Excited state spinmerism in high-field Fe(II)-verdazyl molecular complex: versatile local spins for quantum information

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Abstract

Quantum entanglement between the spin states of a metal centre and radical ligands is suggested in an iron(II) [Fe(dipyvd)2]2+ compound (dipyvd = 1-isopropyl-3,5-dipyridil-6-oxoverdazyl). Wavefunction ab initio (Difference Dedicated Configuration Interaction, DDCI) inspections were carried out to stress the versatility of local spin states. We name this phenomenon excited state spinmerism, in reference to our previous work (see Roseiro et. al., ChemPhysChem, https://doi.org/10.1002/cphc.202200478 (2022)) where we introduced the concept of spinmerism as an extension of mesomerism to spin degrees of freedom. The construction of localized molecular orbitals allows for a reading of the wavefunctions and projections onto the local spin states. The low-energy spectrum is well-depicted by a Heisenberg picture. A 60 cm−1 ferromagnetic interaction is calculated between the radical ligands with the $S_{total} = 0$ and 1 states largely dominated by a local low-spin $S_{Fe} = 0$. In contrast, the higher-lying $S_{total} = 2$ states are superpositions of the local $S_{Fe} = 1$ (17%, 62%) and $S_{Fe} = 2$ (72%, 21%) spin states. Such mixing extends the traditional picture of a high-field $d^6$ Tanabe-Sugano diagram. Even in the absence of spin-orbit coupling, the avoided crossing between different local spin states is triggered by the crystal field generated by radical ligands. This puzzling scenario emerges from versatile local spin states in compounds of interest for spin-qubit generation.

Introduction

The synthesis and characterization of molecule-based magnetic systems has been an intense research area for decades, prompted by the need for information storage devices and advances in quantum technologies (see for example Refs.1–4). The motivations for targeting such complexes stem from their physical-chemical properties ranging from long coherence time5–9 to manipulation possibilities10–15. In the presence of spin-switchable units, the local spin state of archetypical iron(II) or cobalt(II) ($3d^6$ and $3d^7$, respectively) ions can be controlled using external fields. Important structural modifications are then observed, with changes in bond distances of up to 0.2 Å (i.e. 10%)16 and deep changes in charge
distribution (up to 0.5 electrons)\textsuperscript{17}. The latter are responsible for hysteretic behavior in materials,\textsuperscript{18} and have long been underestimated whereas they are the main characteristics of valence tautomers\textsuperscript{19}. Let us stress that the transition between tautomers is not necessarily accompanied by a modification of the spin multiplicity, in contrast with spin-transition systems. More recently, transition metal ions combined with organic ligands have been considered as possible targets in the development of molecular-based quantum units of information, \textit{e.g.} qubits or qudits (see for example Refs.\textsuperscript{1–4}). Theoretical studies have also revealed the potential interest of radical ligands for the manipulation of quantum information via the entanglement of local spin degrees of freedom\textsuperscript{20,21}. A prerequisite is the binding of radical ligands to paramagnetic metal centers without losing their open-shell character. In this respect, oxoverdazyl-based ligands have proven to fulfill such requirement, giving rise to a wealth of magnetic coupling schemes\textsuperscript{22–24}. Furthermore, the flexibility and well-established redox activity of organic-based compounds make such materials particularly interesting. Not only can inter-unit interactions be modulated with speculated spin-crossover behavior\textsuperscript{25}, but the crystal field generated by several open-shell ligands may give rise to unusual and puzzling scenarios.

Recently, it has been suggested that the spectroscopy of a cobalt(II) ion coordinated to open-shell radicals may not be readily interpreted. At the crossroads of exchange coupled and spin-crossover systems, this compound has questioned the traditional pictures emerging from a metal ion, either high-spin or low-spin, in the electrostatic field of neighbouring ligands\textsuperscript{20,26}. Wavefunction-based calculations supported that the spin states are characterized by combinations of various local spin states on the metal center, a feature of entanglement named \textit{spinmerism}. This phenomenon can be seen as an extension of mesomerism to spin degrees of freedom with entanglement in between two local sub-parts of a molecule. Since the ligand field includes Coulomb and direct exchange contributions in a complex built on spin-coupled partners, one may wonder whether different local spin states may coexist on the metal ion. The introduction of radical ligands may indeed disrupt the assumption of a given spin state on the metal centre in the description of ground and excited states.

Inspired by these observations, the pseudo-octahedral iron(II)-oxoverdazyl compound $[\text{Fe(dipyvd)}_2]^{2+}$, with dipyvd = 1- isopropyl-3,5-dipyridil-6-oxoverdazyl (1) was considered as another prototype to be examined (see Figure 1)\textsuperscript{27}. Magnetic and spectroscopic properties were reported in the literature and complemented by density functional theory-based calculations. Iron(II) being a spin-crossover metal ion, any intermediate crystal field should be appropriate to observe the coexistence of a $S_{Fe} = 0$ (low spin) and $S_{Fe} = 2$ (high spin). From the Fe-N bond distances values (ca. 1.9 Å), a low-spin iron center is expected and was indeed confirmed\textsuperscript{27}. However, the $d^6$ Tanabe-Sugano diagram exhibits a crossing between excited triplet and quintet states (see Figure 2). Therefore, \textit{excited state spinmerism} might be anticipated, with total spin states resulting from combinations of local $S_{Fe} = 1$ and $S_{Fe} = 2$. For all these reasons, \textit{ab initio} calculations were carried out to inspect the spectroscopy of compound 1 (shown in Figure 1). The eigen-states were constructed using localized molecular orbitals (LMOs) to allow for projections onto the local spin states of the metal and ligands, $S_{Fe}$ and $S_L$, respectively. The numerical results presented in this work highlight the presence of a strong quantum en-
tanglement between the local spin states, *i.e.* a spinmerism effect, of the metal ion and the radical ligand environment. This evidence reshuffles the standard views in molecular magnetism and simultaneously opens up new perspectives for technological development at the interface of physics and chemistry. The variability of local spin states could provide a pathway to encode quantum information on synthetic molecular systems, paving the way for the generation of molecular spin-qubits.

Figure 2: Low part of the Tanabe-Sugano diagram of an iron(II) d⁶ ion in an octahedral field. The critical ligand field value marking spin-crossover is indicated by a vertical dotted line. The crossing between the excited $S_{Fe} = 1$ and $S_{Fe} = 2$ states is highlighted.

**Computational details**

The presence of multiple open-shells on both metal ion and ligands strongly invites the use of a wavefunction-based method, such as the complete active space self-consistent field (CASSCF) method. The complete active space should include six electrons from the iron center and two from the oxoverdazyl ligands in seven molecular orbitals (CAS[8,7]). However, the active space was reduced to CAS[6,6] by inspecting the occupation numbers of the active molecular orbitals (MOs). The CAS[6,6]SCF sextuplet MOs were then transformed into localized molecular orbitals (LMOs) which are shown in Figure 3. Such transformation allows for a reading of the wavefunctions following a Lewis-like description. In the low-energy spectrum of 1, we checked that the mostly metal d-type LMOs remained doubly occupied (low-spin iron(II)) and the active space was even reduced to CAS[2,2]. All CASSCF calculations were performed on the available Xray structure without any geometry optimization and used the MolCAS 8.0 package. The iron and first coordination sphere atoms were described with 4s3p2d and 3s2p1d basis sets, respectively. Smaller basis sets 3s2p were used for all other atoms whilst hydrogen atoms were depicted with a 1s basis set. The dynamical correlation and polarization effects were included following the Difference Dedicated Configuration Interaction (DDCI) method as implemented in the CASDI code. Given a set of MOs, the structures of the spin states can be directly compared from the CI amplitudes. Depending on the classes of excitations involved in the CI expansion, different levels (CAS + S, CAS + DDC2 and CAS + DDCI) can be reached beyond the CAS pictures (CAS[2,2] or CAS[6,6]). This variational method that follows a step-by-step construction of the wavefunction has produced a wealth of interpretations and rationalizations with a systematic relaxation of the wavefunction (so-called ”fully decontracted method”). The resulting CI eigenfunctions were projected onto the local spin states of the oxoverdazyl ligands pair ($S_L = 0$ or 1) and the iron ion ($S_{Fe} = 0$, 1 or 2). This procedure allows for a decomposition into the different entangled metal-ligand contributions. To implement these projections and conduct our local spin analysis, the open access package QuantNBODY was used. This numerical python toolbox has been recently developed by one of us (SY) to facilitate the manipulation of quantum many-body operators and wavefunctions. Based on this tool, matrix representations (in the many-electron basis) of the local metal and ligands spin operators $\hat{S}_{Fe}^2$ and $\hat{S}_L^2$ were built and diagonalized to access the local spin subspaces. This approach makes it possible to design spin projectors (in the many-electron basis) to target specific local spins con-
tributions for the metal and the ligands in the multi-reference wavefunction.

Results and Discussion

First, CASSCF calculations were conducted on 1. Inspections based on a CAS[8,7] highlight the presence of a MO mostly localized on a 3d iron atomic orbital with occupation number 1.99. Thus, the active space was reduced down to [6,6]. The CAS[6,6]SCF MOs were localized either on the metal center or on each individual dipyvd ligand (see Figure 3). Then, the electronic structure of the environment was inspected following the procedure recently developed on a [Co(dipyvd)$_2$]$_2^{2+}$ compound (cobalt(II)).$^{20,26}$ Based on a fictitious [Zn(dipyvd)$_2$]$_2^{2+}$ (closed-shell divalent metal ion) analogue of the cobalt(II) compound, it was shown that the triplet-singlet energy difference is of the order of 2 cm$^{-1}$.\textsuperscript{20} Considering the geometry changes moving to compound 1, a similar inspection was conducted by substituting iron(II) by zinc(II). A 1.9 cm$^{-1}$ triplet-singlet energy difference was computed at the CAS[2,2] + DDC1 level. The absence of any quantitative exchange coupling between the radical ligands suggests that any projection of the total spin states of 1 may simultaneously involve the local $S_L = 0$ and $S_L = 1$ states. Evidently, the nature of the metal center is likely to modify the exchange coupling constant value, a particular issue we wanted to inspect.

Due to the system size and the number of open-shells, a CAS[6,6] + DDC1 level of calculation is out of reach. Thus, all our conclusions are based on CAS[6,6] + DDC2 excitation energies and corresponding wavefunctions analysis, as summarized in Table 1. First, the ground state is triplet ($2S_{total} + 1 = 3$), dominated by the local spin states $S_{Fe} = 0$ and $S_L = 1$, respectively, followed by a singlet lying 120 cm$^{-1}$ above. This picture is consistent with a $d^6$ metal ion in a high-field environment. Let us mention that the wavefunction includes 13% of charge transfers contributions ($S_{Fe} = 1/2$ and $S_L = 1/2$). Since the CAS[6,6]SCF occupa-

![Figure 3: CAS[6,6] LMOs of 1 generated from a CAS[6,6]SCF calculation for the sextuplet spin state.](image)

| Energy (cm$^{-1}$) | $2S_{total} + 1$ | $S_{Fe}$ | $S_L$ |
|-------------------|-----------------|---------|-------|
| 5326              | 7               | 100% Q  | 100% T|
| 3323              | 5               | 62% T  | 11% S | 72% T |
| 2906              | 5               | 17% T  | 39% S | 50% T |
| 120               | 1               | 84% S  | 84% S |
| 0 (reference)     | 3               | 87% S  | 87% T |

Table 1: Energy spectrum of 1. Quintets and heptuplet energies are calculated at the CAS[6,6] + DDC2 level. The ground state energy is used as a reference energy. Spin multiplicities $2S_{total} + 1$, local spin proportions ($S_{Fe}$ and $S_L$) are given. $S$, $T$ and $Q$ correspond to singlet, triplet and quintet, respectively.
tion numbers of the mostly d-type LMOs are larger than 1.98, the singlet-triplet energy difference was further confirmed from CAS[2,2] + DDCI calculations (CAS[2,2]SCF triplet MOs) and turned out to be 120 cm$^{-1}$. This value is in reasonable agreement with the reported one which may vary depending on the extraction from broken-symmetry calculations.\textsuperscript{27} Thus, the low-energy part of the spectrum of 1 can be viewed as two organic radicals coupled through a closed-shell iron(II) (see Figure 4). Evidently, a Heisenberg Hamiltonian $\hat{H} = -2J\hat{s}_1\hat{s}_2$ can be derived from the singlet-triplet energy difference. The strong ferromagnetic exchange coupling constant $J = 60$ cm$^{-1}$ accounts for the low-temperature magnetic properties experimentally observed.

![Figure 4](image)

Figure 4: Energy spectrum of 1 reflecting a Heisenberg behaviour in the low-energy part, whereas excited state spinmerism is observed higher in energy. The excited quintet states $Q_1$ and $Q_2$ exhibit a strong mixing between $S_{Fe} = 1$ and $S_{Fe} = 2$ local spin states.

Based on this preliminary observation suggesting a $S_L = 1$ crystal field, let us then concentrate on the third ($2S_{total} + 1 = 5$) and fourth ($2S_{total} + 1 = 7$) excited states given in Table 1. The iron(II) spin state is successively dominated by a $S_{Fe} = 1$ (62%) and $S_{Fe} = 2$ (100%) character. Such picture obtained from the spin projections of the wavefunctions is consistent with a high-field $d^6$ Tanabe-Sugano diagram.\textsuperscript{34} However, the quintet excited state $Q_2$ in Figure 4 exhibits a non-negligible contribution from the local $S_{Fe} = 2$ spin state (21%). Such superposition of triplet and quintet metal spin states in the absence of spin-orbit coupling is a manifestation of the recently reported spin-merism effect.\textsuperscript{20} Our analysis supports the appearance of a similar phenomenon in 1, named as excited state spinmerism. This manifestation results from the open-shell character of the environment and the energy crossing between the $S_{Fe} = 1$ and $S_{Fe} = 2$ excited states in the high-field regime of the iron(II) $d^6$ Tanabe-Sugano diagram. The traditional resonance in the Tanabe-Sugano diagram is lifted from the intimate open-shell nature of the crystal field. As expected, the spectroscopy exhibits a second close-in-energy quintet state resulting from this mixing (see $Q_1$ in Figure 4). The latter is found 2906 cm$^{-1}$ above the ground state, with a dominant $S_{Fe} = 2$ character (72%), and a significant mixing between the environment $S_L = 0$ (39%) and $S_L = 1$ (50%) spin state. The entanglement between the spin states of the metal ion and its coordination sphere is manifested in the excited state of the high-field regime of the Tanabe Sugano diagram. In agreement with a recent inspection based on a model Hamiltonian,\textsuperscript{21} the emergence of the two quintet states $Q_1$ and $Q_2$ in Figure 4 from avoided crossing stresses the importance of not only the magnitude of the crystal field (Coulomb contributions), but also the open-shell character of such field (decisive exchange contributions).

**Conclusion**

The spin states structures of a coordination compound [Fe(dipvdz)$_2$]$^{2+}$ built on a spin-crossover ion (iron(II)) and two radical ligands (oxoverdazyl) were analyzed from DDCI wavefunctions calculations. The procedure is based on the generation of localized molecular orbitals and spin projections onto the local spin states. A ground state triplet $S_{total} = 1$ characterized by a $S_{Fe} = 0$ local spin state is found, a reflection of a high-field regime. A strong ferromagnetic interaction $J = 60$ cm$^{-1}$ is calculated featuring the coupling of organic radical spin holders through a low-spin metal ion. Even though the low-energy part of the spectrum can
be rationalized by a Heisenberg spin Hamiltonian, the magnetic picture delivered by a d6 Tanabe-Sugano diagram is deeply reshuffled in the next nearest excited states. The flexibility afforded by the open-shell character of the environment gives rise to marked superpositions of local spin states $S_{Fe} = 1$ and $S_{Fe} = 2$ in the $S_{total} = 2$ excited states. The traditional quasi-degeneracy in the high-field regime is lifted by 417 cm$^{-1}$ with significant contributions from both $S_L = 1$ and $S_L = 0$ on the ligand pair. This observation, which we named excited state spinmerism, extends a phenomenon that was reported in a cobalt(II) analogue. The prerequisite for the manifestation of such entanglement is fulfilled from the presence of an iron(II) ion and radical organic ligands. This particular class of coordination chemistry compounds combining versatile local spin states not only enlarges the traditional pictures in molecular magnetism but might become original targets for spin-qubit generation.

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AUTHOR DECLARATIONS

CONFLICTS OF INTEREST

The authors have no conflicts to disclose.

DATA AVAILABILITY

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

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