.0065 \text{ cm}^{-1}$ for their di-titanium system. In the copper system SOC effects dominate and the $z$ principal axis is defined by the exchange interaction tensor $D_e$ and is perpendicular to the Cu–Cu axis. In the titanium system, however, dipole effects dominate and the axial component is along the Ti–Ti axis as defined by the dipole interaction tensor $D_d$.

In this experiment the rhombic is larger than the axial exchange parameter ($|E_e|>|D_e|$) indicating that SOC effects are larger perpendicular to the Ti–Ti axis than along it.

A technique which has been used to simplify the mathematics involved in the analysis of experimental spectra outlined in Sec. I is the adoption of spin-functions quantized along the principal axes $x, y$, and $z$.  

$$T_x = \frac{1}{\sqrt{2}} (\beta_1 \beta_2 - \alpha_1 \alpha_2),$$

FIG. 3. Schematic representation of the effects of a spin-orbit coupling calculation on $S_0$ and $T_1$ which includes the first 20 singlet ($S_0-S_{19}$) and triplet ($T_1-T_{20}$) states of $D_{2h}$ $H_2Ti(\mu-H)_2TiH_2$.

FIG. 4. Decomposition of the total effect of spin-orbit coupling on $S_0$ and $T_1$ by adding the states included in the calculation a few at a time.
This change of basis from $M_a = \pm 1, 0$ and 1 is not required in our calculation, but to facilitate comparison to experiment, by inspection of the eigenvectors obtained from the diagonalization of the $80 \times 80$ SOC matrix for $D_{2h}$ $\text{H}_2\text{Ti}(\mu - \text{H})\text{H}_2\text{Ti}$ (see Table III) and accounting for orbital phases, we have labeled the split energy levels in Fig. 3 $X$, $Y$, and $Z$ according to the definitions in Eqs. (7)–(9). These labels represent agreement with Samuel et al.’s experiment in that they also show that the rhombic is larger than the axial exchange effect when the $z$ axis is defined along the Ti–Ti direction (see Fig. 1). The eigenvectors also allow determination of the weightings of the adiabatic states which make up the spin-mixed states. The composition of the first four spin-mixed states are shown in Table III, and illustrates why the $T_1$ spin-mixed states are split; that is each component of $T_1$ mixes with a different set of excited states. We now consider this mixing and its effects further.

Figure 4 demonstrates how SOC affects $S_0$ and $T_1$ if the number of states included in the SOC is built up from three ($S_0$–$S_2$, $T_1$–$T_3$), to six ($S_0$–$S_5$, $T_1$–$T_6$), to twelve ($S_0$–$S_{11}$, $T_1$–$T_{12}$). Figure 5 identifies which states are coupled in these calculations and shows cartoon representations of the $d$-orbital interactions deemed responsible for ferromagnetic and antiferromagnetic contributions which make up the total effect when all states are included. For ease of visualization the cartoons do not represent molecular orbitals; in fact each $d$ orbital represents an unpaired electron localized on a Ti center.

When only the first three states ($S_0$–$S_2$, $T_1$–$T_3$) are included, $T_1$ is stabilized preferentially to $S_0$; there is a ferromagnetic effect of 1.167 cm$^{-1}$. Inspection of the SOC eigenvectors and state weightings reveals the interactions responsible are purely between states with $\sigma$ and $\pi$ interactions (see Fig. 5), with no participation of the bridging hydrogens. This is consistent with the findings of Kahn who predicts ferromagnetic interaction when there is no bridging ligand mediation between two $d$ orbitals in an orthogonal orientation. Due to symmetry constraints, the angular momentum operator which gives rise to all of these interactions is $L_z$ which acts along the Ti–Ti internuclear axis (see Fig. 1). This axial splitting is calculated to be only 0.030 cm$^{-1}$. The SOC matrix elements indicate there is no excited state- excited state coupling; this is also due to the symmetry constraints imposed by the angular momentum operators.

The addition of three more states ($S_0$–$S_5$, $T_1$–$T_6$) results in an antiferromagnetic effect of $-0.486$ cm$^{-1}$. The ground state-excited state coupling responsible for this effect (see Fig. 5) is between states with $\sigma$ and $\delta_1$ interactions (see Fig. 2 and Table I) which do include contributions from the bridging hydrogens. Again, this is consistent with the findings of Kahn. The SOC matrix elements indicate introduction of these states and also results in a small amount of coupling between excited states. This enables indirect coupling of more excited states with the ground states. The angular momentum operator that is responsible for the coupling between states with $\sigma$ and $\delta_1$ interactions is $L_x$, where the $x$ axis is perpendicular to the plane of the bridge in the molecular orientation for these calculations (see Fig. 1). The resulting rhombic energy splitting is calculated to be 0.198 cm$^{-1}$, suggesting that the rhombic splitting seen in Fig. 3 is due almost entirely to the effects of the introduction of these three states and the resulting SOC interactions.

The inclusion of the next six states ($S_0$–$S_{11}$, $T_1$–$T_{12}$) has a small effect that brings the energy levels essentially to the same values as those in the full twenty singlet and triplet state SOC. The very small antiferromagnetic effect of
\(-0.020 \text{ cm}^{-1}\) appears to arise from a number of SOC matrix elements of similar magnitude describing both ground state-excited state, and excited state-excited state interactions, though these interactions are clearly very weak as the excited state weightings are too small to appear in Table III. Figure 5 shows a cartoon representation of the former. Negligible additional splitting within \(T_1\) results from the inclusion of these states.

In summary, spin-orbit coupling in \(D_{2h}\) \(\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2\) obtained with the first twenty singlet and twenty triplet states produces a very small ferromagnetic effect that arises from competing ferromagnetic and antiferromagnetic interactions between ground and excited state orbitals, as well as interactions between excited states. In the molecular orientation of Fig. 1 the rhombic energy splitting \(\Delta E(2) = 0.199 \text{ cm}^{-1}\) is caused almost entirely by the introduction of \(S_3 - S_4\), and \(T_4 - T_5\) and the resulting interactions. The angular momentum operator \(L_x\) which acts along the axis perpendicular to the bridge plane (see Fig. 1) is responsible for most of these interactions. In contrast, magnetic dipole-dipole interactions are almost always largest along the internuclear axis \((z)\) axis. If this is true for \(D_{2h}\) \(\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2\), the two effects which result in splitting of the triplet state have their largest components along perpendicular principal axes. This has been observed experimentally both in a di-copper system and a di-titanium system. However, unlike Samuel et al. who can estimate the Ti–Ti separation accurately in their system using the approximation \(D \approx D_d\), because \(D_d\) is small \((0.0012 \text{ cm}^{-1})\), in \(D_{2h}\) \(\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2\), in the relevant orientation, the calculated axial exchange parameter is substantial, \(D_e = -0.086 \text{ cm}^{-1}\) (see the Appendix), so it is possible that \(D \approx D_d\) would not be a good approximation.

IV. CONCLUSIONS

Excited state energies of singlet and triplet \(\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2\) have been calculated. The effect of orbital relaxation (optimizing the orbitals for each state) is found to be small. Dynamic correlation makes a considerable difference in terms of energetics, but has little effect on the ordering of the states.

In dinuclear complexes spin-orbit coupling effects can contribute to the splitting of the triplet state as measured by EPR spectroscopy. Through \textit{ab initio} calculations which include spin-orbit coupling we have identified which states couple in \(D_{2h}\) \(\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2\) to produce these contributions. The calculated rhombic energy splitting, \(\Delta E(2) = 0.199 \text{ cm}^{-1}\), is due almost entirely to coupling brought about by the angular momentum operator perpendicular to the plane of the Ti–H–Ti bridge \((L_z)\). The effect of the operator along the Ti–Ti axis \((L_x)\) was found to be much smaller. The ferromagnetic effect of spin-orbit coupling on the ground state singlet-first excited triplet energy gap is found to be very small relative to the isotropic antiferromagnetic interaction in \(\text{H}_2\text{Ti}(\mu-\text{H})_2\text{TiH}_2\), and therefore plays no role in determination of overall magnetic properties of the system.
Given the importance of dynamic electron correlation both in determining the isotropic interaction energy and in the effect it has on excited state energies, a first step toward achieving reliable values of energy level splittings due to exchange effects can be made with its inclusion in the spin-orbit coupling calculations.

The calculations presented here should be viewed as a first step in using ab initio computational chemistry techniques to determine how the SOC induced exchange contribution to zero-field splittings is moderated by bridging and terminal ligands in paramagnetic dinuclear titanium (III) compounds.

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APPENDIX

The parameters $D$ and $E$ (which are due to both spin-spin and spin-orbit effects), where the molecular orientation and thereby the principal axes are defined such that $|D| \gg |E|$, are related to the triplet splitting energies by the following:  

\begin{align*}
D &= (Z-X) + E, \quad \text{(A1)} \\
E &= (X-Y)/2. \quad \text{(A2)}
\end{align*}

However, in the present study we have calculated energy splittings due to spin-orbit coupling effects only, $\Delta E(1)$ and $\Delta E(2)$ (see Fig. 3). In order to relate these calculated energy splittings to $D_e$ and $E_e$ for comparison with experiment we must consider how the principal axes were defined in the determination of the experimental $D_e$ and $E_e$; that is, whether the principal axes of $D_e$ [calculated using Eq. (4)] are defined such that $|D_e| \gg |E_e|$ or alternatively whether $D_e$ and $E_e$ are found by simply applying Eqs. (5) and (6), the principal axes then being defined by $D$.

In the experiment by Gatteschi et al., applying Eqs. (A1) and (A2) we must realabel the energy levels in Fig. 3 switching $X$ and $Z$, effectively rotating the Ti–Ti axis in $H_2Ti(\mu-H)TiH_2$ to the $x$ principal axis (see Fig. 1).

\begin{align*}
D_e - E_e &= \Delta E(2) = 0.199 \text{ cm}^{-1} \\
2E_e &= \Delta E(1) = 0.226 \text{ cm}^{-1}
\end{align*}

Applying Eqs. (A1) and (A2) gives $D_e = 0.212 \text{ cm}^{-1}$ and $E_e = 0.013 \text{ cm}^{-1}$. In the experiment by Samuel et al. the principal axes are determined by $D$ which is dominated by $D_e$. Here the experimental $D_e$ and $E_e$ are determined using Eqs. (5) and (6). The $z$ principal axis lies along the internuclear axis as in the orientation used for the present calculations on $H_2Ti(\mu-H)TiH_2$ (see Fig. 1). We can therefore apply Eqs. (A1) and (A2) using the principal axes defined in Fig. 3, giving $D_e = -0.086 \text{ cm}^{-1}$ and $E_e = 0.113 \text{ cm}^{-1}$.

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These labels were confirmed by reorientation of the molecule, $x$ axis → $y$ axis, recalculation and reinspeck of the eigenvectors to find the energy level with $M_s = 0$ (it shifted from spin state 3 to 4) thus allowing identification of $Z$ in two different orientations and labeling of $X$, $Y$, and $Z$ in the original orientation (Fig. 1) by deduction.

Reference 17(a), pp. 99 and 333.