Magne\textit{t}ostructural Dependencies in $3d^2$ Systems: The Trigonal Bipyramidal $V^{3+}$ Complex

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We introduce a multiconfigurational approach to study the magnetostructural correlations in $3d^2$ systems. The theoretical framework represents a restricted active space self-consistent field method, with active space optimized to the number of all non-bonding orbitals. To demonstrate the validity and effectiveness of the method, we explore the physical properties of the trigonal bipyramidal spin-one single-ion magnet $(C_6F_5)_3$trenVCN$^+$Bu. The obtained theoretical results show good agreement with the experimental data available in the literature. This includes measurements for the magnetization, low-field susceptibility, continuous wave electron paramagnetic resonance, and photoluminescence spectroscopy. The proposed method may be reliably applied to a variety of $3d^2$ magnetic systems. To this end, and for the sake completeness, we provide detailed analytical and numerical representations for the generic Hamiltonian’s effective matrix elements related to the crystal field, exchange, spin–orbit, and Zeeman interactions.

1. Introduction

Being at the frontier between classical and quantum physics, low-dimensional magnetic systems\cite{1,2,3,4} and molecular magnets\cite{5,6,7,8} have continued to generate an ever-growing interest among researchers in the field of magnetism for the last few decades. Tailoring the underlying quantum features poses a great challenge for their synthesis, experimental, and theoretical characterization. Molecular magnets have great scientific and practical potential. They have been successfully implemented in resonance imaging\cite{9,10,11,12} and stand as promising candidates for building sensor devices\cite{13,14,15} and quantum computing technology\cite{16,17,18} to name a few. Despite recent progress\cite{19,20,21,22}, engineering the magnetic properties of such systems remains a challenging task and it still requires a lot of effort to pave the route toward their rationalization and industrial application. Let us emphasize that the compound’s magnetic behavior is tightly related to the type, number, and coordination of ligands with respect to the composing magnetic centers.\cite{23,24,25,26} These have been the subject of extensive interest; here we mention only some prominent and most recent examples, such as the mononuclear $\beta$-diketonate Dy$^{3+}$ single molecular magnet,\cite{27} tetraneutral lanthanide metalloocene complexes,\cite{28} the tetravanadate $V_4O_{12}$ \cite{29} anion-bridged Cu$^{2+}$ complexes,\cite{30} and the single-ion Co$^{2+}$ one.\cite{31} For an overview on the properties of $3d^2$-type systems, the reader may consult other studies.\cite{32,33,34} Studying the relation between the magnetic properties and the compound’s structure provides a deeper knowledge for the existing zero-field splitting (ZFS)\cite{35,36} quantum character of magnetic anisotropy, and all field-dependent properties. It further elucidates the driving mechanisms behind the magnetic dynamics that opens up the potential for future applications.

The focus of this study is to reveal the role of the ligand structure in shaping the magnetic and spectroscopic properties of $3d^2$ systems and shed light on the relevant contribution of the crystal field, exchange, and spin–orbit interactions. To this end, complementing the quantum perturbation method, we make use of the variational method.\cite{37,38} The associated mathematical framework represents a restrictive active space self-consistent field method with an active space spanning all $3d$ orbitals. To assess the validity of the proposed multiconfigurational approach, we performed a thorough theoretic investigation in the framework of the compound $(C_6F_5)_3$trenVCN$^+$Bu, whose magnetic properties have been experimentally probed.\cite{39} Here, we interpret the experimental data available for magnetization, low-field susceptibility, continuous-wave electron paramagnetic resonance (cw-EPR) spectra, and photoluminescence. As the study unfolds, we discuss the role of the crystal field and spin–orbit interactions in the magnetization and susceptibility behavior and the contribution of the exchange interaction to the absorption and emission features.

We would like to emphasize that the proposed approach may be applied to shed light on the magnetic properties of the whole class of $3d^2$ systems, regardless of their dimensionality in space–molecular magnets or low-dimensional spin systems. Therefore, we provide analytical results for all interaction terms and effective matrix elements.

The rest of the article is structured as follows. In Section 2, we introduce and elaborate on the theoretical methods used to study the compound under consideration. Further, we introduce some basic notations and give explicit representations of the applied Hamiltonian and all initial basis sates. In Section 3, we provide

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details of our computational method that includes representations for all effective matrix elements. Section 4 discusses the obtained energy spectrum and its dependence on the action of externally applied magnetic field. A representation of the obtained ZFS in terms of the axial “D” and rhombic “E” fine structure (FS) parameters is also discussed. Section 5 covers results on the compound’s magnetic and spectroscopic properties. Finally, a summary of the results is given in Section 6. We would like to mention that all numerical results are obtained with the aid of Wolfram Mathematica 12.

2. Theoretical Background

2.1. General Considerations

The magnetic and spectroscopic properties of the compound \((\text{C}_\text{eF}_\text{s})_\text{trenVCN}^\text{Bu}\) are computed and interpreted using a restricted active space self-consistent field approach. The only relativistic contribution accounted for in the calculations is the spin–orbit interaction. In particular, adhering the approximations used in CF theory\(^{[41–43]}\), we describe both unpaired electrons as localized, to a large extent, around the \(\text{V}^{3+}\) metal center. Accordingly, the constructed optimized reaction space is restricted to the existing \(3\text{d}^2\) configuration. Furthermore, complying to the effective field approach used in the Hartree–Fock method\(^{[39,44,45]}\), these electrons are exposed to the average field of all remaining “core” electrons that on average do not contribute neither to the splitting nor to the shifting of energy levels in the ensuing energy spectrum. Thus, the considered transition metal complex may be viewed as a good model of a spin-one system consisting of two 3d electrons distributed among six effective point-like charges. Those are the vanadium center, the four nitrogen ligands, and the isocyanide one. The five ligands reside on the vertices of a distorted trigonal bipyramidal structure (see Figure 1 and Table 1). We would like to emphasize that to overcome the disadvantage of the localized electron approach over the delocalized one used in ligand field theory\(^{[43]}\), we introduce five nonvariational parameters, one for each ligand, to control the ligands’ electric charge that both 3d electrons are exposed to. Moreover, we have one nonvariational parameter to address the effect of electrons’ delocalization into the spin–orbit coupling. The resulting six parameters are then allowed to vary to achieve better agreement between theory and experimental measurements.

We would like to point out, furthermore, that the contributions of all orbital and spin magnetic–dipole interactions related to both 3d unpaired electrons and the constituent nuclei are found negligible and hence omitted from the calculations. Similarly, the hyperfine interactions are also excluded.

Henceforth, we find it convenient to introduce the following notations: \(r_i = (\alpha_i)_\text{i} \in \mathbb{K}\) designates the \(i\)-th electron’s position vector, where \(\mathbb{K} = \{x, y, z\}\) and \(i = 1, 2\). In spherical coordinates, \(\rho_i, \theta_i, \phi_i\) are the \(i\)-th electron’s radial distance, polar, and azimuthal angles, respectively. By \(\hat{\mu}_i = -\mu_0 \vec{l}_i\) and \(\hat{\mu}_s = -g_s \mu_0 \vec{s}_i\), we denote the corresponding orbital and spin magnetic moment operators, where \(\mu_0\) is the Bohr magneton, \(g_e\) is the electron g-factor, \(\vec{s}_i = (s_i^x, s_i^y, s_i^z)_\text{i} \in \mathbb{K}\), and \(\vec{l}_i = (l_i^x, l_i^y, l_i^z)_\text{i} \in \mathbb{K}\) are the respective spin and angular momentum operators. The operator of the total magnetic moment \(\vec{\mu}\) is given by the sum of total spin \(\hat{\mu}_s = \hat{\mu}_{s1} + \hat{\mu}_{s2}\) and orbital \(\hat{\mu}_l = \hat{\mu}_{l1} + \hat{\mu}_{l2}\) ones. The position vector of the \(i\)-th ligand is denoted by \(\vec{d}_i\), with corresponding spherical coordinates \(\varphi_i, \theta_i, \rho_i\).

![Figure 1. Ball and stick representation of the vanadium ion coordinated by the isocyanide and four nitrogen ligands in the trigonal bipyramidal complex (C₆F₅)₃trenVCN'Bu. The blue, green, and gray balls represent the vanadium, nitrogen, and carbon elements with coordinates given in Table 1. The chemical structure of the compound with included three C₆F₅ rings is given by Fatafah et al.© 2022 Wiley-VCH GmbH](image-url)
The Hamiltonian of the considered system reads

\[
\hat{H} = \hat{U}_R(r_1, r_2) + \hat{U}_{CF}(r_1, r_2) + \hat{U}_{SO}(r_1, r_2) + \hat{H}_c
\]

(2.1)

where \(\hat{U}_R\) accounts for the Coulomb repulsion between both electrons, \(\hat{U}_{CF}\) represents the interaction of both electrons with the surrounding ligands (crystal field term), \(\hat{U}_{SO}\) is the relativistic term that takes into account the spin–orbital interactions, and \(\hat{H}_c\) describes the action of the externally applied magnetic field. The last operator \(\hat{H}_c\) on the right-hand-side in (2.1) is an invariant of the Hamiltonian system, that is, \([\hat{H}, \hat{H}_c] = 0\). It produces a constant related to the values of all effective parameters that minimize the energy. It is obtained with respect to the variational function of all bonding and nonbonding “core” electrons. The kinetic terms of both unpaired electrons are also accounted for, as in the case of localized \(d\)-electrons, the relevant expectation values are constants.

In spherical coordinates, the series expansion of the Coulomb term reads\(^{[46,47]}\)

\[
\hat{U}_R(r_1, r_2) \equiv \frac{\gamma}{|r_2 - r_1|} = \sum_{n=0}^{r_2} \rho_n^2 P_n(u), \quad \rho_1 > \rho_2
\]

(2.2)

where \(\gamma = e^2/4\pi\) and for all \(n\), \(P_n(u)\) are the Legendre polynomials, with \(u = \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) + \cos\theta_1 \cos\theta_2\).

The total CF operator is given by the sum

\[
\hat{U}_{CF}(r_1, r_2) = \sum_j (\hat{U}_j(r_1) + \hat{U}_j(r_2))
\]

(2.3)

where \(j\) runs over the number of all ligands. Here, the series expansion of the potential energy accounting for the interaction between the \(k\)-th ligand and the \(i\)-th electron is given by\(^{[41,42,46]}\)

\[
\hat{U}_k(r_i) \equiv \frac{\gamma Z_i}{|r_i - d_k|} = \sum_{n=0}^{\rho_n^2} \rho_n^2 P_n(v_{i,k}), \quad \rho_k > \rho_i, \quad \forall i, k
\]

(2.4)

where, \(v_{i,k} = \sin\theta_i \sin\theta_k \cos(\phi_1 - \phi_k) + \cos\theta_i \cos\theta_k\) and \(Z_i\) is the charge number of the \(k\)-th ligand to which both 3d electrons are exposed. Notice that \(Z_i\), for all \(k\), are fitting parameters that allow one to distinguish between the different ligands. Within the used approximations their values may not be integers, but their lowest value is unity.

The spin–orbit interaction term is given by

\[
\hat{U}_{SO}(r_1, r_2) \equiv \frac{g_s \mu_B \hbar^2}{2\pi} \sum_i \rho_i^2 \hat{l}_i \cdot \hat{s}_i, \quad i = 1, 2
\]

(2.5)

where \(Z\) is the charge number of the vanadium metal center with respect to both electrons.

Finally the operator describing the interaction with the externally applied magnetic field reads

\[
\hat{U}_Z \equiv -\mu_B \sum B \cdot (\hat{l}_i + g_s \hat{s}_i), \quad i = 1, 2
\]

(2.6)

2.3. Initial Basis States

The active space is restricted to the number of all nonbonding orbitals. In other words, we have five \(3d\) orbitals and two unpaired electrons. As a result, we end up with 45 quantum basis states including only active orbitals

\[
|\psi_{1,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xz}, d_{yz}\rangle + (-1)^m|d_{xy}, d_{sz}\rangle)|s, m\rangle
\]

\[
|\psi_{2,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xz}, d_{xy}\rangle + (-1)^m|d_{xz}, d_{yz}\rangle)|s, m\rangle
\]

\[
|\psi_{3,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xz}, d_{xz}\rangle + (-1)^m|d_{xz}, d_{yz}\rangle)|s, m\rangle
\]

\[
|\psi_{4,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xz}, d_{xy}\rangle + (-1)^m|d_{xy}, d_{sz}\rangle)|s, m\rangle
\]

\[
|\psi_{5,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xz}, d_{xy}\rangle + (-1)^m|d_{xy}, d_{sz}\rangle)|s, m\rangle
\]

\[
|\psi_{6,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xz}, d_{xy}\rangle + (-1)^m|d_{xz}, d_{xy}\rangle)|s, m\rangle
\]

\[
|\psi_{7,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xy}, d_{xy}\rangle + (-1)^m|d_{xz}, d_{xy}\rangle)|s, m\rangle
\]

\[
|\psi_{8,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xy}, d_{xy}\rangle + (-1)^m|d_{xz}, d_{xy}\rangle)|s, m\rangle
\]

\[
|\psi_{9,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xy}, d_{xy}\rangle + (-1)^m|d_{xy}, d_{xy}\rangle)|s, m\rangle
\]

\[
|\psi_{10,m}\rangle \equiv \frac{1}{\sqrt{2}}(|d_{xy}, d_{xy}\rangle + (-1)^m|d_{xy}, d_{xy}\rangle)|s, m\rangle
\]

and five core orbital states

\[
|\psi_{11,0,0}\rangle \equiv |d_{xz}, d_{xz}\rangle|0, 0\rangle, \quad |\psi_{12,0,0}\rangle \equiv |d_{yz}, d_{yz}\rangle|0, 0\rangle
\]

\[
|\psi_{13,0,0}\rangle \equiv |d_{xz}, d_{xy}\rangle|0, 0\rangle, \quad |\psi_{14,0,0}\rangle \equiv |d_{xz}, d_{yz}\rangle|0, 0\rangle, \quad |\psi_{15,0,0}\rangle \equiv |d_{xz}, d_{xz}\rangle|0, 0\rangle
\]

(2.7b)

where \(s = 0.1\) and \(m = \pm s\) are the total spin and spin–magnetic quantum numbers. Explicit representation of each \(d\)-state is given in Appendix A.
3. Computational Details

3.1. Coulomb Terms

Calculating the average values of the Coulomb interaction \((2.2)\) up to the fourth order in the series expansion in the basis \((2.7)\), we obtain zero off-diagonal matrix elements. For the diagonal ones, with \(\langle \psi_{i,m,n} \mid U_{CF} \mid \psi_{i,m,n} \rangle = E_{i,m,n}\), we have

\[
\begin{align*}
E_{1,s,m} &= V_1 + (-1)^s \delta_{s,1} L_1, & E_{2,s,m} &= V_4 + (-1)^s V_7 \\
E_{3,s,m} &= V_4 + (-1)^s V_7, & E_{4,s,m} &= V_5 + (-1)^s V_8 \\
E_{5,s,m} &= V_4 + (-1)^s V_7, & E_{6,s,m} &= V_4 + (-1)^s V_7 \\
E_{7,s,m} &= V_5 + (-1)^s V_8, & E_{8,s,m} &= V_2 + (-1)^s \delta_{s,2} L_2 \\
E_{9,s,m} &= V_6 + (-1)^s V_9, & E_{10,s,m} &= V_6 + (-1)^s V_9 \\
E_{11,0,0} &= V_1 + \frac{1}{2} L_1, & E_{12,0,0} &= V_1 + \frac{1}{2} L_1 \\
E_{13,0,0} &= V_2 + \frac{1}{2} L_2, & E_{14,0,0} &= V_2 + \frac{1}{2} L_2 \\
E_{15,0,0} &= V_3
\end{align*}
\]

where the explicit representations of \(\{ V_j \}_{j=1}^9\) and \(\{ L_1, L_2 \}\), with \(Z\) being the only parameter, are provided in Appendix B. The subscript \(m\) shows the threefold degeneracy of the corresponding energy levels.

3.2. CF Terms

Within the selected active space, the mixing of states by CF is prominent. In general, we have \(\langle \psi_{i,m,n} \mid U_{CF} \mid \psi_{j,m,n} \rangle = U_{i,j,m,n}\). For the sake of clarity, we denote the respective diagonal elements by \(U_{i,m}\) to get

\[
\begin{align*}
U_{1,s,m} &= U_{xz} + U_{yz}, & U_{2,s,m} &= U_{xz} + U_{xy} \\
U_{3,s,m} &= U_{xz} + U_{xy}, & U_{4,s,m} &= U_{xz} + U_{xz} \\
U_{5,s,m} &= U_{yz} + U_{xy}, & U_{6,s,m} &= U_{yz} + U_{xz} \\
U_{7,s,m} &= U_{yz} + U_{yz}, & U_{8,s,m} &= U_{xy} + U_{xy} \\
U_{9,s,m} &= U_{xy} + U_{xy}, & U_{10,s,m} &= U_{yz} + U_{xy} \\
U_{11,0,0} &= 2U_{xz}, & U_{12,0,0} &= 2U_{yz} \\
U_{13,0,0} &= 2U_{xy}, & U_{14,0,0} &= 2U_{xy} \\
U_{15,0,0} &= 2U_x
\end{align*}
\]

The off-diagonal entries are nonzero for all \(s' = s\) and \(m' = m\). Therefore, applying the shorthand notation \(U_{i,j,m,n} \rightarrow U_{i,j,m}\), we have

\[
\begin{align*}
U_{2,1,s,m} &= U_{yz,xy}, & U_{3,1,s,m} &= U_{yz,xz} \\
U_{4,1,s,m} &= U_{yz,z}, & U_{5,1,s,m} &= (-1)^s U_{xz,xy} \\
U_{6,1,s,m} &= (-1)^s U_{xz,xz}, & U_{7,1,s,m} &= (-1)^s U_{xz,z} \\
U_{3,2,s,m} &= U_{xy,xz}, & U_{4,2,s,m} &= U_{xy,z} \\
U_{5,2,s,m} &= U_{xz,yz}, & U_{8,2,s,m} &= (-1)^s U_{xz,xz} \\
U_{9,2,s,m} &= (-1)^s U_{xz,z}, & U_{4,3,s,m} &= U_{z,yz}, \ z^2 \\
U_{6,3,s,m} &= U_{xz,yz}, & U_{8,3,s,m} &= U_{xz,xy} \\
U_{10,3,s,m} &= (-1)^s U_{xz,z}, & U_{7,4,s,m} &= U_{x,yz} \\
U_{9,4,s,m} &= U_{xz,xy}, & U_{10,4,s,m} &= U_{xz,xz} \ (3.3a) \\
U_{6,5,s,m} &= U_{xy,yz}, & U_{5,5,s,m} &= U_{xy,z} \\
U_{8,5,s,m} &= (-1)^s U_{yz,xz}, & U_{9,5,s,m} &= (-1)^s U_{yz,xy} \\
U_{7,6,s,m} &= U_{yz,yz}, & U_{10,6,s,m} &= U_{yz,xz} \\
U_{10,7,s,m} &= U_{yz,yz}, & U_{9,8,s,m} &= U_{y,yz}, \ z^2 \\
U_{10,8,s,m} &= (-1)^s U_{xy,xy}, & U_{10,9,s,m} &= U_{xy,xz} \ (3.3b)
\end{align*}
\]

Moreover, the average values associated with the singlet-only states are given by

\[
\begin{align*}
U_{11,1,0,0} &= \sqrt{2} U_{xz,yz}, & U_{12,1,0,0} &= \sqrt{2} U_{xz,yz} \\
U_{11,2,0,0} &= \sqrt{2} U_{xz,xy}, & U_{12,2,0,0} &= \sqrt{2} U_{xz,xy} \\
U_{11,3,0,0} &= \sqrt{2} U_{xz,xz}, & U_{12,3,0,0} &= \sqrt{2} U_{xz,xz} \\
U_{11,4,0,0} &= \sqrt{2} U_{xz,z}, & U_{12,4,0,0} &= \sqrt{2} U_{xz,z} \\
U_{11,5,0,0} &= \sqrt{2} U_{yz,yz}, & U_{12,5,0,0} &= \sqrt{2} U_{yz,yz} \\
U_{11,6,0,0} &= \sqrt{2} U_{yz,xz}, & U_{12,6,0,0} &= \sqrt{2} U_{yz,xz} \\
U_{11,7,0,0} &= \sqrt{2} U_{yz,z}, & U_{12,7,0,0} &= \sqrt{2} U_{yz,z} \\
U_{11,8,0,0} &= \sqrt{2} U_{x,y}, & U_{12,8,0,0} &= \sqrt{2} U_{x,y} \\
U_{11,9,0,0} &= \sqrt{2} U_{y,z}, & U_{12,9,0,0} &= \sqrt{2} U_{y,z} \\
U_{11,10,0,0} &= \sqrt{2} U_{x,y}, & U_{12,10,0,0} &= \sqrt{2} U_{x,y} \ (3.3b)
\end{align*}
\]

The explicit representation of the functions \(U_{\alpha}\) and \(U_{\beta,\epsilon}\), with \(\alpha \neq \beta \in \{xz, yz, xy, x^2 - y^2, z^2\}\), is shown in Appendix C. We would like to point out that all functions in Section 3.2 are real, with parameters being the ligands’ coordinates, \(Z_1, \ldots, Z_5\) and \(Z\). The computations are performed up to the fourth order in \((2.4)\).

3.3. Spin–Orbit Terms

All diagonal matrix elements associated with the total spin-orbit operator \((2.5)\) are zero. For both electrons, the corresponding spin-orbit coupling \(\zeta = \langle \frac{\hbar}{m_e} \mu_0 Z / 2\pi \rangle = (35.604 \times 10^{-4}) Z^4\) meV. To write down the respective matrix elements in a transparent way, we introduce the parameter \(\eta = \zeta / 2\sqrt{2}\), with \(0 \leq \kappa \leq 1\). The prefactor \(\kappa\) is included to account for a possible delocalization of both electrons. In other words, if \(\kappa \approx 1\), then the initial assumption of localized, to a large extent electrons, holds. In contrast, if \(\kappa < 1\), it would be a sign
that the considered electrons may be partially delocalized. Now, for \( \langle \psi_{i,m} | U_{SO} | \psi_{i',m'} \rangle = Y_{i,m,i',m'} \), we get

\[
Y_{2,1,1,1,0} = (±1)\eta, \quad Y_{1,1,1,1,0} = ±i(±1)\eta,
Y_{4,1,1,1,0} = ±i\sqrt{3}(±1)\eta, \quad Y_{5,1,1,1,0} = -i(±1)\eta,
Y_{6,1,1,1,0} = (±1)\eta, \quad Y_{7,1,1,1,0} = ±i\sqrt{3}(±1)\eta,
Y_{1,1,1,2,0} = (±1)\eta, \quad Y_{3,1,1,2,0} = ±i2\sqrt{2}\eta,
Y_{5,1,1,2,0} = (±1)\eta, \quad Y_{8,1,1,2,0} = ±3(±1)\eta.
\]

and

\[
Y_{9,1,1,2,0} = -3(±1)\eta, \quad Y_{6,1,1,3,0} = ±3(±1)\eta,
Y_{10,1,1,3,0} = ±i2\sqrt{2}\eta, \quad Y_{12,1,1,3,0} = ±i\sqrt{3}(±1)\eta.
\]

Further, the spin–orbit interactions mix the single orbital states (2.7b) with the remaining ones, such that

\[
Y_{2,1,1,1,0} = ±i\sqrt{2}\eta, \quad Y_{1,1,1,1,0} = ±3(±1)\eta,
Y_{4,1,1,1,0} = ±3(±1)\eta, \quad Y_{5,1,1,1,0} = ±i2\sqrt{2}\eta,
Y_{6,1,1,1,0} = ±3(±1)\eta, \quad Y_{7,1,1,1,0} = ±i2\sqrt{2}\eta,
Y_{8,1,1,1,0} = ±3(±1)\eta, \quad Y_{9,1,1,1,0} = ±3(±1)\eta.
\]

3.4. Zeeman Terms

Due to the symmetry of the orbitals in (2.7), the diagonal matrix elements obtained from (2.6), \( Z_{i,m} = \langle \psi_{i,m} | Z | \psi_{i,m} \rangle \), depend only on the total spin. Thus, we have \( Z_{i,0} = g_s \mu_B m \beta_B \). Furthermore, as we work in the basis of the spin z component, there are 40 spin-only off-diagonal elements corresponding to the mixing between \( m = 0 \) and \( m = ±1 \) states. For all \( i = 1, \ldots, 10 \), the nonconjugate ones read \( Z_{i,1,±1,0} = -g_s \mu_B (B_z \mp B_i) / \sqrt{2} \). The remaining off-diagonal elements depend exclusively on the mixing of orbitals. Using the substitution \( Z_{i,m,j,m} \rightarrow Z_{i,j,m} \), with respect to the states (2.7a), we obtain

\[
Z_{2,1,3,0} = -i \mu_B B_y, \quad Z_{3,1,3,0} = -i \mu_B B_x,
Z_{4,1,3,0} = -i \sqrt{3} \mu_B B_y, \quad Z_{5,1,3,0} = i (±1) \mu_B B_x,
Z_{6,1,3,0} = -i (±1) \mu_B B_y, \quad Z_{7,1,3,0} = -i \sqrt{3} \mu_B B_y,
Z_{8,1,3,0} = i \mu_B B_x, \quad Z_{9,1,3,0} = i \mu_B B_y,
Z_{10,3,0} = -i \sqrt{3} \mu_B B_x, \quad Z_{2,3,0} = i \mu_B B_x,
Z_{3,3,0} = -i \mu_B B_y, \quad Z_{4,3,0} = -i \mu_B B_y.
\]

and with the consideration of singlet states (2.7b), we get

\[
Z_{11,1,0,0} = i \sqrt{2} \mu_B B_z, \quad Z_{12,1,0,0} = -i \sqrt{2} \mu_B B_z,
Z_{11,2,0,0} = -i \sqrt{2} \mu_B B_z, \quad Z_{12,2,0,0} = i \sqrt{2} \mu_B B_z,
Z_{11,3,0,0} = i \sqrt{2} \mu_B B_z, \quad Z_{12,3,0,0} = -i \sqrt{2} \mu_B B_z,
Z_{11,4,0,0} = -i \sqrt{2} \mu_B B_z, \quad Z_{12,4,0,0} = i \sqrt{2} \mu_B B_z,
Z_{11,5,0,0} = i \sqrt{2} \mu_B B_z, \quad Z_{12,5,0,0} = -i \sqrt{2} \mu_B B_z,
Z_{11,6,0,0} = i \sqrt{2} \mu_B B_z, \quad Z_{12,6,0,0} = -i \sqrt{2} \mu_B B_z,
Z_{11,7,0,0} = i \sqrt{2} \mu_B B_z, \quad Z_{12,7,0,0} = -i \sqrt{2} \mu_B B_z,
Z_{11,8,0,0} = -i \sqrt{2} \mu_B B_z, \quad Z_{12,8,0,0} = i \sqrt{2} \mu_B B_z.
\]

4. Energy Spectrum

4.1. Zero-Field Spectrum

The energy spectrum of the considered vanadium complex is obtained by direct diagonalization of the total matrix given by the sum of the four matrices corresponding to the interactions in Hamiltonian (2.1) and with elements given in Section 3. The spectrum is nondegenerate and hence it is built up of 16 energy levels for both cases \( B = 0 \) and \( B ≠ 0 \). As the value of the ground-state energy does not affect the final splitting and shifting of levels, the respective eigenvalues are normalized such that the ground-state energy equals zero. The resulting energy-level sequence depends on two sets of parameters. On the one hand, we have the ligands’ coordinates given in Table 1 and on the other the fitting parameters \( k, Z_i \), and \( Z_{k,i} \), for \( k = 1, \ldots, 5 \). The relevant structural parameters are experimentally determined and provided in the study by Fatafah. \(^{[40]}\) The values of all \( Z \) parameters are given in the penultimate row of Table 1 and in conjunction with \( k = 0.43 \) their values are fit in accordance with the low-field susceptibility, magnetization, cw-EPR experimental, and photoluminescence data from the study by Fatafah. \(^{[40]}\)

The energy spectrum in the absence of an external magnetic field is shown in Figure 2a. The value of each energy level is
ground state as a mixing involving only trigonal bipyramidal geometry, see Figure 1, determine the levels, which represent the obtained ZFS\(^{37,48}\) states, that is
dependence on \(\kappa\) provided in Appendix D. Figure 2b depicts the first three energy levels, which represent the obtained ZFS\(^{37,48-51}\) and its dependence on \(\kappa\).

The combined effect of spin–orbital interactions and distorted trigonal bipyramidal geometry, see Figure 1, determine the ground state as a mixing involving only \(m = 0\) and \(m = -1\) spin states, that is

\[
|\Psi_1\rangle = (-0.14 + 0.14i)|\psi_{1,1,0}\rangle + (0.14 + 0.15i)|\psi_{1,1,0}\rangle + (0.25 - 0.24i)|\psi_{2,1,0}\rangle + (0.25 + 0.27i)|\psi_{2,1,1}\rangle - (0.13 - 0.13i)|\psi_{3,1,0}\rangle - (0.13 + 0.14i)|\psi_{3,1,1}\rangle - (0.24 - 0.23i)|\psi_{5,1,0}\rangle - (0.25 + 0.25i)|\psi_{5,1,1}\rangle + (0.29 - 0.28i)|\psi_{6,1,0}\rangle + (0.29 + 0.31i)|\psi_{6,1,1}\rangle - (0.065 - 0.063i)|\psi_{8,1,0}\rangle - (0.066 + 0.071i)|\psi_{8,1,1}\rangle + \sum_{n \geq 2} O(10^{-n})|\psi_{...}\rangle
\]

(4.1)

Therefore, we have a probability of \(\approx 47\%\) to observe the system in \(m = 0\) state and \(53\%\) in a state with \(m = -1\). Consequently, with expectation values given in Bohr magneton units, for the total magnetic moment, we have \(\mathbf{\mu}_1 = (-0.0171, 1.4091, -1.0865)\). The orbital contribution is negligible, thus, \(\mathbf{\mu}_s = (-0.0181, 1.4103, -1.0612)\) and \(\mathbf{\mu}_l = (0.001, -0.0011, -0.0253)\).

The distortion in coordination geometry also determines the first excited state as a superposition of only \(m = 1\) spin states.

\[
|\Psi_2\rangle = \begin{pmatrix} 0.19 - 0.21i \mid \psi_{1,1,1} \rangle - 0.34 - 0.37i \mid \psi_{2,1,1} \rangle \\ 0.17 - 0.20i \mid \psi_{3,1,1} \rangle + 0.33 - 0.35i \mid \psi_{5,1,1} \rangle \\ 0.39 - 0.44i \mid \psi_{6,1,1} \rangle + 0.089 - 0.098i \mid \psi_{8,1,1} \rangle \end{pmatrix} + \sum_{n \geq 2} O(10^{-n})|\psi_{...}\rangle
\]

(4.2)

where \(\mathbf{\mu}_2 = (0.0157, 0.0037, 2.0509)\) and \(\mathbf{\mu}_s = (0.0, 0.19994)\). Thus, any excitation to \(E_2\) would be associated with an almost fully polarized magnetic moment. An illustration of both vectors \(\mathbf{\mu}_1\) and \(\mathbf{\mu}_2\) is shown in Figure 1.

The second excited state, \(|\Psi_3\rangle\), is given by the same superposition of initial basis states as the ground state (4.1), but with different probability coefficients values, see (D.1). The corresponding total magnetic moment is \(\mathbf{\mu}_3 = (0.0036, -1.4241, -0.9634)\), with contribution from the spin component \(\mathbf{\mu}_s = (0.0182, -1.4105, -0.9379)\).

It is essential to emphasize that the first almost total singlet state, with \(\approx 99\%\) probability to observe \(s = 0\), is

![Figure 2](image-url)
\[ \psi_{26} = 0.092 |\psi_{11,0,0}\rangle - 0.24 |\psi_{12,0,0}\rangle - 0.34 |\psi_{13,0,0}\rangle \\
+ 0.18 |\psi_{14,0,0}\rangle - 0.26 |\psi_{2,0,0}\rangle + 0.31 |\psi_{3,0,0}\rangle \\
+ 0.74 |\psi_{4,0,0}\rangle - 0.11 |\psi_{6,0,0}\rangle - 0.23 |\psi_{8,0,0}\rangle \\
+ \sum_{n \geq 2} O(10^{-n}) |\psi_{\ldots}\rangle \\
\] (4.3)

The corresponding energy level lies very high in the zero-temperature energy spectrum shown in Figure 2a. It is approximately 1.846 eV. Such a large exchange coupling is typical for transition metal complexes with localized around the metal-center electrons and suggests a possible phosphorescence observation. On the other hand, the small energy gap \( \Delta E_{21} \approx 0.17 \) and \( \Delta E_{31} \approx 0.36 \) meV make the zero-field and low-field magnetic properties of the considered complex highly sensitive to the variations in temperature. This feature is clearly demonstrated by the temperature dependence of the susceptibility depicted in Figure 3 and the magnetization behavior shown in Figure 4 at \( B = 1 \) T. This point will be discussed in Section 5.

According to all approximations taken into account in Section 2.1, the obtained ZFS results due to the spin–orbit interactions acting within the CF basis. Therefore, any consideration with \( \kappa \rightarrow 0 \) leads to a threefold degenerate ground state. For further details, see Figure 2b. On the other hand, for \( \kappa \rightarrow 1 \), the ZFS increases to the extent that the theory is no longer able to reproduce the overall experimental observations. To gain insight into the interrelationship between the two physically different notions, ZFS and CF, we recommend the interested reader to consult other studies. [36, 37]

4.2. The Magnetic Field Effect

The interaction of the considered complex with the externally applied magnetic field is taken into account by the Zeeman effective matrix with elements given in Section 3.4. The zero-field spectrum is not degenerate with respect to \( m \), due to the distorted geometry, and so no Zeeman splitting can be observed. As a consequence, we witness only shifting of the energy levels. However, the change of the ground state takes place in a way that resembles the Zeeman effect.

An example of how the energy levels shift under the action of the externally applied magnetic field, for \( B_z \equiv B = 7 \) T, is demonstrated in Figure 2c. The superscript “\( f \)” indicates the selected magnetic field direction and the magnitude. The resulting shifting is related to a change of the eigenstates. The first excited state from the zero-field spectrum (4.2) is now the ground state. Thus, we have \( |\psi_2\rangle \rightarrow |\psi_1^f\rangle \), where the variation in the probability coefficients value is negligible, such that \( \mu_2 \rightarrow \mu_1^f = (0.015, 0.0048, 2.0288) \). This is not the case with the first excited state \( |\psi_3^f\rangle \), which is a transformation of the zero-field ground state (4.1). We get

\[ |\psi_3^f\rangle = (0.18 - 0.21i)|\psi_{1,1,0}\rangle + (0.048 + 0.043i)|\psi_{1,1,1}\rangle - (0.32 - 0.37i)|\psi_{1,2,0}\rangle - (0.081 + 0.074i)|\psi_{1,2,1}\rangle \\
+ (0.17 - 0.19i)|\psi_{1,3,0}\rangle + (0.040 + 0.039i)|\psi_{1,3,1}\rangle \\
+ (0.31 - 0.36i)|\psi_{5,1,0}\rangle + (0.081 + 0.069i)|\psi_{5,1,1}\rangle \\
+ (0.38 - 0.43i)|\psi_{5,3,0}\rangle - (0.096 + 0.086i)|\psi_{5,3,1}\rangle \\
+ (0.084 - 0.098i)|\psi_{8,1,0}\rangle + (0.022 + 0.020i)|\psi_{8,1,1}\rangle \\
+ \sum_{n \geq 2} O(10^{-n}) |\psi_{\ldots}\rangle \]

(4.4)

Hence, the orbital and spin terms given in Section 3.4 enhance the probability of observing the \( m = 0 \) state from 47\% at \( B = 0 \) T to \( \approx95\% \) in the considered case. At the same time, the value of the corresponding energy level increases and \( E_1 \rightarrow E_1^f \). Respectively, the expectation values of the total magnetic moment also change. We get \( \mu_1 \rightarrow \mu_1^f = (0.0022, 0.6102, -0.1193) \).
The second excited state $|\Psi_2^i\rangle$ is a transformation of $|\Psi_1^i\rangle$, and it favors the $m = -1$ outcome with $\approx 94.8\%$ probability rather than 46.4\% obtained for the zero-field case. As a result, we get $\mu_1 \rightarrow \mu_1^f = (0.0011, -0.6053, -1.9755)$. For the explicit representation of the second excited quantum state, see for example, (D.2).

We would like to point out that the observed shifting of energy levels and the absence of a genuine Zeeman splitting in the present study is similar to the same feature found for the magnetic behavior of Ni$_8$Mo$_{12}$ molecular magnet[52] and Er$_3$ complexes[53] except that for the latter compounds, such a dependence of the FS on an externally applied magnetic field is more complex and it is tightly related to the exchange interactions.[54]

4.3. Orbital Energy Diagram

In addition to the energy spectrum, we introduce the splitting of the 3$d$ orbitals. The corresponding diagram is depicted on the top right in Figure 1. Each single electron 3$d_\alpha$ orbital has an energy $U_\alpha$ given in Appendix C, where \( \alpha \in \{xz, yz, x^2 - y^2, z^2\} \). As expected, due to the presence of CN ligand, the $d_z$ orbital is the highest in energy. For the same reason $d_{xz}$ and $d_{yz}$ orbitals are higher in energy than the $d_{xy}$ and $d_{x^2 - y^2}$ ones, which is opposite to the case of identical ligands.

Each eigenstate can be schematically represented as a superposition of such diagrams with included spin configurations. For example, the first excited state given in (4.2) is the superposition of six spin–orbital configurations shown in Figure 5. The approximate probability of observing each one is given in percentage.

4.4. The Determination of the ZFS Parameters $D$ and $E$

Since we have neglected all dipole–dipole magnetic interactions, the obtained FS shown in Figure 2b is entirely determined from the spin–orbit interactions within CF basis states (2.7). Thus, quantifying the ZFS in terms of the corresponding parameters resulting from the quantum perturbational approach and related algebraic representations (see, e.g., the study by Rudowicz[56] and references therein), we need only the spin Hamiltonian

$$\hat{h} = \hat{S} \cdot \mathbf{D} \cdot \hat{S}$$

where $\hat{S} = (\hat{S}_\alpha)_{\alpha \in \mathbb{K}}$ is the effective spin-one operator of the considered system and $\mathbf{D}$ is a symmetric tensor, with elements $D_{\alpha\beta} \in \mathbb{R}$, $\alpha, \beta \in \mathbb{K}$. Hereafter, we will see that a direct mapping between the spectrum of (4.5) and those depicted in Figure 2b is not feasible.

With respect to the applied method, the FS relevant to the low-energy levels is quantified by the energy gaps $\Delta E_{21} = 0.1708$, $\Delta E_{31} = 0.3649$, and $\Delta E_{12} = 0.1941$ meV. The associated functions are the ground state (4.1), first (4.2), and second (D.1) excited states. Represented only within the effective spin space, they read $|\Psi_1^i\rangle \rightarrow C(|0\rangle - |\uparrow\rangle)$, $|\Psi_2^i\rangle \rightarrow |1\rangle$, and $|\Psi_3^i\rangle \rightarrow C(|0\rangle + |\uparrow\rangle)$, respectively, where $C = 1/\sqrt{2}$. Here, the superposition of the ground and second excited states cannot be addressed by the spin Hamiltonian (4.5) as in our case the CF contributes significantly to the mixing of states. As a consequence, we could perform a sort of mapping and extract useful information for the elements of $\mathbf{D}$ only by increasing the complex’s symmetry to $C_{3v}$ and preserving the overall ZFS that equals 0.3649 meV. Now, calculating the energy-level sequence and associated eigenstates in the case of ideal trigonal bipyramidal geometry, we have $D_{\alpha\beta} = 0$ for all $\alpha \neq \beta$, $D_{yy} = D_{zz} = \Delta E_{31}/3$, and $D_{xx} = -2\Delta E_{31}/3$ meV. Owing to the relation between ZFS parameters ($D$, $E$) and the tensor elements,[48,55] we get $D = -\Delta E_{31}$ and $E = 0$.

In contrast to the positive value of $D$ obtained in the study by Fataftah[49] and hence $|0\rangle$-spin one ground state, our calculations suggest the opposite scenario. In other words, the ground-state energy level should be twofold degenerate and represented by the $|1\rangle$ and $|\uparrow\rangle$ states, with $D \approx -2.943$ cm$^{-1}$ and $|0\rangle$ being the excited state.

5. Magnetic and Spectroscopic Properties

5.1. Magnetization and Susceptibility

The obtained FS in the zero-field energy spectrum shown in Figure 2b, with energy gaps smaller than half of a meV, clearly indicates that the compound’s magnetic moment

$$m(T) = \Omega^{-1} \sum_{n=1}^{45} \mu_n e^{-E_n/k_B T}$$

with $\Omega = \sum_{n=1}^{45} e^{-E_n/k_B T}$

(5.1)

rapidly decreases by magnitude with increasing temperature. The dependence on $k$ and therefore on the overall ZFS is shown in Figure 7a, where $0 \leq k \leq 1$. Thus, for $k \leq 0.1$, the effect of temperature is most prominent in the domain 0.1 to 1 K. On the contrary, when the ZFS is large, or $k = 1$, in the same temperature domain, the magnitude of $m$ remains almost unchanged. Moreover, as it is depicted in Figure 6a, $m$ also deviates from its initial direction when $T \rightarrow 0$. 

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Even at low-magnetic field values, the small ZFS renders the magnetic behavior of the considered complex very susceptible to temperature variations, see Figure 7b. An exception is the domain \(0 \leq \kappa \leq 0.086\) for \(T \leq 0.1\) K, where the contribution of the externally applied magnetic field to the mixing of the ground state is greater than the spin–orbit one. Hence, the smaller the ZFS, the greater the population of the first two excited states for a given temperature. As an example, for \(\kappa = 0.43\), \(T = 10\) K, and \(B = 0.1\) T, the population rates of the first two excited energy levels are almost equal. In particular, we have the probability to observe 40% of the constituents in the powder sample at the ground state, \(p_0 = 0.33\) in the first excited state and \(p_1 = 0.26\) in the third one. As a result, we obtain a prompt decrease in the low-field susceptibility in the temperature domain \(0 < T \leq 10\) K. A comparison between theory and experiment is depicted in Figure 3, where the fraction between the corresponding molar mass and density is found to be \(\approx 0.975\) cm\(^3\) mol\(^{-1}\).

As the zero-field spectrum is nondegenerate, the action of the externally applied magnetic field changes the FS of the energy spectrum by only increasing the corresponding energy gaps, see, for example, Figure 2c. The eigenstates also change, such that their magnetic sequence resembles the spin Zeeman splitting. Thus, while reaching saturation of the magnetization, the probability of observing a fully polarized magnetic moment, along the magnetic field direction, at the ground state equals unity.

With magnetization data collected on a powder sample, the magnetization \(M(B, T)\) is computed as an arithmetic mean of the magnetic moments \(m\) of all complexes that can be represented as parity transformation one to another regarding their local reference frame shown in Figure 1. The temperature dependence of magnetization per complex, \(M = |M(T)|\), for some external magnetic field values is depicted in Figure 4. The consistency with the experimental data from the study by Fatafah et al.\(^{[40]}\) is obtained for values of the model parameters in Table 1 and the angle \(\nu\) between \(M(B, T)\) and \(B\) in the bottom row of Table 2.
Table 2. Magnetization (fourth row) for given magnetic field value $B$ and temperatures to the saturation values (first row). The last row indicates the variation of the effective angle $\nu$ between the vectors of the applied magnetic field and the magnetization with the change of $B$. For comparison, the third row shows the $z$ component of the molecule’s magnetic moment at the same temperature and magnetic field values, where in this case $\nu$ represents the angle between the magnetic field and $z$-axis of the compound’s reference frame.

| $T$ [K] | 0.1 | 0.2 | 0.6 | 1 | 1.35 |
|---------|-----|-----|-----|---|------|
| $m_z [\mu_0]$ | -1.0865 | -0.4666 | 1.3382 | 1.7712 | 1.9240 |
| $M [\mu_0]$ | 0 | 0.5952 | 1.5434 | 1.7920 | 1.9046 |
| $\nu [^\circ]$ | 47.6481 | 34.8129 | 24.6142 | 16.9022 |

At 7 T and $T \leq 1$ K, the magnetization is $\approx 0.963$ times its maximal value reached at about $B = 10$ T. In the case of low-field values, the obtained small reduction of the magnetization at $B = 1$ T and $T \leq 0.8$ K, shown in Figure 4, is due to the presence of single-ion anisotropy; see the energy barriers depicted in Figure 8 and 9. As an example, taking $B = 1$ T and $T = 0.8$ K, for the magnetization of a powder sample, we have $M = 0.6413$. Yet calculating the magnetic moment (5.1), for $\{B = x, B = y, B = z\} = \{58.53^\circ, 58.53^\circ, 47.46^\circ\}$, we get $m = (0.582, 1.455, -0.215)$ and $m = (-0.739, 0.195, 0.466)$. Hence, the energy required to fully polarize a single molecule strongly depends on the direction of the externally applied magnetic field in the compound’s reference frame. To shed more light on the existing single-ion anisotropy, we explore how the complex's energy depends on the direction angles $(a, b, c)$ \cite{46,48,56} of the magnetic moment (5.1) taken with respect to the reference frame shown in Figure 1. As the $z$-axis coincides with the principle axis of the ideal trigonal geometry case and we do not have a $\perp C_2$ axis of symmetry, we set $(a, b, c) = (m_x, m_y, m_z)$. Moreover, in view of the fact that at $T = 0.1$ K the ground state is about 100% populated, excited energy levels have a negligible contribution to the obtained energy barrier profile. Therefore, we obtain a small energy barrier with height $E_{br} \approx \Delta E_{z}$ [meV], shown by the inset in Figure 8 and 9. The barrier separates two different states of equal population in the case $T = 0.1$ K, one of which is the ground state (4.1) indicated by a green circle. The representation of the second state, shown by a red circle, depends on the axis along which the magnetic moment $m$ reverses. For example, considering the $z$-axis, with barrier depicted in Figure 8a, we find that the second state is (4.2). The evolution of the energy barrier with respect to $B$ is depicted on the background in Figure 8 and 9. The value of $E_{br}$ depends on the direction of the applied magnetic field. Taking the $z$-axis, for example, with $B = (0, 0, B_z)$, we get $E_{br} \approx \Delta E_{z}$ [meV]. On the other hand, for $B = (0, 0, -B_z)$, the barrier’s height is $\approx 1.6$ meV. The most prominent value of $E_{br}$ is obtained in the case $B = (0, -B_y, 0)$, reaching nearly 2 meV. The energy barrier rapidly vanishes with increase in temperature. The corresponding dependence is shown in Figure 10a and is intrinsically related to the evolution of $m$ depicted in Figure 6a. Moreover, Figure 9 shows that the barrier’s height reduces significantly by decreasing the value of $\kappa$, demonstrating how it depends on the ZFS shown in Figure 2b. Note that as expected no energy barrier is observed along the $x$-axis, by virtue of the temperature dependence of $m_x$ shown in Figure 6a.

5.2. cw-EPR

According to the cw-EPR experimental observations reported in the study by Fataftah et al. \cite{40}, the vanadium-based complex responds to 240 GHz microwave radiation at $\approx 3.75$, 6.55, and 10.4 T magnetic field values and $T = 8$ K. As all three transitions are related to spin-triplet states, the selection rules are $\Delta S = 0$ and $|\Delta m| = 1, 2$. We would like to point out that these transitions are selected for the sake of convenience and for mixed states the
associated selection rules should be interpreted in accordance with other studies.\cite{48,57} The corresponding excitations, with energy \( \approx 0.992 \text{ meV} \), are reasonably well reproduced by the present theoretical approach. They are related to the existing anisotropy that determines the \( y \) component of the magnetic moment (5.1) as a dominant transverse component in the whole temperature range; see Figure 6a and the energy barriers depicted in Figure 8. In other words, with respect to the compounds’ reference frame illustrated in Figure 1, the resonance condition is satisfied only when the magnetic field vector lies in the \((2\pi)\) plane and forms a certain angle with the \( z \)- and \( \gamma \)-axes. Thus, only certain units in the powder sample with the appropriate orientation with respect to the direction of \( \textbf{B} \) will be magnetically excited, contributing on average to the change in magnetization from the perspective of laboratory reference frame.

By taking \( \textbf{B} = \textbf{n} \), where \( \textbf{n} = (n_x, n_y, n_z) \) is the field’s unit vector with respect to the compound’s reference frame, we obtain that the resonance occurs for \( n_x = 0, 0.4212 \leq n_y \leq 0.4338 \), and \(-0.901 \leq n_z \leq -0.907 \).

The first transition at 3.75 T refers to magnetic excitation with \( |\Delta m| = 2 \). It involves the ground and the second excited states. The population rate at the ground state is 62.5\% and represented by a superposition of the three spin-one triplets with coefficients given in percentage; it reads \( |\Psi_{1}^{\text{1.75}}\rangle \rightarrow 0.1\%|1, 1\rangle + 23.8\%|1, 0\rangle + 76.1\%|1, \bar{\u03c8}\rangle \). Respectively, for the second excited state, we get \( |\Psi_{2}^{\text{1.75}}\rangle \rightarrow 81.3\%|1, 1\rangle + 16.3\%|1, 0\rangle + 2.4\%|1, \bar{\u03c8}\rangle \).

The second excitation at 6.55 T is associated with transition between the ground and the first excited states, with \( |\Delta m| = 1 \). The calculated population of the ground state is about 75.2\%, which explains the higher intensity of the relevant peak compared with that of the first excitation. With respect to the probabilities’ distribution among the three spin triplets, both states read \( |\Psi_{1}^{\text{6.55}}\rangle \rightarrow 1.7\%|1, 1\rangle + 18.9\%|1, 0\rangle + 80.4\%|1, \bar{\u03c8}\rangle \) and \( |\Psi_{2}^{\text{6.55}}\rangle \rightarrow 13.2\%|1, 1\rangle + 68.4\%|1, 0\rangle + 18.4\%|1, \bar{\u03c8}\rangle \).

The third peak at \( \approx 10.4 \text{ T} \) is associated with transition between the first and second excited states that can be represented as \( |\Psi_{1}^{\text{10.4}}\rangle \rightarrow 11.9\%|1, 1\rangle + 72.4\%|1, 0\rangle + 15.7\%|1, \bar{\u03c8}\rangle \) and \( |\Psi_{2}^{\text{10.4}}\rangle \rightarrow 88.5\%|1, 1\rangle + 11\%|1, 0\rangle + 0.5\%|1, \bar{\u03c8}\rangle \), respectively. The corresponding selection rule is \( |\Delta m| = 1 \). The population of the first excited level at 8 K is about 10.1\%, which is consistent with the observed low intensity of the peak.\cite{40}

5.3. Photoluminescence

The photoluminescence spectroscopy performed on \( (C_6F_5)_3\text{trenVCN}^+\text{Bu} \) in 2-methyltetrahydrofuran at 77 K, reported in the study by Fatafah et al.,\cite{40} shows a continuous near-infrared emission with spectral peak at \( \approx 1.240 \mu m \) in the excitation wavelength range 550 – 750 nm. According to the \( s = 1 \) ground state, the transitions to all photoexcitations are triplet–singlet related. Respectively, the observed phosphorescence is associated with a singlet–triplet relaxation process. Furthermore, the large difference between the excitation and emission energies suggests that the overall relaxation pathway

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{The ground-state energy of a single molecule as a function of the direction angle "c" between \( \textbf{m} \) and the \( z \)-axis of the compounds reference frame and its dependence on the reduction parameter \( \kappa \) to the spin–orbit coupling. No angle dependence is observed at \( \kappa = 0 \). The energy is normalized to the value obtained in the case \( \textbf{B} = 0 \), indicated with a black circle. For additional details, see Figure 8a. The inset depicts a detailed view of the energy barrier profile.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{a) Temperature dependence of the energy barrier calculated with respect to the \( z \)-axis. The excited states contribute for \( T > 0.1 \text{ K} \). More details are shown in the inset in Figure 8a. Subfigure b) depicts how the barrier’s height along the \( z \)-axis changes with respect to the cyanide charge number \( Z_1 \) at \( T = 0.1 \text{ K} \).}
\end{figure}
may incorporate transitions with different vibronic modes. To this end, in an attempt to reproduce the photoluminescence data, we simulate variations in the polar and azimuthal angles for all ligands with a value no larger than 0.63°, as within the domain (−0.63°, 0.63°), the ZFS depicted in Figure 2b remains invariant. This simulation allows us to trace the corresponding change of the electronic energy levels and the extent of spin–multiplet mixing in the resulting eigenstates. Actually, the phonon energies and interactions are not considered. Moreover, for brevity, variations in the radial position of the ligands are not computed.

For Δθi = 0° and Δφi = 0°, i = 1, ..., 5, the function (4.3) is the first singlet state with energy E26 = 1.84694 eV; see Appendix D. At this point, the group of eigenstates (Ψ23,Ψ24,Ψ25) is all s = 1 states with more than 99.9% probability. For example

$$|\Psi_{23}\rangle = 0.55i |\psi_{10,1,0}\rangle - 0.38 |\psi_{10,1,1}\rangle + 0.045 |\psi_{9,1,0}\rangle - 0.031 |\psi_{9,1,1}\rangle - 0.08 |\psi_{7,1,0}\rangle + 0.055 |\psi_{7,1,1}\rangle + 0.048 |\psi_{4,1,0}\rangle - 0.033 |\psi_{4,1,1}\rangle + \sum_{n=2} O(10^{-n}) |\psi_{...}\rangle$$

In this case, the lower possible excitation wavelength lies in the experimentally observed domain and is ≈671 nm. However, the only spin-allowed emission near the observed one, with no intersystem crossing (ISC), is of low probability and related to the transition $|\Psi_{26}\rangle \rightarrow |\Psi_{15}\rangle$. It is about 1.16 μm, where

$$|\Psi_{15}\rangle = (-0.61 - 0.27i) |\psi_{1,1,0}\rangle + (0.26 - 0.6i) |\psi_{1,1,1}\rangle - (0.17 + 0.08i) |\psi_{2,1,0}\rangle + (0.07 - 0.17i) |\psi_{2,1,1}\rangle + (0.039 + 0.018i) |\psi_{5,1,0}\rangle - (0.017 - 0.039i) |\psi_{5,1,1}\rangle - (0.1 + 0.044i) |\psi_{6,1,0}\rangle + (0.042 - 0.099i) |\psi_{6,1,1}\rangle + (0.113 + 0.051i) |\psi_{8,1,0}\rangle - (0.048 - 0.112i) |\psi_{8,1,1}\rangle + \sum_{n=2} O(10^{-n}) |\psi_{...}\rangle$$

A better theoretical description of the photoluminescence spectroscopy is obtained by varying the polar and azimuthal angles of all ligands with an amount of ±0.63° to their initial values given in Table 1. The resulting emission wavelengths take values in the range of 1.230 – 1.250 μm. A particular case with Δθi = 0.585° and Δφi = 0° for all i = 1, ..., 5 is depicted in Figure 11a. The most considerable is the shifting related to the observed emission involving the set of energy levels $E_{11}, E_{14}, E_{15}$. An absorption band and a possible relaxation pathway are depicted by curved arrows, where the absorption at 705 nm is of very low probability rate for T < 300 K. The corresponding radiative decay at about 1240 nm is a singlet–triplet transition. In particular, the compound undergoes a transition from $|\Psi_{23}\rangle$ to $|\Psi_{15}\rangle$, where the former state is now the 99.5% singlet:

![Figure 11](image-url)

Figure 11. a) Energy-level diagram of (C6F5)i, trenVCNBu up to 2 eV with possible absorption bands and relaxation pathway reproducing the photoluminescence and UV–vis–NIR spectroscopy measurements reported in the study by Fataftah et al.\textsuperscript{40} For all i = 1, ..., 5 the black lines represent the case with Δθi = 0° and Δφi = 0° shown in Figure 2a. The gray solid fields depict bands of energy levels associated with possible continuous or discrete variations in the angular positions of all ligands, in the intervals $-0.63° \leq \Delta \theta_i \leq 0.63°$ and $-0.63° \leq \Delta \phi_i \leq 0.63°$. The blue, violet, and orange arrows refer to spin-allowed ground- and excited-state transitions, respectively, where Δθi = 0.585° and Δφi = 0°. Accordingly, the olive green arrow depicts singlet–triplet radiative decay at 1240 nm related to the observed emission, see the study by Fataftah et al.\textsuperscript{40} Nonradiative decays are illustrated by solid noncurved arrows. The light-green arrow shows a transition at about 3 μm. b) A magnification shows the FS for the case with Δθi = 0.585° and Δφi = 0°, with possible ISC and magnetic dipole transitions (MDT) depicted by the dashed gray arrow.

$$|\Psi_{21}\rangle = -0.11 |\psi_{1,0,0}\rangle + 0.25 |\psi_{2,0,0}\rangle - 0.2 |\psi_{1,0,0}\rangle - 0.73 |\psi_{5,0,0}\rangle - 0.016 |\psi_{6,0,0}\rangle - 0.031 |\psi_{7,0,0}\rangle + 0.25 |\psi_{8,0,0}\rangle + 0.045 |\psi_{9,0,0}\rangle - 0.051 |\psi_{11,0,0}\rangle + 0.26 |\psi_{12,0,0}\rangle + 0.38 |\psi_{13,0,0}\rangle - 0.13 |\psi_{14,0,0}\rangle + \sum_{n=1} O(10^{-n}) |\psi_{...}\rangle$$

A better theoretical description of the photoluminescence spectroscopy is obtained by varying the polar and azimuthal angles of all ligands with an amount of ±0.63° to their initial values given in Table 1. The resulting emission wavelengths take values in the range of 1.230 – 1.250 μm. A particular case with Δθi = 0.585° and Δφi = 0° for all i = 1, ..., 5 is depicted in Figure 11a. The most considerable is the shifting related to the observed emission involving the set of energy levels $E_{11}, E_{14}, E_{15}$. An absorption band and a possible relaxation pathway are depicted by curved arrows, where the absorption at 705 nm is of very low probability rate for T < 300 K. The corresponding radiative decay at about 1240 nm is a singlet–triplet transition. In particular, the compound undergoes a transition from $|\Psi_{23}\rangle$ to $|\Psi_{15}\rangle$, where the former state is now the 99.5% singlet:

$$|\Psi_{21}\rangle = -0.11 |\psi_{1,0,0}\rangle + 0.25 |\psi_{2,0,0}\rangle - 0.2 |\psi_{1,0,0}\rangle - 0.73 |\psi_{5,0,0}\rangle - 0.016 |\psi_{6,0,0}\rangle - 0.031 |\psi_{7,0,0}\rangle + 0.25 |\psi_{8,0,0}\rangle + 0.045 |\psi_{9,0,0}\rangle - 0.051 |\psi_{11,0,0}\rangle + 0.26 |\psi_{12,0,0}\rangle + 0.38 |\psi_{13,0,0}\rangle - 0.13 |\psi_{14,0,0}\rangle + \sum_{n=1} O(10^{-n}) |\psi_{...}\rangle$$

The superposition in the energy eigenstate $|\Psi_{21}\rangle$ has almost the same expression as (5.2). For more details, see Appendix E. In addition, Figure 11b depicts the FS of this transition. Depending on the values of Δθi and Δφi, the calculations predict a different extent of ISC between two group of levels related to the states $|\Psi_{21}\rangle, |\Psi_{26}\rangle, |\Psi_{27}\rangle, |\Psi_{28}\rangle$. The relaxation to the ground state after emission involves only spin–triplet states and is assumed to be related to vibrational modes.

In spite of the fact that the proposed approach sheds light on the experimentally observed phosphorescence, the decay corresponding to a wavelength of nearly 3 μm remains unresolved (see Figure 11a).
We would like to point out that the isocyanide member may allow significant stretching of its bond to the vanadium center, as is discussed in the study by Fataftah et al.\(^{[40]}\) In this respect, variations equal or less than $\pm 0.05$ Å in the corresponding radial position have no significant contribution to the energy spectrum shown in Figure 11a. Yet, any value closer to $\pm 0.1$ Å considerably increases the shifting of the energy levels and leads to a different ZFS.

6. Conclusion

To gain useful insight into the magnetostructural dependencies in 3d\(^2\) systems and the mutual influence of crystal field, exchange, and spin–orbit interactions on their magnetic behavior, we performed an extensive and detailed theoretical investigation of the magnetic and spectroscopic properties of the compound $(C_6F_5)_2$trcnVNCN$^{1}$Bu. Using a multiconfigurational method with active space restricted to all five $d$ orbitals, we reproduce and interpret the available in literature experimental data.\(^{[40]}\) This includes calculations for the magnetization, low-field susceptibility, cw-EPR, and photoluminescence spectroscopy. For more details, see, for example, Section 5.

In general, in the parameterization scheme associated with the proposed method, there are three sets of nonvariational parameters. The first set includes the coordinates of all ligands, obtained from the structural analysis. The second comprises the charge numbers of all ligands and metal centers, see Section 2.2, in particular (2.4). Moreover, the second set accounts for a control parameter to the spin–orbit coupling, denoted in the present study by $\kappa$ and discussed in the beginning of Section 3.3. Finally, the third contains the components of the unit vector associated with the applied magnetic field, taken with respect to the compound’s reference frame (see, e.g., Figure 1). It further includes all derived quantities, such as the effective angle given in Table 2. Let us stress that these parameters uniquely characterize the compound under consideration.

In particular, the study of $(C_6F_5)_2$trcnVNCN$^{1}$Bu points out that the electrons are partially delocalized. This may be traced back to the lower than expected values of the prefactor $\kappa$ and charge number $Z$ of the vanadium ion; see Table 1. This is also evident from the larger than expected value of $Z_1$. Furthermore, the calculations show that the difference between the values of the charge number of nitrogen and isocyanide ligands plays a significant role in shaping the low-field low-temperature magnetic properties. Accordingly, there is an optimal range for this difference where one obtains good agreement with the available experimental data. For example, reducing the value of $Z_1$ from Table 1 results in better agreement with the low-susceptibility measurements and in worse reproduction of the low-field magnetization, cw-EPR, and photoluminescence data. This is due to the corresponding decrease in energy of the $d_{xz}$ and $d_{yz}$ orbitals and increase in ZFS. However, the value of $Z_1$ does not contribute considerably to the zero-field ground-state magnetic properties. In particular, setting $Z_i = Z_1$, for all $i = 2, \ldots, 5$, with $Z_1$ shown in Table 1, the orientation of the total magnetic moment at the ground state slightly changes from $\mu_1 = (-0.0171, 1.4091, -1.0865)$ to $\mu_1 = (-0.02695, 1.36805, -1.01942)$ (see Figure 6a and Section 4.1). As a result, for $T \to 0$, the magnitude and orientation of $\mu$ given in (5.1) slightly change. The $d_{xz}$ and $d_{yz}$ orbitals are now lower in energy than the $d_{xy}$, $d_{x^2-y^2}$ ones and the ZFS is stronger. We have $\Delta E_{z1} = 0.2855$, $\Delta E_{z1} = 0.5785$, and $\Delta E_{z1} = 0.2929$ meV. Consequently, the population of the corresponding levels changes, leading to a different temperature dependence of the magnetic moment (5.1) in the case of $T > 0$. Furthermore, the anisotropy energy\(^{[36,58,59]}\) also changes, such that the corresponding energy barrier’s height increases. An example is depicted in Figure 10b, where for $T = 0.1$ K and $Z_1 = 1.157$ with respect to the $z$ axis, we have $E_{z1} \approx 0.084$ meV.

Let us stress that in the case of ideal trigonal bipyramidal geometry, we obtain an energy-level sequence that can be directly related to the conventional ZFS Hamiltonian.\(^{[36,60]}\) Thus, one has the case of twofold degenerate ground state and an excited state related to $m = 0$ spin state, with $D < 0$ and $E \to 0$. Nevertheless, the proposed multiconfigurational scheme still gives the energy eigenstates as a linear combination of different configuration functions. The comparison with the axial $D$ and rhombic $E$ ZFS parameters is provided in Section 4.4.

An essential feature observed in the presence of the external magnetic field is the evolution of FS. The shifting of energy levels due to the action of $B$ is discussed in Section 4.2. Nevertheless, another example of how the Zeeman and spin–orbit terms interfere causing this effect is evident from the dependence of magnetic moment (5.1) on the reduction coefficient $\kappa$. This effect is prominent for low-temperatures and is demonstrated in Figure 7b. Within the studied low-symmetry complex, there exists a minimum value of $|m|$ that corresponds to maximal degeneracy of the ground-state energy level in the case of $B \neq 0$. With respect to the case depicted in Figure 7b, for $\kappa = 0.086$ and $B \parallel B_z = 0.2$ T, the ground-state level is twofold degenerate. As a result, the magnitude of $m$ drops below its zero-field value, shown in Figure 7a, marking the crossing point of the competition between Zeeman and spin–orbit terms.

Within the considered localized electron approach, the exchange interactions do not contribute to the ground-state magnetic properties of the studied compound. Generally, this is true for all 3d\(^2\) compounds as the corresponding energy gaps are larger than 1 eV. For example, the first singlet state in the energy spectrum shown in Figure 2 is $E \approx 1.846$ eV, see Equation (4.3). Therefore, the only exchange-related magnetic transitions occur due to absorption or emission.

This study provides analytical and numerical results for the expectation values of all possible interaction terms, energy eigenstates, and the related magnetic moments. In general, the used method and the ensuing analytical expressions can be directly applied to all 3d\(^2\) single-molecular magnets and low-dimensional systems. Some candidates, for example, are those consisting of Ti$^{2+}$, Cr$^{4+}$, and Mn$^{3+}$ metal centers.

### Appendix A. State Representation

The single electron 3d states in (2.7) are given by the product between the radial wavefunction $R_{2l}(\rho)$, the spherical harmonics $Y^{m_i}_l(\theta, \phi)$\(^{[46,61]}\) and the spin states $|m_s\rangle$, where $m_s = 0, \pm 1, \pm 2$.
and $m_\Sigma = \pm 1/2$. For example, $|d_{z^2}|m_\Sigma \to R_{32}(\rho)Y^0_{2\Sigma}|m_\Sigma\rangle$.

Omitting the spin term, we have

$$
|d_{z^2}| \to R_{32}(\rho) \frac{1}{\sqrt{2}} \left( Y_2^1(\theta, \phi) - Y_2^3(\theta, \phi) \right)
$$

$$
|d_{1z}| \to R_{32}(\rho) \frac{i}{\sqrt{2}} \left( Y_2^1(\theta, \phi) + Y_2^3(\theta, \phi) \right)
$$

$$
|d_{xy}| \to R_{32}(\rho) \frac{i}{\sqrt{2}} \left( Y_2^2(\theta, \phi) - Y_2^2(\theta, \phi) \right)
$$

$$
|d_{x^2-y^2}| \to R_{32}(\rho) \frac{1}{\sqrt{2}} \left( Y_2^2(\theta, \phi) + Y_2^2(\theta, \phi) \right)
$$

### Appendix B. Exchange Integrals

The exchange integrals $\{V_i\}_{i=1}^5$ and $\{L_1, L_2\}$ in (3.1) read

$$
V_1 = \frac{4201}{483840} \frac{Z}{r_B^7}, \quad V_2 = \frac{43459}{483840} \frac{Y}{r_B^7}, \quad V_3 = \frac{29731}{322560} \frac{Z}{r_B^7},
$$

$$
V_4 = \frac{8121}{967680} \frac{Z}{r_B^7}, \quad V_5 = \frac{2783}{322560} \frac{Y}{r_B^7}, \quad V_6 = \frac{26689}{322560} \frac{Z}{r_B^7},
$$

$$
V_7 = \frac{507}{967680} \frac{Y}{r_B^7}, \quad V_8 = \frac{949}{322560} \frac{Y}{r_B^7}, \quad V_9 = \frac{169}{35840} \frac{Z}{r_B^7},
$$

$$
L_1 = \frac{3991}{483840} \frac{Z}{r_B^7}, \quad L_2 = \frac{65}{13824} \frac{Y}{r_B^7}
$$

### Appendix C. CF Integrals

The functions $U_{\alpha}$ and $U_{\alpha|\beta}$, with $\alpha \in \{xz, yz, xy, x^2 - y^2, z^2\}$, are the sum of five terms $U^{(i)}_{\alpha}$ and $U^{(i)}_{\alpha|\beta}$, respectively, where $i = 1, \ldots, 5$. For example, $U_{xz} = \sum_{i=1}^5 U^{(i)}_{xz}$. For all $i$, the functions that enter into the diagonal elements read

$$
U^{(i)}_{xz} = \frac{\gamma Z_i}{32g_i^2Z_i^2} \left( -21870r^4_B + 144\alpha_i^2r^2_\Sigma Z^2 + 32\alpha_i^4Z^4 + 54r^2_B \right) \times 
\frac{1}{(675r^2_B + 8\alpha_i^2Z^2)\cos[2\varphi_i] - 42525r^4_B\cos[2(\varphi_i - 2\theta_i)]}
$$

$$
+ 24300r^4_B\cos[2(\varphi_i - 2\theta_i)] - 216\alpha_i^2r^2_\Sigma Z^2\cos[2(\varphi_i - 2\theta_i)] - 48600r^4_B\cos[2\varphi_i] + 432\alpha_i^2r^2_\Sigma Z^2 \cos[2\varphi_i - 2\theta_i] - 85050r^4_B \times 
\cos[4\varphi_i] + 24300r^4_B\cos[2(\varphi_i + \theta_i)] - 216\alpha_i^2r^2_\Sigma Z^2 \times 
\cos[2(\varphi_i + \theta_i)] - 42525r^4_B\cos[2(\varphi_i + 2\theta_i)]
$$

$$
U^{(i)}_{yz} = \frac{\gamma Z_i}{32g_i^2Z_i^2} \left( -21870r^4_B + 144\alpha_i^2r^2_\Sigma Z^2 + 32\alpha_i^4Z^4 + 54r^2_B \right) \times 
\frac{1}{(675r^2_B + 8\alpha_i^2Z^2)\cos[2\varphi_i] - 42525r^4_B\cos[2(\varphi_i - 2\theta_i)]}
$$

$$
+ 24300r^4_B\cos[2(\varphi_i - 2\theta_i)] - 216\alpha_i^2r^2_\Sigma Z^2\cos[2(\varphi_i - 2\theta_i)] - 48600r^4_B\cos[2\varphi_i] + 432\alpha_i^2r^2_\Sigma Z^2 \cos[2\varphi_i - 2\theta_i] - 85050r^4_B \times 
\cos[4\varphi_i] + 24300r^4_B\cos[2(\varphi_i + \theta_i)] - 216\alpha_i^2r^2_\Sigma Z^2 \times 
\cos[2(\varphi_i + \theta_i)] - 42525r^4_B\cos[2(\varphi_i + 2\theta_i)]
$$

Furthermore, $V_i$, for the functions (3.3), we have

$$
U^{(i)}_{xz,yz} = \frac{27r^7_B}{4g_i^2Z_i^4} \left( (1152r^4_B + 4\alpha_i^2Z^2 + 1575r^6_B) \cos[2\varphi_i] \right) \times 
\frac{1}{2(90\varphi_i)\sin^2[\theta_i]}
$$

$$
U^{(i)}_{xz,xy} = \frac{27r^7_B}{16g_i^2Z_i^4} \left( 6300r^4_B \cos[\varphi_i] \sin[3\varphi_i] \sin^3[\theta_i] \right) \times 
(225r^5_B - 6\alpha_i^2Z^2 + 1575r^6_B \cos[2\varphi_i]) \times 
\frac{1}{2(90\varphi_i)\sin[\theta_i]}
$$

$$
U^{(i)}_{xz,x^2-y^2} = \frac{27r^7_B}{32g_i^2Z_i^4} \left( (1185r^4_B + 4\alpha_i^2Z^2 + 1575r^6_B) \cos[2\varphi_i] \right) \times 
4 \cos[\varphi_i] \sin[2\varphi_i] - 1575r^6_B \times 
\cos[\varphi_i] + 3\sin[\varphi_i] \sin[4\varphi_i]
$$

$$
U^{(i)}_{xz,x^2+y^2} = \frac{9\sqrt{3}r^7_B}{8g_i^2Z_i^4} \left( 675r^4_B + 8\alpha_i^2Z^2 + 4725r^6_B \cos[2\varphi_i] \right) \times 
\frac{1}{2(90\varphi_i)\sin[\varphi_i] \sin[\theta_i]}
$$

$$
U^{(i)}_{yz,xy} = \frac{27r^7_B}{8g_i^2Z_i^4} \left( (675r^4_B + 8\alpha_i^2Z^2 - 1575r^6_B) \cos[2\varphi_i] \right) \times 
\frac{1}{2(90\varphi_i)\sin^2[\varphi_i] \sin[4\varphi_i] \cos[\varphi_i]}
$$

$$
U^{(i)}_{yz,x^2-y^2} = \frac{27r^7_B}{2g_i^2Z_i^4} \left( \cos[\theta_i] \sin[\varphi_i] \sin[\theta_i] \right) \times 
(450r^5_B - 4\alpha_i^2Z^2 + 1575r^6_B \cos[2\varphi_i] \sin^2[\theta_i])
$$

$$
U^{(i)}_{yz,x^2+y^2} = \frac{9\sqrt{3}r^7_B}{8g_i^2Z_i^4} \left( 675r^4_B + 8\alpha_i^2Z^2 + 4725r^6_B \cos[2\varphi_i] \right) \times 
\frac{1}{2(90\varphi_i)\sin[\varphi_i] \sin[\theta_i]}
$$

$$
U^{(i)}_{y^2,x^2-y^2} = \frac{42525r^7_B}{8g_i^2Z_i^4} \sin[4\varphi_i] \sin^4[\theta_i]
$$
\[ U_{xy,z}^{(i)} = \frac{9\sqrt{3}r_{\parallel}^{2}}{8q_{\parallel}^{2}}Z_{\parallel} \left( 3375r_{\parallel}^{2} - 16q_{\parallel}^{2}Z_{\parallel} + 4725r_{\parallel}^{2} \cos[\theta] \right) \times \sin[2\varphi_{\parallel} \sin^{2}[\theta]] \]

and

\[ U_{x'-y',z'}^{(i)} = \frac{9\sqrt{3}r_{\perp}^{2}}{8q_{\perp}^{2}}Z_{\perp} \left( 3375r_{\perp}^{2} - 16q_{\perp}^{2}Z_{\perp} + 4725r_{\perp}^{2} \cos[\theta] \right) \times \cos[2\varphi_{\perp} \sin^{2}[\theta]] \]

**Appendix D. Energy spectrum**

The zero-field values, in eV, of all energy levels depicted in Figure 2a are provided hereafter. Starting from the highest one on the left to the ground-state energy level on the right, we have the array

\[
(5.81233, 3.90346, 3.75779, 3.32676, 3.16796, 2.92855, 2.92845, 2.92835, 2.8337, 2.7857, 2.78561, 2.7854, 2.77113, 2.43523, 2.40827, 2.32306, 2.13117, 1.98332, 1.91452, 1.84694, 1.82376, 1.82358, 1.82344, 1.6839, 1.68375, 1.68362, 1.6435, 1.9804, 1.9803, 1.9803, 0.77873, 0.778659, 0.778587, 0.287733, 0.287647, 0.287533, 0.212738, 0.212734, 0.212714, 0.204263, 0.204227, 0.204211, 0.000364953, 0.000170839, 0).
\]

The second excited state in the zero-field energy spectrum depicted in Figure 2b reads

\[
|\Psi_{1}^{(2)}\rangle = (-0.16 + 0.14i)|\psi_{1,1,0}\rangle + (0.13 + 0.15i)|\psi_{1,1,1}\rangle \\
+ (0.28 - 0.24i)|\psi_{2,1,0}\rangle - (0.22 + 0.26i)|\psi_{2,1,1}\rangle \\
- (0.15 - 0.12i)|\psi_{3,1,0}\rangle + (0.11 + 0.14i)|\psi_{3,1,1}\rangle \\
- (0.27 - 0.23i)|\psi_{3,1,0}\rangle + (0.22 + 0.25i)|\psi_{3,1,1}\rangle \\
+ (0.33 - 0.28i)|\psi_{6,1,0}\rangle - (0.25 + 0.31i)|\psi_{6,1,1}\rangle \\
- (0.074 - 0.063i)|\psi_{6,1,0}\rangle + (0.058 + 0.07i)|\psi_{6,1,1}\rangle \\
+ \sum_{n\geq2} O(10^{-n})\psi_{\ldots}\]

\[ (D.1) \]

In the case shown in Figure 2c, the state (D.1) transforms into

\[
|\Psi_{2}^{(2)}\rangle = (-0.046 + 0.043i)|\psi_{1,1,0}\rangle + (0.19 + 0.21i)|\psi_{1,1,1}\rangle \\
+ (0.080 - 0.076i)|\psi_{2,1,0}\rangle - (0.32 + 0.36i)|\psi_{2,1,1}\rangle \\
- (0.042 - 0.038i)|\psi_{3,1,0}\rangle + (0.16 + 0.20i)|\psi_{3,1,1}\rangle \\
- (0.077 - 0.072i)|\psi_{5,1,0}\rangle + (0.32 + 0.35i)|\psi_{5,1,1}\rangle \\
+ (0.096 - 0.087i)|\psi_{6,1,0}\rangle - (0.38 + 0.43i)|\psi_{6,1,1}\rangle \\
- (0.022 - 0.021i)|\psi_{8,1,0}\rangle + (0.086 + 0.097i)|\psi_{8,1,1}\rangle \\
+ \sum_{n\geq2} O(10^{-n})\psi_{\ldots}\]

\[ (D.2) \]

**Appendix E. Photoluminescence**

For the explicit representation of the 15-th energy state, related to the emission with 1240 nm wavelength obtained in the case \(\Delta \theta = 0.585^\circ\) and \(\Delta \varphi = 0^\circ\) for all \(i = 1, \ldots, 5\), we have

\[
|\Psi_{15}^{(2)}\rangle = (0.34 + 0.56i)|\psi_{1,1,0}\rangle - (0.55 - 0.35i)|\psi_{1,1,1}\rangle \\
+ (0.11 + 0.18i)|\psi_{2,1,0}\rangle - (0.17 - 0.11i)|\psi_{2,1,1}\rangle \\
- (0.022 + 0.036i)|\psi_{5,1,0}\rangle + (0.036 - 0.022i)|\psi_{5,1,1}\rangle \\
+ (0.044 + 0.071i)|\psi_{6,1,0}\rangle - (0.069 - 0.044i)|\psi_{6,1,1}\rangle \\
- (0.073 + 0.12i)|\psi_{8,1,0}\rangle + (0.117 - 0.074i)|\psi_{8,1,1}\rangle \\
+ \sum_{n\geq2} O(10^{-n})\psi_{\ldots}\]

To compare the last superposition with that in the case of no change in the ligands angles, see (5.2).

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

magnetostructural correlations, molecular magnets, vanadium
