

RESEARCH ARTICLE

An Unprecedented Square Planar Fe(III) Complex Exhibiting Spin Crossover Between the Spin-Admixed States

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ABSTRACT

The presence of strong spin-orbit coupling, which is comparable to the crystal field in certain ferric-porphyrin/phthalocyanine derivatives, results in a spin-admixed state between the high-spin (HS; $S = 5/2$) and intermediate-spin (IS; $S = 3/2$) states. However, there are no literature precedents for spin admixing between the IS ($S = 3/2$) and low-spin (LS; $S = 1/2$) states, which are purely governed by axial ligation. It is also true that systems showing spin-admixed behavior do not exhibit thermal equilibrium between the spin states, that is, spin crossover (SCO). In this article, we report a unique and rare square planar ferric ion complex, $[\text{Na}(\text{DME})_3][\text{Fe}(\text{L}^{2-})_2]$ (**1**), which exhibits two different physical phenomena: SCO is observed between the spin-admixed states, a phenomenon unprecedented in this context. Field- and temperature-dependent Mössbauer spectra, variable temperature X-band EPR spectra, multifrequency EPR (MF-EPR), and temperature-dependent magnetic susceptibility measurements reveal that the spin-admixed state has contributions from IS ($S = 3/2$) and LS ($S = 1/2$), unlike other reports in the literature. The detailed electronic structure of **1**, along with the rationale for quantum spin admixing and SCO, is well supported by theoretical calculations.

1 | Introduction

Determining the correct electronic structure of a complex or the active site of an enzyme is of utmost importance for understanding and fine-tuning properties. For example, oxygen binding with hemoglobin [1], various oxidases [2], halogenases [3], electron transfer proteins [4, 5], and so forth. Even in certain natural enzymes and biomimetic model complexes, two-state reactivity is invoked for their superior catalytic performance, thanks to the detailed theoretical calculations that shed light on the electronic structure, besides the experimental supports [6].

However, in certain bacterial electron transfer proteins called ferricytochrome c' [7], two distinct proposals were made to explain the nature of the ground state associated with these hemoproteins: (i) the ground state possesses an average magnetic moment of a thermal mixture (temperature-dependent spin crossover) of high-spin (HS; $S = 5/2$) and an intermediate-spin state (IS; $S = 3/2$); (ii) a unique and independent spin state originates due to the *quantum mechanical spin—admixing (QMA)* of HS and IS of Fe(III) ions [8]. However, this longstanding puzzle was unfolded by the pioneering work of Maltempo, Moss, and coworkers, where the latter proposal was found

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to be true. The presence of QMA in these systems can be uniquely identified by the significantly deviated effective g -tensors (in particular, the $g_{\perp}^{eff}$) of the Fe(III) ion ($6 > g_{\perp}^{eff} > 4$) and the reduced magnetic moment from the pure HS state [7]. Besides the theoretical basis for QMA, the authors have also provided the selection rules and conditions to realize the quantum mechanical spin-admixed state, which is described elsewhere [7]. Following this ground-breaking discovery, not only were the various ferricytochrome c' extracted from different bacterial sources investigated, but also various bio-mimetic models [9–12]. Therefore, not surprisingly, the literature is flooded with ferric-porphyrin/porphycenes derivatives where the presence of sterically crowded nonplanar saddled and ruffled conformations results in a QMA phenomenon [13, 14]. It has also been noticed that QMA is observed only in a handful of five-coordinate Fe(III) complexes, which are predominantly in tetragonal geometry and very few in trigonal bipyramidal geometry [12–16]. Without any exception, in all these complexes (both porphyrin and nonporphyrin), the HS ($S = 5/2$) state is admixed with the IS state ($S = 3/2$) [7, 17, 18], while the other possible admixing combination ($S = 3/2$ with $S = 1/2$) is not witnessed so far.

A protein or a discrete molecule that shows QMA would correspond to a single magnetic species with magnetic properties distinct from either of the pure spin species, that is, the spin-admixed state tends to obey the Curie law, which is the case for all the reported systems [7]. Therefore, such a system is not expected to show spin transition or spin crossover (SCO), which will be distinctly visible in the temperature-dependent magnetic susceptibility measurements. SCO is usually observed in 3d metal ions in its octahedral geometry with d^4 – d^7 electronic configurations. Among the four electronic configurations, SCO is predominantly observed in d^6 , Fe(II) ion [19, 20]. In contrast, observation of the SCO phenomenon in d^5 , Fe(III) ion, even in an octahedral geometry, is relatively scarcer than Fe(II) [21–24]. This is even slimmer when Fe(III) has a five-coordinate (trigonal bipyramidal or square pyramidal) geometry [25, 26]. To the best of our knowledge, the SCO phenomenon is not witnessed in four coordinate Fe(III) square planar geometry because stabilizing a square planar geometry around a ferric ion is a challenging task. This is directly evident from the number of such complexes that were structurally characterized (less than five, based on CSD search as of 13 Mar 2026).

The spin-admixed phenomenon and SCO properties were observed independently in hundreds of complexes; however, the existence of these two distinct phenomena simultaneously in one system is not reported [8, 19, 21, 27–29]. Also, due to the rarity of square planar ferric ions, their corresponding electronic and magnetic properties are extremely scarce in the literature [17, 30–34]. Therefore, we sought to unveil a synthetic method to stabilize this exotic square planar geometry around the Fe(III) ion and to investigate various physical phenomena. In this article, we report an uncommon square planar ferric ion complex employing a redox-active phenanthro-imino-quinone ligand (L1) (Scheme S1 and Figures S1 and S2) that is structurally characterized with the molecular formula $[\text{Na}(\text{DME})_3][\text{Fe}(\text{L}^{2-})_2]$ (**1**). Complex **1** was found to show both QMA and SCO (between the QMA states) simultaneously. The presence of these two distinct phenomena was unambiguously confirmed by the combined analytical

techniques, such as field and temperature-dependent Mössbauer spectroscopy, multifrequency EPR (MF-EPR) spectroscopy, and temperature-dependent magnetic susceptibility measurements in a polycrystalline sample of **1**. Further, experimental observations are rationalized by theoretical calculations, besides the electronic structure of **1**.

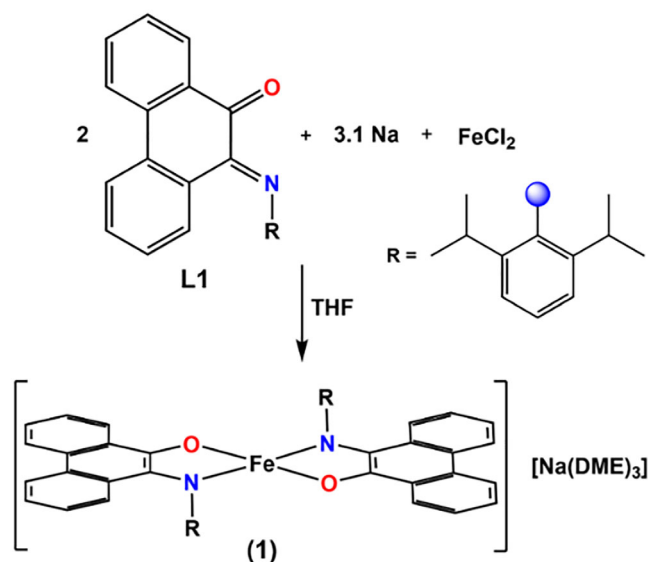
2 | Results and Discussion

2.1 | Structural Description of **1**

The neutral ligand L1 was reduced with sodium metal in THF. The resultant reduced L1 was treated with anhydrous FeCl_2 , which led us to isolate dark green color single crystals in a diethyl ether/DME mixture (Scheme 1). The single-crystal X-ray data collection and structure solution reveal the molecular formula of $[\text{Na}(\text{DME})_3][\text{Fe}(\text{L}^{2-})_2]$ (**1**). Complex **1** crystallized in the orthorhombic, $P2_12_12_1$ space group (Table S1).

The crystal structure determination reveals that **1** is a mononuclear iron ion in its distorted square planar geometry (Figure 1), and the entire molecule is present in the unit cell as an asymmetric unit (Figure S3). All four coordination sites of the iron are completed by two bidentate reduced L1 ligands. The average Fe–O and Fe–N bond lengths were observed to be 1.847(3) Å and 1.876(2) Å, respectively (see also Table S2 for selected bond lengths and bond angles of **1**, Table S3 for the CShM deviation). Based on the oxidation state and the noninnocent nature of L1 (see Scheme S3), we have assigned the oxidation state of the metal ion in **1** as +3, which is consistent with the Mössbauer data. The detailed structural description of **1** is given in the Supporting Information.

Attempts to isolate **1** upon reducing the L1 by two equivalents of sodium metal straight away and in the presence of Fe(III) precursor have failed, that is, we only obtained a five-coordinate Fe(III) complex [35], rather than a four-coordinate, square planar complex **1** (Scheme S2 and Figure S3A). Usually, the Fe^{3+} ion prefers to crystallize in the most thermodynamically stable



SCHEME 1 | The general synthetic procedure followed to isolate **1**.

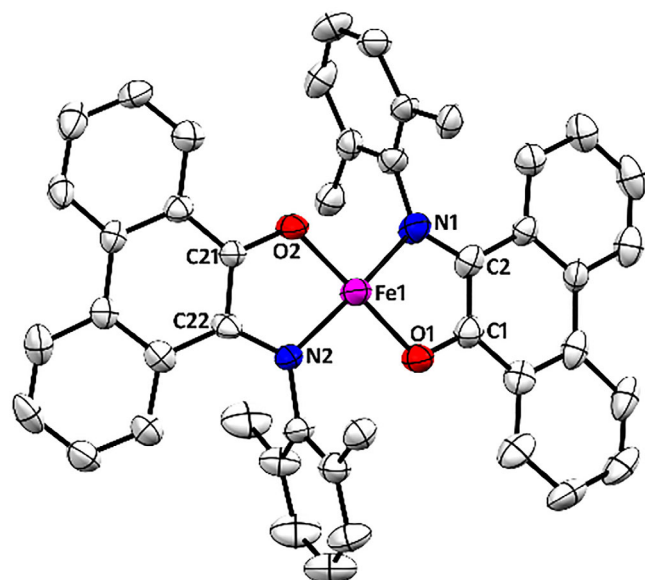


FIGURE 1 | Thermal ellipsoid picture of the crystal structure of the anionic core of **1**. The hydrogen atoms and side-chain carbon atoms are removed for clarity. Color code: Magenta = Fe; Red = O, Blue = N, and Gray = C.

geometry, such as tetrahedral or octahedral. Isolation of a square planar ferric ion is extremely challenging, which is reflected directly from the number of such complexes structurally characterized until now [17, 30–34]. In this respect, **1** becomes a unique complex that is facilitated by the redox noninnocent ligand employed over here. Further, the bulk phase purity of **1** has been confirmed by elemental analysis (see the experimental section in Supporting Information) and powder X-ray diffraction studies (Figure S4) before proceeding to other powder/bulk phase measurements.

2.2 | Mössbauer Spectroscopy

To determine the spin state and oxidation state of the metal ion in **1** variable temperature and field, Mössbauer measurements were performed on a polycrystalline sample of **1**. Figure 2A reproduces the zero-field Mössbauer spectrum recorded at 6 K on a powder sample of **1**. A single doublet is observed that is almost unchanged upon raising the temperature to 80 K (Figures 2F and S5). The obtained isomer shift value (δ) value of 0.23 mm s^{−1} and quadrupole splitting (ΔE_Q) of 2.16 mm s^{−1} (values at 6 K) suggests a +3 oxidation state of the iron in **1**, which is consistent with the δ value of the various ferric ions reported in the literature [8, 17, 34, 36].

To get insights into the electronic structure of **1**, spectra were recorded at ca 6 and 80 K using an external magnetic field with increasing magnitude (see Figure 2B–E,G–J). Attempts to reproduce the series of spectra were performed assuming either an effective spin $S_{\text{eff}} = 1/2$ or an $S = 3/2$ system. Satisfying simulations are obtained in both cases. However, the best result was obtained for the effective spin of $S_{\text{eff}} = 1/2$, assuming the effective g -values derived from the multifrequency EPR studies (*vide infra*). The corresponding simulations are displayed in

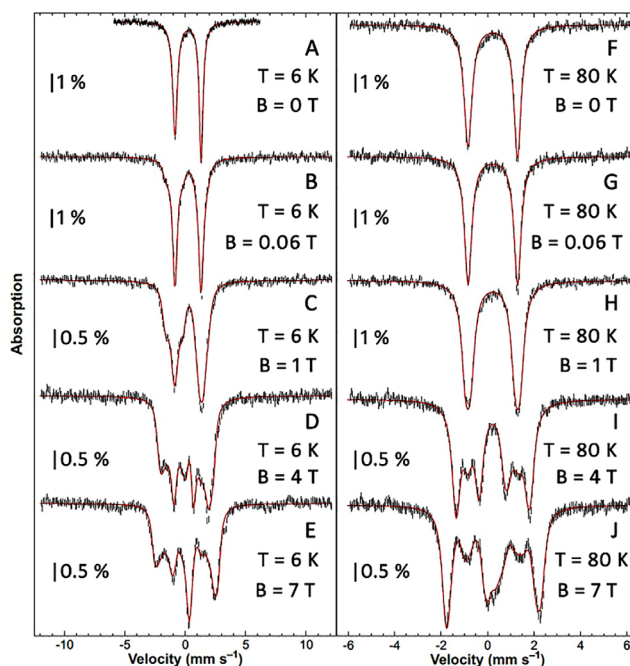


FIGURE 2 | Experimental Mössbauer spectra recorded on a powder sample of **1** at ca 6 (A–E) and 80 K (F–J) at zero-field (A and F) or with a 0.06 T (B and G), 1 T (C and H), 4 T (D and I) and 7 T (E and J) magnetic field applied parallel to the γ -rays (vertical bars). Simulations assuming an effective spin $S = 1/2$ state and using the parameters listed in Table 1 and Table S4 are overlaid as solid red lines.

TABLE 1 | Common electronic and nuclear parameters were used to reproduce the 6 and 80 K Mössbauer spectra assuming an effective spin $S_{\text{eff}} = 1/2$ state. The computed Mössbauer parameters of various optimized spin surfaces ($S = 1/2, 3/2$, and $5/2$) of **1** and on the X-ray structure of **1** are shown for comparison purposes.

δ (mm s ^{−1})	0.23		
ΔE_Q (mm s ^{−1}) ^a η	2.16/2.13	0.67	
Euler angles (deg) (α, β, γ) ^b	155	90	0
g_k $k = x, y, z$ ^c	2.03	2.31	3.57
$A_k/g_N\mu_N$ (T) ($k = x, y, z$) ^d	−0.6	−8.8	14.0
DFT optimized geometry (X-ray)			
Spin	1/2	3/2	5/2
δ (mm s ^{−1})	0.23	0.26 (0.20)	0.38
$ \Delta E_Q $ (mm s ^{−1})	1.22	2.21 (2.41)	2.44

^aThe quadrupole splitting is slightly lower at 80 K compared to that at 6 K.

^bEuler angles are those for the g -matrix versus the EFG tensor.

^cFixed values (derived from X-band EPR).

^dThe hyperfine tensor is colinear with the g -matrix.

Figure 2 as solid red lines, and parameters are listed in Table 1 and Table S4. Results obtained assuming a $S = 3/2$ state are given in the Supporting Information (see Figures S6 and S7 and Tables S5 and S6). Spectra recorded at 6 K under low-field, namely 0.06 T and 1 T, could be reproduced assuming the same set of electronic and nuclear parameters but with both slow and fast relaxing components (see Figure S8 for the deconvolution).

However, the 1 T spectrum is better reproduced within the effective spin 1/2 hypothesis. The contribution of the fast-relaxing component is more important as the external field diminishes. Mixing two different relaxing systems to reproduce the Mössbauer spectra has been previously observed for HS ferrous systems with large spin-orbit coupling [37]. It was evidenced that the contribution of the slow relaxing component increased with the magnitude of the external magnetic field, as observed here. Whatever the spin state, the obtained hyperfine tensor is anisotropic, with one negative and one positive component and a third one close to zero. Two negative and one positive components have been previously observed for IS ferric compounds [38–40], whereas an inverted distribution, that is, one negative and two positive values, has been mostly determined for low-spin ferric systems [41]. However, published values are larger in absolute value than those obtained here. Indeed, it is worth noticing that the isotropic part of the hyperfine tensor of **1** is very weak ($A_{\text{iso}}/g_N\mu_N = 1.5$ T for $S_{\text{eff}} = 1/2$ and 1.1 T for $S = 3/2$), much weaker than those observed in the previously investigated $S = 3/2$ and $S = 1/2$ systems. This may originate from a strong spin-orbit coupling in compound **1**.

2.3 | Electron Paramagnetic Resonance (EPR) of **1**

To gain a comprehensive understanding of the electronic structure of polycrystalline sample of **1**, we conducted an extensive series of EPR experiments, spanning a wide range of frequencies: starting from the X-band (9.4 GHz) and extending to high-frequency EPR measurements up to 413 GHz; all performed at a low-temperature of 5 K (Figure 3A). The data obtained from these multifrequency EPR studies revealed well-resolved rhombic features (Figure 3A inset), providing critical insights into the anisotropic characteristics of the system. Additionally, the temperature-dependent X-band EPR experiments conducted in the 5–280 K temperature range (Figure S9) suggest Curie-like behavior, where the signal intensity decreases as the temperature increases, that is, the signals originated from the ground state, and no EPR signal is observed at higher temperatures.

EPR spectral simulations were performed considering an effective spin of $S = 1/2$ using the following spin Hamiltonian.

$$\mathcal{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{S}. \quad (1)$$

Here, $\hat{S}$ is the vector operator describing the effective spin $S = 1/2$ of the Fe(III) ion, μ_B is the electron Bohr magneton, $\vec{B}$ is the applied external magnetic field vector, $\vec{g}$ is the effective g-tensor with principal values g_x , g_y , and g_z , describing the electron Zeeman interaction. Since hyperfine interactions are not resolved, we do not consider them when simulating the spectra.

The g-tensor components determined from the plot of resonance positions versus frequency (see Figure 3B) and spectral simulations (see Figure 3A) are $g_x = 2.03(1)$, $g_y = 2.31(1)$, and $g_z = 3.57(2)$. These values indicate a rhombic symmetry and remain consistent across all frequency regimes examined. On the other hand, the g-values of the pure low-spin Fe(III) complexes were observed to be in the range 2.6–1.6, which was reported elsewhere [42–44]. It is

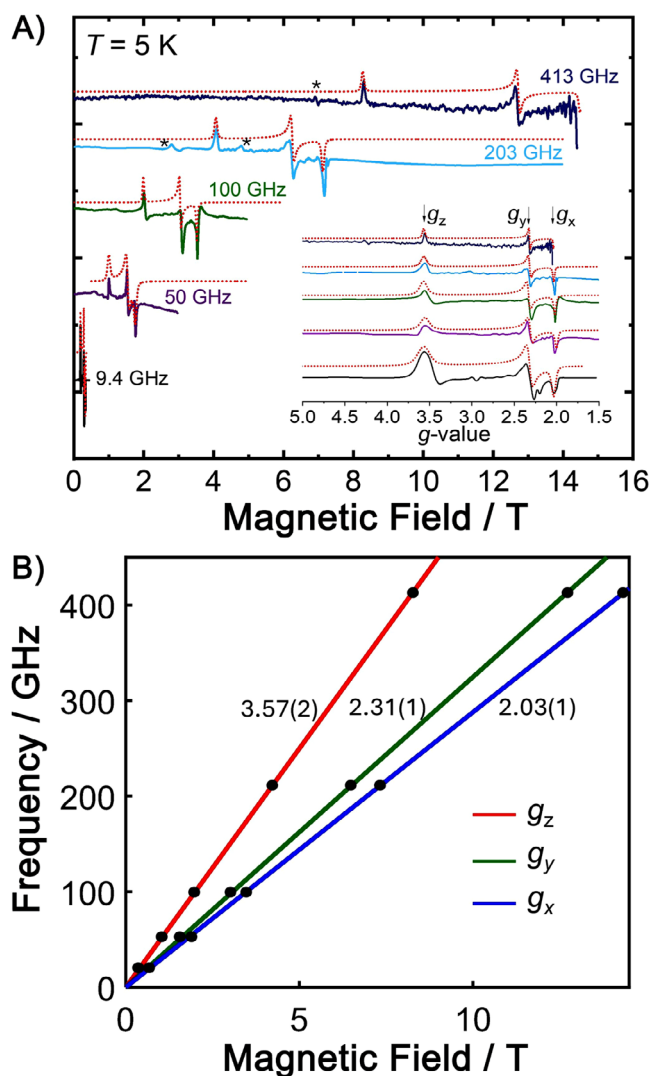


FIGURE 3 | (A) Multifrequency EPR experiments conducted on a polycrystalline powder sample of **1**, spanning frequencies from 9.4 to 413 GHz at 5 K. Inset: spectra are plotted against g-values (solid lines correspond to the experimental spectra, while dotted red lines are simulations; * corresponds to oxygen peaks). (B) Plot of the resonance positions in (A) versus frequency (solid black circles). The solid lines are linear fits from which the g-tensor components can be deduced: $g_x = 2.03(1)$, $g_y = 2.31(1)$, $g_z = 3.57(2)$ (see legend); the error bars in (B) are within the data points and are therefore not shown.

also witnessed in the literature that for a system that is stabilized with a pure IS state, the effective g-value $g_{\perp}$ must be close to 4.0, and the reduction in this value discloses the presence of a spin-admixed state [7]. The average $g_{\perp}^{\text{eff}} = 2.17$ value obtained for **1** unambiguously reveals that the IS state $S = 3/2$ is admixed with $S = 1/2$.

The QMA of the IS state with the HS state $S = 5/2$ always results in the effective $g_{\perp}$ falling in the range $6.0 > g_{\perp}^{\text{eff}} > 4.0$, which is well exemplified and rationalized in the literature [8, 18]. Qualitatively, the percentage of $S = 1/2$ mixed with the $S = 3/2$ to the QMA state of **1** was calculated using $g_{\perp}^{\text{eff}} = 4(a_{3/2})^2 + 2(b_{1/2})^2$ and $(a_{3/2})^2 + (b_{1/2})^2 = 1$ (assuming pseudo C_{4v} geometry). The $(a_{3/2})^2 = (g_{\perp}^{\text{eff}} - 2)/2$ and $(b_{1/2})^2 = (1 - (a_{3/2})^2)$ indicate the contribution of

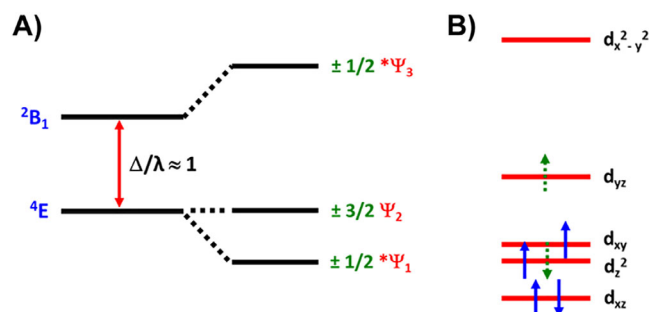


FIGURE 4 | (A) Schematic representation of spin admixture between the IS state and the LS state of **1**. Spin-admixed doublets are represented with an asterisk (*) mark. (B) The representative d-electron configuration of the quantum admixed state in **1**.

the IS (8.5%) and low spin (91.5%), respectively, to the quantum mechanical spin-admixed state observed. A slight variation in the reported percentage contribution might be possible as the symmetry around the ferric ion is not strictly C_{4v} . [9, 13–16, 45] The temperature-independent ΔE_Q and δ value observed for **1** in an applied field of 0.06 T supports the spin-admixed phenomenon. Moreover, the QMA observed in **1** is consistent with the selection rules proposed by Maltempo coworkers, that is, $\Delta S = \pm 1$ and $\Delta S_z = 0, \pm 1$ [7, 46].

QMA in complex **1** is schematically illustrated in Figure 4. For instance, the ground Kramers doublet Ψ_1 (QMA state 1) comprises approximately 91.5% LS ($|^2B_1\pm\frac{1}{2}\rangle$) and 8.5% IS ($|^4E\pm\frac{1}{2}\rangle$). In contrast, the spin composition of Ψ_3 (QMA state 2) is complementary to that of Ψ_1 , consisting of 91.5% $|^4E\pm\frac{1}{2}\rangle$ and 8.5% $|^2B_1\pm\frac{1}{2}\rangle$. Meanwhile, Ψ_2 corresponds to a pure spin $|^4E\pm\frac{3}{2}\rangle$ state.

Contrary to the scenario observed in **1**, the literature is dominated by the quantum mechanical spin-admixing of HS and IS of various ferric-porphyrin or porphycene derivatives in its tetragonal five-coordinate geometry and very few other geometries, for example, an organometallic ferric ion in square planar geometry [13, 17, 46, 47]. In all these cases, the extent of mixing of the IS with HS is dictated by the Fe-axial ligand bond length, which in turn directly correlates to the energy of the $d_{x^2-y^2}$ and $d\pi$ (d_{xz} and d_{yz}) orbitals, that is, the weaker the Fe-axial bond distance (that destabilizes the $d_{x^2-y^2}$ and $d\pi$ orbitals), the larger the mixing of $S = 3/2$ state with HS $S = 5/2$. Besides this, the solvent polarity also has a nonzero influence on the spin-admixing, which is elegantly shown by Nakamura and co-workers [9, 18].

2.4 | Direct Current Magnetic Susceptibility

The temperature-dependent magnetic susceptibility measurements were performed on the polycrystalline sample of **1** in the presence of a 0.1 T external magnetic field in the range of 1.8 to 280 K (Figure 5). The $\chi_M T$ value at 280 K is $2.84 \text{ cm}^3 \text{ K mol}^{-1}$ which decreases abruptly below this temperature. At 200 K, the $\chi_M T$ value of $1.29 \text{ cm}^3 \text{ K mol}^{-1}$ was observed, which gradually decreases upon further decreasing the temperature and reaches a final value of $0.82 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. The observed room temperature $\chi_M T$ value for **1** is significantly lower than the theoretically expected $\chi_M T$ value of a pure HS ($4.375 \text{ cm}^3 \text{ K}$

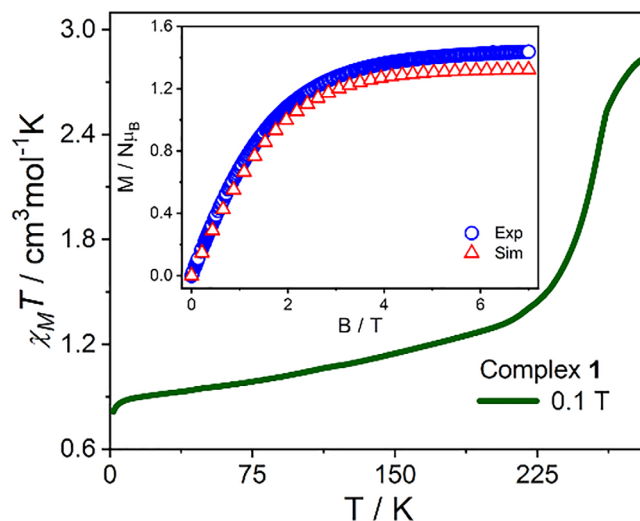


FIGURE 5 | Direct current magnetic susceptibility measurement was performed on a polycrystalline sample of **1**, in the presence of an external magnetic field of 0.1 T. Inset: Magnetization data collected at 2 K in the range 0–7 T. The blue symbol indicates the experimental data, and the red symbol indicates the simulation done using the parameters extracted from the EPR data.

mol^{-1} , assuming $g = 2$) and higher than a pure low-spin Fe^{3+} ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$, assuming $g = 2$) ion. Therefore, the room temperature $\chi_M T$ value suggests that **1** possesses an IS character at room temperature predominantly (Figure 5).

The temperature-dependent $\chi_M T$ profile observed for **1** is indicative of thermal spin equilibrium between the QMA states of **1**, that is, a SCO between the QMA states Ψ_1 and Ψ_3 (see Figure 4). Although the percentage composition of Ψ_1 was determined from low-temperature MF-EPR measurements, determining the corresponding composition for Ψ_3 was hindered by the inherently fast relaxation of the spin states in complex **1**, as no EPR signals were detectable above 60 K.

The rationale for this observation is detailed in the theoretical section (vide infra). Also, we would like to point out that at 1.8 K the observed $\chi_M T$ value ($0.82 \text{ cm}^3 \text{ K mol}^{-1}$) is significantly higher than the pure $S = 1/2$ state (with an average g value of 2). Consistent with the $\chi_M T(T)$ profile, the isothermal magnetization data were collected at 2.0 K between 0 and 7 T, showing a larger magnetic moment value ($1.43 N\mu_B$ at 7.0 T) than expected for a pure $S = 1/2$ state. These measurements also indicate the QMA exists between $S = 3/2$ and $1/2$. This observation is in parallel with the Mössbauer and EPR data collected on **1**. Moreover, a better agreement between the experimental $M(H)$ data and the simulation was obtained using the effective g -tensors extracted from the EPR measurements (see inset of Figure 5).

Variable temperature X-ray structural data were collected to infer the structural changes induced by the SCO phenomenon in **1** (Figure S10). In contrast to the other commonly known six coordinate Fe^{n+} ($n = 2$ or 3) SCO complexes [21, 48–53], we observe marginal changes in Fe–O and Fe–N bond lengths in **1** (Table S7), which are well within the experimental error. However, we noticed a slight change in the unit cell parameter along the

c-axis (Figure S11). This is attributed to the disorder observed in the cationic part $[\text{Na}(\text{DME})_3]^+$ in **1** at higher temperatures, which stacks between the anions along the c-axis. The rationale for no/negligible change in the bond lengths is provided in the theoretical section (vide infra). An attempt to collect the Mössbauer data at 295 K to support the SCO phenomena in **1** was unsuccessful. This may be due to a severe decrease in the Lamb-Mössbauer factor as the temperature is increased from 80 to 295 K. However, the SCO phenomenon is evidently visible in the magnetic data of **1**.

2.5 | Theoretical Studies of **1**

To get further insight into the observed spin-admixed and SCO phenomena in **1**, we have employed DFT and ab initio CASSCF/NEVPT2 calculations on **1**. To begin our study, we have performed geometry optimization (see computational details and Figures S12–S14, also Tables S8–S12) of the sextet, quartet, and doublet spin states of **1** using DFT methods (see computational details in Supporting Information). The DFT computed energies on the optimized geometry reveal that the quartet is the most stable spin state of **1**. The doublet and sextet spin state energies are estimated to be ca. 0.06 eV (457.1 cm^{-1} /5.4 kJ/mol) and 0.27 eV (2157.5 cm^{-1} /25.6 kJ/mol), respectively, compared to the quartet ground spin state employing DFT calculations. The small energy gap of 0.06 eV (5.4 kJ/mol) between the quartet and doublet spin states suggests the possibility of the spin-admixed ground state of **1**. Also, we computed the spin-orbit coupling constant (ξ) value of 0.05 eV (428 cm^{-1}) for **1**. The small energy gap between the two spin states (Δ), which is comparable to that of the spin-orbit coupling constant, is proposed as a condition for the spin-admixed phenomenon, that is, $\Delta/\xi \leq |1|$ [7]. Therefore, the calculations rationalize the existence of spin-admixed behavior in **1**. Since the energy gap between the quartet and doublet states is well below 0.2 eV (20 kJ/mol), a SCO phenomenon is also anticipated. Such a scenario is witnessed in several complexes that exhibit thermal equilibrium [53, 54].

To understand why quartet and doublet states are nearly degenerate, we plot the DFT computed eigenvalue plot of 3d orbitals of **1** in Figure 6A. A large energy gap of 1.52 eV (12238.1 cm^{-1} /146.4 kJ/mol) between the d_{yz} and $d_{x^2-y^2}$ orbitals suggests that the sextet state will be higher in energy than other spin states. The electronic configurations of the quartet and doublet spin states differ in the electron filling of the d_{yz} orbitals. The unexpected non-degeneracy of the d_{xz} and d_{yz} orbitals was attributed to the stronger electron donation from the oxygen donor atom of L1, preferentially destabilizing the d_{yz} orbital. This effect is further reinforced by several noncovalent C—H $\cdots$ Fe interactions aligned along this direction, as confirmed through NBO and AIM analyses (see Figure S13 and Table S11).

The rationale for not observing a significant change in the bond length of the structures collected at variable temperature single-crystal X-ray diffraction (VT-SCXRD) during the spin transition are: (i) the energy of the $d_{x^2-y^2}$ orbital computed from DFT is 1.52 eV (146.4 kJ/mol), which means this antibonding orbital cannot be populated even at room temperature, (ii) the spin transition that occurs in **1** does not favor the population of the antibonding $d_{x^2-y^2}$ orbital, (iii) although the d_z^2 orbital is paired in the low-

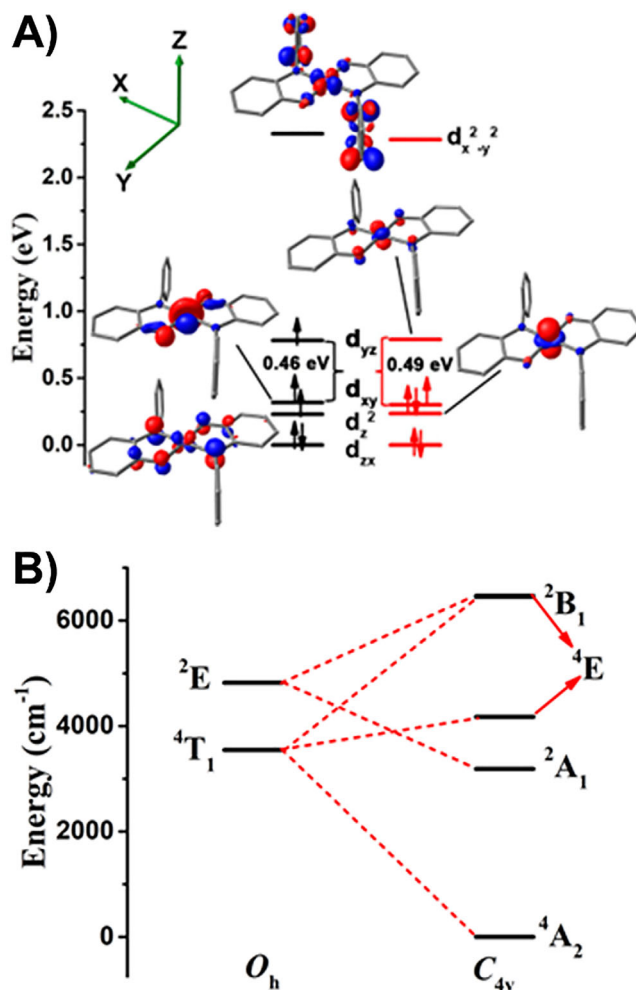


FIGURE 6 | (A) The Eigenvalue plot (DFT) of 3d orbitals for the quartet and doublet spin states of **1**. The quartet and doublet energy levels are represented by black and red horizontal lines, respectively. (B) The CAS(7,6)SCF/NEVPT2 computed energy diagram of the splitting of $4T_1$ and $2E$ terms with lowering of symmetry from O_h to C_{4v} . The red arrows indicate the splitting of the two $4E$ levels (the higher $4E$ level is mixed with the $2B_1$ state).

spin state, it does not significantly influence the structure since the complex does not have ligands along this axis, as **1** exists in square planar geometry. There are no significant changes in the structural parameters in the DFT-optimized geometry of the two spin states, again supporting our experimental findings (Table S8).

Finally, to gain further insight into the spin-admixed state, we have performed ab initio CASSCF/NEVPT2 calculations (see computational details in Supporting Information) on **1**. The calculations were performed with CAS(7,6) active space, including one ligand orbital to capture the metal–ligand covalency. To mention, in pseudo C_{4v} symmetry, the orbital triplet $4T_1$ term splits into $4A_2$ and $4E$ irreducible representations (see Figure 6B). Similarly, a doubly degenerate $2E$ first excited state further splits into $2A_1$ and $2B_1$ in pseudo C_{4v} symmetry. The $2A_1$ is found to be 3187.2 cm^{-1} higher in energy than the $4A_2$ ground state (Figure 6B and Table S13). Moreover, the ground quartet state was found to have a strong multiconfigurational character (Table S14).

Therefore, the ab initio calculations also support the strong spin admixing between the quartet and doublet states of complex **1**.

3 | Conclusion

A unique synthetic strategy led us to isolate a rare square planar ferric complex with the molecular formula $[[\text{Na}(\text{DME})_3][\text{Fe}(\text{L}^{2-})_2]$ (**1**), which is characterized by single-crystal X-ray diffraction. The oxidation state of the metal ion in **1** is unambiguously assigned based on the Mössbauer spectroscopy, which is firmly supported by X-ray structural parameters. The detailed temperature and field-dependent Mössbauer, variable temperature X-band EPR, MF-EPR, and dc magnetic susceptibility data unveil that **1** possesses both a spin-admixed state and thermal equilibrium between these spin-admixed states, which is unveiled for the first time. The strong equatorial bonding combined with the absence of an axial ligand around Fe(III) in **1** results in the sextet state being significantly higher in energy compared to the other two spin states (IS and LS). The ideal condition ($\Delta/\xi \approx 1$) that was observed in **1** promotes QMA between $S = 3/2$ and $S = 1/2$ states. Further, the experimental observations and the detailed electronic structure of **1** were rationalized through detailed theoretical calculations. Spin state-dependent reactivities of the complexes are very well known in the literature, and, therefore, the reactivities and various catalytic activities of **1** as a function of the magnetic field, besides the influence of substituents on L1 on the observed phenomenon in **1**, are targeted in our laboratory.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File 1: chem70994-sup-0001-SuppMat.docx.