Single-Ion Magnets

Single-Ion Magnetic Behaviour in an Iron(III) Porphyrin Complex: A Dichotomy Between High Spin and 5/2–3/2 Spin Admixture

Marta Viciano-Chumillas,^[a] Geneviève Blondin,^{*[b]} Martin Clémancey,^[b] Jurek Krzystek,^{*[c]} Mykhaylo Ozerov,^[c] Donatella Armentano,^[d] Alexander Schnegg,^[e] Thomas Lohmiller,^[f] Joshua Telser,^[g] Francesc Lloret,^[a] and Joan Cano^{*[a]}

Abstract: A mononuclear iron(III) porphyrin compound exhibiting unexpectedly slow magnetic relaxation, which is a characteristic of single-ion magnet behaviour, is reported. This behaviour originates from the close proximity (\approx 550 cm⁻¹) of the intermediate-spin *S*=3/2 excited states to the high-spin *S*=5/2 ground state. More quantitatively, although the ground state is mostly *S*=5/2, a spin-admixture model evidences a sizable contribution (\approx 15%) of *S*=3/2 to the ground state, which as a consequence experiences

Introduction

The design of molecules that show nanomagnet behaviour, collectively called single-molecule magnets (SMMs), has been a challenge in the last decades.^[1] The main rationale for this

[a]	Dr. M. Viciano-Chumillas, Prof. F. Lloret, Dr. J. Cano
	Institut de Ciència Molecular (ICMol)
	Universitat de València, 46980 Paterna (Spain)
	E-mail: joan.cano@uv.es

- [b] Dr. G. Blondin, Dr. M. Clémancey CNRS, CEA, IRIG, CBM, Université Grenoble Alpes CEA-Grenoble, 38000 Grenoble (France) E-mail: genevieve.blondin@cea.fr
- [c] Dr. J. Krzystek, Dr. M. Ozerov National High Magnetic Field Laboratory Florida State University, Tallahassee, FL 32310 (USA) E-mail: krystek@magnet.fsu.edu
- [d] Prof. Dr. D. Armentano
 Dipartimento di Chimica e Tecnologie Chimiche (CTC)
 Università della Calabria, 87030 Rende, Cosenza (Italy)
- [e] Dr. A. Schnegg EPR Research Group, MPI for Chemical Energy Conversion Stiftstrasse 34–36, 45470 Mülheim Ruhr (Germany)
- [f] Dr. T. Lohmiller
 EPR4Energy Joint Lab
 Department Spins in Energy Conversion and
 Quantum Information Science
 Helmholtz-Zentrum Berlin für Materialien und Energie
 Kekuléstrasse 5, 12489 Berlin (Germany)
- [g] Prof. Dr. J. Telser Department of Biological, Physical and Health Sciences Roosevelt University, 430 S. Michigan Avenue, Chicago, IL 60605 (USA)

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large and positive axial anisotropy ($D = +19.2 \text{ cm}^{-1}$). Frequency-domain EPR spectroscopy allowed the $m_s = |\pm 1/2\rangle \rightarrow |\pm 3/2\rangle$ transitions to be directly accessed, and thus the very large zero-field splitting in this $3d^5$ system to be unambiguously measured. Other experimental results including magnetisation, Mössbauer, and field-domain EPR studies are consistent with this model, which is also supported by theoretical calculations.

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trend has been their (still-hypothetical) applications as miniaturised memory units or quantum computing qubits.^[2-7] Initial attention focussed on polynuclear complexes such as the archetypal Mn₁₂ and Fe₈ clusters.^[1] The single-magnet properties of such systems are reasonably well understood and depend on the energy barrier between the ground $|-m_s\rangle$ and $|+m_s\rangle$ states, which in turn requires a negative axial zero-field splitting (ZFS, D < 0). More recently, the effort has increasingly concentrated on coordination complexes with a single paramagnetic centre, commonly known as mononuclear SMMs or single-ion magnets (SIMs).^[8-11] The reason is to achieve better control of the magnetic anisotropy compared with polynuclear complexes. In polynuclear systems the effective ZFS parameter of a cluster is a function of the ZFS of all the constituents, which differ in orientation and often in magnitude as well, making the ZFS hard to predict and control. Even magnetic couplings between the paramagnetic centres can make some contribution to the magnetic anisotropy. On the contrary, in SIMs the magnetic anisotropy results from the ligand (or in the case of f-orbital ions, crystal) field of a single metal ion and its spin-orbit coupling (SOC).

A general prerequisite for an SMM is slow relaxation of the magnetisation. However, in SIMs, unlike in clusters, the requirement of an energy barrier imposed by D < 0 has been recently questioned by the observation of slow relaxation in cobalt(II) complexes with D > 0,^[12-18] or even in systems with S = 1/2 spin ground state based on copper(II) or cerium(III) ions.^[19-22] Moreover, the need for an external magnetic field to observe slow relaxation of the magnetisation in most SIMs (field-induced SIMs) raises additional questions.^[8-11] Indeed, magnetic relaxation is determined by different mechanisms, which are difficult to discriminate and quantify. Therefore, fundamental studies

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on SIMs are still needed to investigate and understand the processes and mechanisms responsible for the slow relaxation of their magnetisation. The most promising hypothesis to date suggests that the spin–lattice relaxation occurs through spin– phonon coupling.^[7,23-27]

The most productive candidate for 3d metal complexes exhibiting SIM behaviour has so far been the 3d⁷ cobalt(II) ion $(S=3/2; t_{2g}{}^5e_{g}{}^2)$, as recently reviewed.^[8–11] Conversely, the high-spin 3d⁵ iron(III) ion $(S=5/2; t_{2g}{}^3e_{g}{}^2)$ in an octahedral ligand field is an unlikely candidate because it is generally electronically isotropic $(D\approx 0)$.^[28] This is due to the negligible orbital contribution in the free-ion ground state, so that SOC acts only in the second order. However, intermediate-spin (S=3/2) iron(III) complexes have proven in a few recent examples to be anisotropic, and show a magnetisation reversal barrier.^[29–31]

Porphyrins are good ligands for the design of SIMs.^[32,33] In particular, iron(III) porphyrins are known to have ground spin states dependent on the ligand strength, especially that of axial ligands.^[34–36] While six-coordinate complexes with strong field axial ligands such as imidazole and cyanide have a low-spin state (S = 1/2), five-coordinate complexes with an anionic ligand such as a halide exhibit a high-spin state (S = 5/2). In rare cases, an intermediate spin (S = 3/2) occurs with weak anionic ligands. Maltempo showed, however, that yet another case is possible, namely a quantum spin-admixed ground state.^[37] In such a case the wavefunction of the ground state is composed of both the S = 3/2 and S = 5/2 spin states, so that they are no longer good quantum numbers.^[38]

Herein we present mononuclear iron(III) compound $[Fe(TPP)(H_2O)_2]CIO_4$ (1), where H_2TPP is 5,10,15,20-tetraphenyl-21H,23H-porphine (meso-tetraphenylporphyrin). Scheidt and co-workers previously reported compounds with the same iron(III) porphyrin unit exhibiting structural parameters similar to those found in 1,^[39,40] but no detailed investigation of the magnetic properties was reported. Compound 1 is a mononuclear iron(III) complex behaving very much as a high-spin system (S = 5/2) with a large positive axial magnetic anisotropy. We demonstrate that 1 is the first high-spin iron(III) complex with D > 0 exhibiting slow magnetic relaxation, with blocking of the magnetisation that is most likely related to spin-lattice relaxation. Detailed high-frequency and -field electron paramagnetic resonance (HFEPR) and Mössbauer spectroscopic measurements determined the sign of the ZFS and hinted at its magnitude. Frequency-domain magnetic resonance techniques, alternatively called frequency-domain Fourier-transform terahertz EPR (FD-FT THz-EPR) or far-infrared magnetic spectroscopy (FIRMS), allowed us to probe the excitation from the $m_{\rm s} = |\pm 1/2\rangle$ ground to the $m_{\rm s} = |\pm 3/2\rangle$ first excited Kramers doublet, which directly determines the ZFS in 1. The large magnitude of the ZFS is supported and explained by quantum-chemical calculations.

Results

Synthesis and crystal structure

Recrystallisation from xylene solution under aerobic conditions of the solid obtained by reaction of [Fe(TPP)CI] and AgClO₄ in hot THF yielded **1** (details in Supporting Information). Thermogravimetric analysis (TGA) of **1** showed a mass loss of 4% below 150°C, which is in agreement with the loss of two water molecules (Figure S1 in Supporting Information), and proves its stability at room temperature. Thus, the bis-aqua axial coordination of the iron(III) ion seen in the room-temperature crystal structure (Figure 1) is intact at the lower temperatures used for all physical/spectroscopic measurements.



Figure 1. Perspective drawing (a) and top (b) and side (c) views of the cationic mononuclear iron(III) unit of **1**. Colour code: brown, iron; blue, nitrogen; red, oxygen; grey, carbon; white, hydrogen.

Crystallographic (Table S1) and structural data (Table S2) can be found in the Supporting Information. The iron(III) ion is in an elongated octahedral coordination geometry, exactly in the equatorial plane formed by the porphyrin nitrogen atoms, as expected for a metalloporphyrin with two identical axial ligands. The Fe-N distances are 2.024(3) and 2.038(4) Å, and the Fe-O distance (axial) is 2.130(3) Å. The cis N-Fe-N angles are 89.7(1)° and 90.3(1)°, whereas the O–Fe–O and trans N–Fe–N angles are linear. The coordination geometry of the iron(III) ion is thus not far from an ideal octahedron, even though there are modest tetragonal and rhombic distortions. These data are consistent with other reported high-spin S = 5/2 iron(III) porphyrin complexes.^[34, 39, 40] Hydrogen bonding between the coordinated water molecules and the perchlorate anion gives rise to chains (Figure S2 and Table S3 in Supporting Information) with an Fe--Fe distance of 10.33 Å. The shortest Fe--Fe intermolecular distance is 8.03 Å between iron(III) ions of adjacent chains.

Static magnetic properties

The direct current (dc) magnetic properties of **1** were measured as $\chi_{\rm M}T$ versus *T* and *M* versus *H*/*T*, as shown in Figure 2. The $\chi_{\rm M}T$ value of **1** at room temperature (3.56 cm³Kmol⁻¹) is lower than that previously reported^[39] and the spin-only value for S = 5/2 (4.37 cm³Kmol⁻¹), but significantly higher than the

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Figure 2. Plots of $\chi_M T$ versus *T* in the range 2–300 K at 0.025 T (*T* < 20 K) and 0.5 T (*T* ≥ 20 K) applied field and *M* versus *H*/*T* (inset) for **1** in the 2–10 K temperature range. The solid lines are the best-fit curves (see text).

value for S = 3/2 (1.87 cm³ Kmol⁻¹). This $\chi_M T$ value slightly increases on cooling to reach 3.68 cm³ Kmol⁻¹ at 140 K and then decreases to 2.30 cm³ K mol⁻¹ at 5 K. This behaviour is characteristic of iron(III) complexes showing a 5/2-3/2 spin-admixed ground state and is due to the presence of higher-lying guartet states close in energy to the sextet ground state. This proximity in energy, modelled through the appropriate choice of crystal field strengths,^[37,38,41] promotes a notable interaction between these states, leading to a ground state that is best described as a mixture of a sextet and one or more quartet electronic configurations. Additionally, the depopulation of these nearby quartet states in favour of the sextet ground state on cooling causes a slight and gradual increase of $\chi_{\rm M} T$ in the high-temperature region. The magnetisation at 5 T and 2 K is 2.72 $N\beta$ (Figure 2 inset). This value is below the saturation limit of 5 N β for one S=5/2 ion with q=2. The isothermal magnetisation curves in the 2-10 K temperature range do not superimpose at high H/T values, and this suggests a significant ZFS, since the iron(III) ions are magnetically well isolated (Fe---Fe distance > 8 Å).

The physical principles underlying the spin-admixed and ZFS models are the same, and only the amplitude of the interaction between the sextet ground and nearest quartet excited states determines the point at which one model is more suitable than the other. Owing to the small change in $\chi_{\rm M}T$ at high temperature (300–40 K) pointing to a modest extent of spin admixture, the lowest-lying Kramers doublets can be described by a ZFS model for S = 5/2. Although analysis of the $\chi_{\rm M}T$ versus T plot at higher temperatures with the ZFS model is limited, adding a temperature-independent paramagnetism (TIP) that accounts for a depopulation of the first quartet excited state with decreasing temperature is a useful alternative to the spin-admixed model.^[42–44] Such depopulation on cooling can lead to an increase of the $\chi_{\rm M}T$ product and a negative value of the TIP.

The experimental magnetic susceptibility and magnetisation data of **1** were fitted with the VPMAG program^[45] by using a standard spin-Hamiltonian for S = 5/2

$$\left[\widehat{H}_{\text{Spin}} = \widehat{H}_{\text{Zeemann}} + \widehat{H}_{\text{ZFS}} = \mu_{\text{B}} B_0 g \widehat{S} + D \left(\widehat{S}_z^2 - \frac{1}{3} S(S+1)\right) + E \left(\widehat{S}_x^2 - \widehat{S}_y^2\right)\right],$$

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where *D* and *E* are the axial and rhombic ZFS parameters. The obtained best-fit parameters are $D = +17.9 \text{ cm}^{-1}$, E/D = 0.002, $g_{\perp} = 1.84$, $g_{||} = 2.03$, and TIP × 10⁶ = -1091.3 cm³ mol⁻¹ with $F = 1.8 \times 10^{-5}$ (*F* is the agreement factor defined as $\Sigma [P_{\text{exp}} - P_{\text{calcd}}]^2 / \Sigma [P_{\text{exp}}]^2$, where *P* is the physical property under study).

Magnetic resonance spectroscopy

FD-FT THz-EPR spectroscopy, or FIRMS, allows a direct, highly accurate and precise measurement of large ZFS.^[46,47] Low-temperature (4.6 K) FD-FT THz-EPR spectra of 1 recorded up to 4.5 T at the BESSY II facility (Berlin) are shown in Figure 3. They are depicted as magnetic-field division spectra (MDS), in which the measured spectral intensities at the indicated fields are divided by each other to remove all signals from non-magnetic transitions, invariant to the field, from the spectra. The experiment was repeated independently at NHMFL (Tallahassee), with the resulting spectra shown in Figure S3 (Supporting Information), by using a different method to suppress the nonmagnetic transitions (see Experimental Section). In both experiments, we could observe the intra-Kramers $m_{
m S}$ = $|-1/2\rangle$ \rightarrow $|+1/2\rangle$ transition, which is shifted by the magnetic field into the observation window of the BESSY II synchrotron-based experiment, as observed in the 4.5 T/4 T spectrum. Similarly, application of magnetic fields higher than 6 T shifts this transition



Figure 3. Experimental FD-FT THz-EPR MDS of 1 measured at 4.6 K (black solid line) and simulations thereof (red dashed line). Spectra depicted above 14 cm⁻¹ were acquired by using the Hg arc lamp of the FTIR spectrometer, and the spectrum at the top depicted in the range 5–37 cm⁻¹ by using synchrotron radiation (BESSY II, low- α mode). In the relative transmittance MDS obtained by division of a raw spectrum at B_0 +1 T by one measured at B_0 , or one measured at 4.5 T by one at 4 T, maxima correspond to stronger absorption at lower B_0 , and minima to increased absorption at higher B_0 .



into the observation window of the FIRMS experiment at NHMFL. More importantly, we were able to observe in both experiments the inter-Kramers $m_s = |\pm 1/2\rangle \rightarrow |\pm 3/2\rangle$ transitions. In the 1 T/0 T FD-FT THz-EPR spectrum, the ZFS energy can be directly determined from that transition as $\Delta = 2\sqrt{D^2 + 3E^2} = 38.5 \text{ cm}^{-1}$ (Figure 3). The FIRMS experiment (Figure S4 in Supporting Information) yielded $\Delta = 38.3 \text{ cm}^{-1}$. A consensus value for Δ between the two independent experiments can thus be safely assumed as $38.4(1) \text{ cm}^{-1}$. Since the ZFS tensor of complex 1 is almost exactly axial (see below), this yields the axial ZFS parameter $D = \Delta/2 = +19.2 \text{ cm}^{-1}$.

We also performed a least-squares fitting of simulations to the field-dependent MDS, which yielded further spin Hamiltonian parameters: $g_{\perp} = 1.87$, $g_{||} = 2.00$ (fixed), E = 0.28 cm⁻¹ ($E/D \approx 0.015$). Inclusion of a *D* strain of $\Delta D = 1.6$ cm⁻¹ ($\Delta D/D =$ 7.8%) was found to be necessary to account for the observed line widths. The field dependence of the sublevel energies of the S = 5/2 spin manifold is shown in Figure S5 in the Supporting Information.

Field-domain experiments were conducted in the form of HFEPR spectroscopy in a 100-650 GHz frequency range. A typical low temperature spectrum is shown in Figure S6 and is symptomatic of S = 5/2 and positive D much larger than the sub-THz wave energy quantum, consisting exclusively of turning points of the intra-Kramers $m_{\rm S} = |-1/2\rangle \rightarrow |+1/2\rangle$ transition. In such a case, typically no information on the ZFS parameter D can be obtained; however, we used the D value known from frequency-domain experiments (19.2 cm⁻¹) as a constant, and subjected the other S = 5/2 spin Hamiltonian parameters to a fit using the tunable-frequency methodology,^[48] as depicted in Figure S7 of the Supporting Information. In this way, we obtained the values $E = 0.28 \text{ cm}^{-1}$, $g_{\perp} = 1.87$ and $g_{\parallel} = 2.00$, which agree very well with the frequency-domain results. Note that E in HFEPR was obtained from the visible splitting of the perpendicular turning point of the intra-Kramers transition (Figure S6), which is not resolved in the frequency-domain experiment (Figure 3). Although in principle that splitting can also originate from in-plane q anisotropy $(q_x \neq q_y)$, it is far more sensitive to the rhombicity of the ZFS tensor than to that of the *g* tensor. We can thus conclude that $E/D \approx 0.015$.

These results agree with the fits of the magnetometric and Mössbauer data (see below and Table 1). Specifically, the low

Table 1. Spin Hamiltonian parameters for 1 obtained by different techniques.						
Technique	g_	g_{\parallel}	<i>D</i> [cm ⁻¹]	E/D		
magnetometry FD-FT THZ-EPR FIRMS HFEPR Mössbauer ($S = 5/2$ model analy- sis) Mössbauer ($S = 5/2-3/2$ spin ad- mixed model analysis)	$\begin{array}{c} 1.84 \\ 1.87 \\ 1.87 \\ 1.88 \\ 1.88 \pm 0.10 \\ 1.91 \pm 0.02^{(b)} \end{array}$	2.03 2.00 ^[a] 2.00 ^[a] 2.0 ^[a] 2.0 ^[a]	+ 17.9 + 19.25 + 19.15 + 19.2 ^[a] + 18 ± 3 + 20 ± 3 ^[b]	0.002 0.015 - 0.015 < 0.02		
[a] Fixed value. [c] Calculated according to Equations (S3) and (S4) of the Supporting Information						

 g_{\perp} value is confirmed and responsible for the low $\chi_{\rm M} T$ value at room temperature.

Mössbauer spectroscopy

Figure 4 shows the Mössbauer spectrum recorded on a powder sample of 1 at 5 K with a 7 T external magnetic field applied perpendicular to the γ -radiation (hatched bars). Additional spectra are presented in Figure S9 of the Supporting Information. Previously published measurements, which were performed at 78 and 298 K in zero field, allowed only the determination of the isomer shift and quadrupole splitting.^[39] All the Mössbauer spectra of 1 are also very similar to those reported for the picket-fence porphyrin complex $[(TPpivP)Fe^{III}(OSO_2CF_3)(OH_2)]$.^[49] Given the large *D* value obtained by magnetometry and magnetic resonance, we considered multiple approaches to spectral analysis. In a first approach, axial symmetry was assumed. Assuming 1 is a pure S =5/2 system, simultaneous fitting of the six spectra reported in Figure 4 and Figure S9 of the Supporting Information, leads to the following electronic and nuclear parameters: $D = +18 \pm$ 3 cm⁻¹, $g_{\perp} = 1.88 \pm 0.10$, $g_{\parallel} = 2.0$ (fixed), $A_{\perp}/(g_{\rm N}\mu_{\rm n}) = -17.7 \pm$ 0.2 T, $A_{\parallel}/(g_N \mu_n) = -29 \pm 3$ T, $\Delta E_0 = 2.0 \pm 0.1$ mm s⁻¹ for T < 100 K, $\Delta E_{\rm O} = 2.15 \pm 0.20 \ {\rm mm \, s^{-1}}$ for $T > 100 \ {\rm K}$, $\delta = 0.43 \pm 0.03 \ {\rm mm \, s^{-1}}$ for T < 100 K and δ = 0.41 \pm 0.10 mm s⁻¹ for T > 100 K (see solid lines in Figure 4 and Figure S9 of the Supporting Information). In a second step, fits were performed under the assumption of rhombic ZFS. The quality of the simulations was not significantly improved and the E/D ratio was < 0.02; this validated the initially assumed axial symmetry. The D and q_{\perp} parameters were also found to be in excellent agreement with the values deduced from the magnetic data and from the frequency- and field-domain EPR measurements.

Compound **1** was alternatively analysed as a spin-admixed (S = 5/2-3/2) system, as had been reported for [(TPpivP)Fe^{III}(OSO₂CF₃)(OH₂)].^[49] Equally satisfying simulations were obtained for the six Mössbauer spectra, as shown in Figure S10 of the Supporting Information. Within this model, de-



Figure 4. Experimental Mössbauer spectrum of 1 recorded at 5 K with a 7 T external magnetic field applied perpendicular to the γ -beam (hatched bars). The solid red line is a simulation obtained with parameters given in the text for a pure axial S = 5/2 spin system.



veloped in the 1970s by Maltempo,^[37,50] the critical electronic parameters are the single-electron SOC constant ξ and, in D_{2h} symmetry, the energy gap between the ground ${}^{6}A_{g}$ and the excited ${}^{4}B_{1g}$ states ($\Delta_{3/2-5/2}$), taken as positive here for the S = 5/2 ground state. The obtained values of $\Delta_{3/2-5/2} = 550 \pm 50 \text{ cm}^{-1}$ and $\xi = 230 \pm 20 \text{ cm}^{-1}$ indicate that the ground spin state has a dominant S = 5/2 character ($86 \pm 3\%$), but also a significant contribution ($14 \pm 3\%$) of the first S = 3/2 excited spin state. The relationship between spin-admixed and ZFS models is expressed through Equations (S3) and (S4) of the Supporting Information and, in agreement with magnetometry and FD-FT THz-EPR and HFEPR spectroscopy, this result leads to values of $D = +20 \pm 3 \text{ cm}^{-1}$ and $g_{\perp} = 1.91 \pm 0.02$.

Computational studies

Ligand-field theory can first be used to provide a simple picture of the origin of the spin Hamiltonian parameters in highspin d⁵ complexes. The major contributions of quartet excited states to the ZFS parameter and the *g* values are described by the following equations for D_{2h} symmetry:^[51] [Eqs. (1)–(4)]

$$D = \frac{\xi^2}{10} \left[\frac{2}{E({}^4B_{1g})} - \left(\frac{1}{E(1{}^4B_{2g})} + \frac{1}{E(1{}^4B_{3g})} \right) \right]$$
(1)

$$E = \frac{\xi^2}{10} \left[\frac{1}{E(1^4 B_{2g})} - \frac{1}{E(1^4 B_{3g})} \right]$$
(2)

$$g_{\perp} = g_e - \frac{\xi}{5} \frac{2}{E({}^4B_{1g})}$$
(3)

$$g_{\parallel} = g_e + \frac{\xi}{5} \left(\frac{1}{E(1^4 B_{2g})} + \frac{1}{E(1^4 B_{3g})} \right)$$
(4)

where g_e is the free-electron g value (\approx 2.00) and the relative energies of various quartet excited states are given by $E({}^{4}B_{1a})$, and so on. Similar equations were used with the Maltempo model for the Mössbauer spectroscopy simulations (see Supporting Information). The ⁴B_{1g} state contributes oppositely to D versus the $1^{4}B_{2q}$ and $1^{4}B_{3q}$ states, but since the first of these is much lower in energy in a tetragonal system, the sign of D is positive (see Figure S11 of the Supporting Information). This contribution of the ${}^{4}B_{1a}$ state also leads to a deviation of g_{\perp} from g_e to a lower value [see Eq. (3)], while g_{\parallel} deviates above $g_{\rm e}$ [see Eq. (4)] due to the interaction with the other two quartet states. A reduction of the molecular symmetry from D_{4h} to D_{2h} infers an energy gap between the $1^{4}B_{2q}$ and $1^{4}B_{3q}$ states leading to rhombicity of the ZFS tensor $[E \neq 0$, see Eq. (2)]. This splitting is small since the porphyrin ligand enforces nearly fourfold symmetry (see Table S4 of the Supporting Information).

DFT calculations were performed to reproduce the experimental results and analyse their origin. DFT calculations based on the broken-symmetry approach were also employed on models with two neighbouring iron porphyrin units to confirm the absence of intermolecular magnetic interactions. In the crystallographic geometry, the calculated ZFS parameters for a spin sextet ($D = +23.8 \text{ cm}^{-1}$, E/D = 0.27) support the large and positive D value but not the small E/D ratio, which is usually more difficult to evaluate by theoretical methods. However, when the calculations are done on the optimised geometry, the resulting E/D ratio is lower than 0.005 (see Table S5 of the Supporting Information). The spin-spin coupling (SSC) contribution to ZFS is always negligible (around 0.02%), and the SOC contribution is almost entirely from the guartet excited states, as Equation (1) and the spin-admixed model used to analyse the Mössbauer data suggest. Evaluation of the relative energies of the excited states by DFT methods is difficult, particularly when the ground and excited states exhibit different spin multiplicity, resulting in over-stabilised excited states. Only sophisticated techniques such as the constrained-DFT method can help to solve this problem.^[52-55] However, changing the occupation of the frozen SOMOs composed mostly of d orbitals of the iron(III) ion and avoiding any relaxation of the wavefunction can provide a better approach for the energies of the quartet excited states, although slightly overestimated. This approach, not detailed here, suggests that the first quartet excited state should be placed at only 1000 cm⁻¹ (E_1). Other theoretical results obtained by using ab initio post-Hartree-Fock methods and the problem of covering the covalence of the metal-ligand bond fully through dynamical correlation are further discussed in the Supporting Information (Figures S12 and S13).

Dynamic magnetic properties

Alternating current (ac) magnetic susceptibility studies on 1 were performed to study its relaxation properties. No $\chi_{M}^{''}$ signals were observed down to 1.9 K in absence of a dc magnetic field even at the highest frequency used (10 kHz). However, a frequency-dependent component appears both in χ'_{M} and χ''_{M} below approximately 5 K in the presence of an applied field (Figure 5, Figures S14-S17 of the Supporting Information). The presence of a dc-magnetic field usually hampers relaxation through a quantum tunnelling mechanism (QTM) and nonzero $\chi_{M}^{''}$ signals are observed. QTM is typically observed for SMM systems having large negative D values and high energy barriers.^[1] However, no barrier occurs for systems exhibiting easyplane slow relaxation magnetisation (D > 0), a common feature in 3d SIMs.^[8-11] In these cases, an intra-Kramers transition within the magnetic ground Kramers doublet rather than QTM should be invoked to describe the SIM behaviour.

The experimental data were analysed through a Debye model described by the parameters χ_{S} , $\chi_{\overline{\nu}} \tau$ and α , which are the static and infinite frequency magnetic susceptibilities, the relaxation time and the exponential factor, respectively, the last-named of which describes the spectral breadth. The simultaneous fit of χ'_{M} and χ''_{M} versus ν is the best approach,^[56] which nicely reproduces $\chi'_{M}-\nu$, $\chi''_{M}-\nu$, and the Cole–Cole plots with a unique set of values (Figure 5, Figures S14–S17 of the Supporting Information). Moreover, the standard errors for the parameters are usually smaller than those for the analysis of the Cole–Cole plots. Nevertheless, the correlation matrices indi-

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Figure 5. Frequency dependence of χ'_{M} (top left) and χ''_{M} (top right) and Cole–Cole plots (bottom left) of 1 under a dc applied static field of 0.15 T with \pm 0.5 mT oscillating field in the temperature range of 2–4.5 K (from blue to red). Thermal dependence of α (bottom right) under dc-applied static fields from 0.05 to 0.5 T. Standard deviations appear as vertical error bars.

cate that the fit parameters are not independent. Also, the values of α decrease in the temperature range $2.0 \le T \le 4.5$ K, but they continuously increase for T > 4.5 K (Figure 5). Either the strong correlation among the parameters or the presence of a second relaxation process could account for this last anomaly. In fact, despite the small values of $\chi_{M'}^{"}$, an additional weak signal in the $\chi_{M}^{"}-\nu$ plots is discerned above 7 K (Figure S18 of the Supporting Information). These issues combined limited our analysis to the data at $T \le 4.5$ K.

The obtained results are illustrated by Figures 5 and 6, where $\alpha < 0.2$ at any temperature and in any explored dc magnetic field (0.075–0.5 T). This feature supports a single relaxation process and rejects any spin-glass behaviour. On the other hand, the temperature-dependent relaxation times, $\tau = 1/2\pi\nu$,



Figure 6. Arrhenius plots for **1** under applied static fields from 0.05 to 0.5 T. The solid lines are the best-fit curves for a model that combines Raman and direct processes. Standard deviations appear as vertical error bars.

as Arrhenius plots, begin to superimpose as the applied dc magnetic field increases up to 0.3 T. At higher fields, other relaxation mechanisms emerge. Thus, these curves were fitted by using any of the following combinations of relaxation mechanisms: Raman plus direct $[1/\tau = CT^n + AT]$, Orbach and direct $[1/\tau = (1/\tau_0)\exp(-E_a/k_BT) + AT]$, and two Orbach processes $[1/\tau = (1/\tau_{01})\exp(-E_{a1}/k_BT) + (1/\tau_{02})\exp(-E_{a2}/k_BT)]$.

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Due to the positive value of *D*, the Orbach process is not related to an energy barrier arising from the ZFS, but to the need for reaching a most likely vibrational excited state to allow fast relaxation. Concerning the Raman plus direct combination, although the values of *n* (5.2–7.2) are roughly in the physically expected range (6–8), they depend on the magnetic field. Still, this unusual dependence on the magnetic field also occurs for the *C* parameter (Raman, Figure 7 top) and the coefficient for the direct relaxation does not follow the expected dependence $A \propto H^2$ (Figure 7 bottom).^[57] The latter observation is also reproduced in the case of Orbach plus direct mechanisms (Figure S19). Finally, the values of the energy barrier (E_a) for the Orbach-direct combination cover the range 14–19 cm⁻¹ under most of the applied dc fields, with somewhat



Figure 7. Dependence of the parameters defining a model that combines Raman (top; parameters *C* and *n*; see text) and direct (bottom; parameter *A*; see text) relaxation mechanisms on the applied dc magnetic field for **1**. Standard deviations appear as vertical error bars.

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smaller values at the lowest magnetic fields following a linear dependence.

Discussion

Up to now, the few reported iron(III) SIMs have shown negative values of the anisotropy in the range from -1.2 to -50 cm^{-1} with an S=3/2 ground state.^[29-31] A high-spin 3d⁵ complex should be magnetically isotropic (D=0), but the proximity of the excited quartet (S = 3/2) states, which depends on the ligand fields, can significantly affect the ground state, inducing anisotropy. Only recently, SIM behaviour (with D < 0), was observed for S = 5/2 iron(III) compounds.^[58–60] The ground state in iron(III) porphyrins in particular can be tuned by the ligand field, as observed in such complexes showing S = 1/2, 3/2, and 5/2 ground states, [34-36] including those with S = 5/2and positive and sizable D values.^[61-63] In **1**, the ligand field of the water molecules at axial positions is not strong enough to induce an intermediate S = 3/2 ground state,^[64] but is sufficient to bring the quartet excited states close in energy and thus to induce magnetic anisotropy and SIM behaviour in the presence of an external magnetic field.

The small $\chi_{\rm M}T$ value at room temperature, its unusual hightemperature behaviour and the Mössbauer spectroscopic study indicate the presence of at least one very close excited quartet state (545 ± 50 cm⁻¹). This fact not only explains the large ZFS found in 1, but it also suggests the occurrence of a slight spin admixture in such a way that the ground state no longer corresponds to a pure sextet state but a mixture with a quartet state in 86:14 ratio.

The magnetic relaxation process for systems with m_s states close in energy is typically due to the presence of an energy barrier attributed to an axial D < 0 anisotropy, as occurs in manganese(III) compounds.^[32,65,66] However, in systems with large ZFS, such as octahedral cobalt(II) complexes, the sign of the anisotropy is not decisive to observe slow magnetic relaxation, because different mechanisms, for example, spin-phonon coupling, direct and Raman processes, can be responsible for such behaviour.^[67] Since there is no energy barrier (D > 0) in 1, the lowest molecular vibrational frequencies might instead be the basis for the slow magnetic relaxation.^[7,24,25,27,68-71] At temperatures at which no excited vibrational level is significantly occupied, the magnetisation cannot effectively relax and it is blocked. However, a slight increase in temperature populates the first levels of the low-lying vibrational modes in the molecule, or by extension, phonons in the lattice, causing greater dynamics that favour faster relaxation of the magnetisation. Theoretical analysis of low-energy vibrational modes was done (see the Supporting Information, which includes videos of the first three vibrational modes) to understand the magnetic relaxation. These vibrational modes correspond mainly to motions involving the phenyl rings of the porphyrin. The first vibrational mode appears at 12.5 cm⁻¹ and the next around 25 cm⁻¹, which is consistent with a non-magnetic transition observed at 21.6 cm⁻¹ in FD-FT THz-EPR spectra (Figure S8 of the Supporting Information). The first observed relaxation process thus might be related to relaxation through spin-phonon coupling. A spin–lattice relaxation phenomenon was proposed to be the preponderant mechanism responsible for the intermediate electronic relaxation process detected by Mössbauer spectroscopy for [(TPpivP)Fe(OSO₂CF₃)(OH₂)].^[49] Owing to the similarity of the nuclear and electronic parameters of both complexes, this experimental evidence supports our conjectured role of vibrational modes in **1**.

Conclusion

We have reported here the first example of a mononuclear high-spin d^5 (S = 5/2) iron(III) compound, namely six-coordinate porphyrin complex 1, that shows both an in-plane magnetic anisotropy and SIM behaviour with applied external magnetic field. Despite the expected isotropic spin ground state, the compound has a large and positive magnetic anisotropy value (axial ZFS with $D = +19.2 \text{ cm}^{-1}$), which can be attributed to the contribution of quartet excited states (i.e., a spin-admixed character to the ground state). Magnetisation, field- and frequency-domain magnetic resonance techniques and Mössbauer measurements confirm this result, which is also supported by theoretical calculations. The slow relaxation of the magnetisation of 1 may be modulated by low-energy molecular vibrational modes. Future work will explore the role of axial ligands in this class of porphyrinic compounds to clarify their effect on the SIM behaviour and how they can relate to the low-energy molecular vibrational modes.

Experimental Section

Materials

All chemicals were obtained from commercial sources and used as received. [Fe(TPP)CI] was synthesised as described in the literature.^[72] **Caution!** Perchlorate salts are potentially explosive. They should be used in small quantities and be treated with utmost care at all times.

Synthesis of [Fe(TPP)(H₂O)₂]ClO₄ (1)

[Fe(TPP)CI] (203 mg, 0.288 mmol) and AgClO₄ (78 mg, 0.373 mmol) were dissolved in boiling THF and stirred for a few minutes under aerobic conditions. After filtration, heptane was added to the solution to afford purple crystals, which were collected by filtration. Single crystals of **1** were obtained by recrystallisation of the solid from xylene solution under aerobic conditions. Yield: 169 mg (73%). IR: \tilde{v}_{max} = 3520 (s, coordinated H₂O), 1072 cm⁻¹ (br, ClO₄⁻).

Physical measurements

IR spectra (4000–300 cm⁻¹) were recorded on a Nicolet 5700 spectrophotometer as KBr pellets. The thermogravimetric analysis (TGA) was performed on single-crystals of 1 under a dry N₂ atmosphere with a Mettler Toledo TGA/STDA 851e thermobalance in the temperature range 25–250 °C.

Static dc measurements were carried out on 1 by powdering and restraining the samples to prevent any displacement due to the magnetic anisotropy. Variable-temperature (2.0–300 K) dc magnetic susceptibility under applied fields of 0.025 (T < 20 K) and 0.5 T (T ≥ 20 K) and variable-field (0–5.0 T) magnetisation in the temperature



range from 2 to 10 K were recorded with a Quantum Design SQUID magnetometer. Variable-temperature (2.0–10 K) ac magnetic susceptibility measurements under \pm 0.5 mT oscillating field at frequencies in the range of 0.1–10 kHz were carried out on crystalline samples in different applied static dc fields in the range 0.0–0.5 T with a Quantum Design Physical Property Measurement System (PPMS). The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

HFEPR spectra of 1 were recorded at 4.5 K on polycrystalline samples (20–25 mg) by using a homodyne spectrometer associated with a 15/17 T superconducting magnet and a frequency range from 52 to 610 GHz. Detection was provided with an InSb hot electron bolometer (QMC Ltd., Cardiff, UK). The magnetic field was modulated at 50 kHz for detection purposes. A Stanford Research Systems SR830 lock-in amplifier converted the modulated signal to dc voltage. The single-frequency spectra were simulated with the SPIN software.

Mössbauer spectra were recorded between 5 and 160 K with a strong-field Mössbauer spectrometer equipped with an Oxford Instruments Spectromag 4000 cryostat containing an 8 T split-pair superconducting magnet. The spectrometer was operated in constant-acceleration mode in transmission geometry. The isomer shifts were referenced against that of a room-temperature metallic iron foil. Analysis of the data was performed with a homemade program^[73,74] that was adapted to treat the quantum spin admixture.

FD-FT THz-EPR data were acquired at the THz-EPR user station of the electron storage ring BESSY II. The setup is described in detail elsewhere. $^{[46,75]}\mbox{THz}$ coherent synchrotron radiation (CSR) or broadband, unpolarised THz radiation emitted by the Hg arc lamp of an FTIR spectrometer (Bruker IFS 125) were used as broad band (\approx 4– 50 cm⁻¹ and > 12 cm⁻¹, respectively) excitation sources. The radiation was transmitted by a quasi-optical evacuated transmission line through the FTIR spectrometer and focused on the sample contained in a 10 T superconducting magnet (Oxford Spectromag). Spectra were recorded in Voigt geometry. The transmitted signal was detected by a Si bolometer detector (IR labs) and Fouriertransformed to yield frequency-domain EPR spectra. The experimental resolution was 0.5 cm⁻¹. Polycrystalline 1 (23 mg) was homogenised in a mortar with polyethylene powder (36 mg) and pressed into a pellet mounted in the variable-temperature insert of the magnet. FD-FT THz-EPR, as an FTIR-based technology, requires the measurement of a reference spectrum. Referencing between spectra recorded at different temperatures or fields was done as described elsewhere.[46,62]

Frequency-domain spectra were simulated by using the EasySpin toolbox.^[76-78] The spin Hamiltonian included the electron-Zeeman and the ZFS interactions [Eq. (5)]:

$$\widehat{H}_{\text{Spin}} = \underbrace{\mu_{B}B_{0}g\widehat{S}}_{\widehat{H}_{\text{Zeeman}}} + \underbrace{D\left(\widehat{S}_{z}^{2} - \frac{1}{3}S(S+1)\right) + E\left(\widehat{S}_{x}^{2} - \widehat{S}_{y}^{2}\right)}_{\widehat{H}_{\text{Zes}}}$$
(5)

where $\mu_{\rm B}$ is the Bohr magneton, B_0 the external magnetic field, g the g matrix and \hat{S} the electron spin operator. The g and D (ZFS) interaction matrices were assumed to be collinear. The relative transmittance T in MDS at two magnetic fields B_i and B_{ji} experimentally obtained from the measured spectral intensities I as $T_{\rm exp} = I_{B_i}/I_{B_j}$, are calculated from the simulated absorbance spectra A as $T_{\rm sim} = 10^{A_{\rm BJ}-A_{\rm BJ}}$.

High-field THz spectra (FIRMS) were collected at the National High Magnetic Field Laboratory with a Bruker Vertex 80v FTIR spectrometer coupled with a 17 T vertical-bore superconducting magnet in Voight configuration. The experimental setup was equipped with a mercury lamp and a composite silicon bolometer (Infrared Laboratories), as THz radiation source and detector, respectively. An *n*-eicosane pellet containing the studied compound (\approx 7 mg) was measured in the spectral region between 14 and 730 cm⁻¹ (0.42–22 THz) with a resolution of 0.3 cm⁻¹ (9 GHz). Both sample and bolometer were cooled by low-pressure helium gas to 4.6 K. The relative transmittance spectra were calculated as the THz intensity spectrum at each magnetic field divided by the THz intensity spectrum averaged for all fields.

Single-crystal XRD

XRD data of 1 were collected with a Bruker-Nonius X8APEXII CCD area detector diffractometer by using graphite-monochromated $Mo_{K\alpha}$ radiation at T=90 K. All calculations for data reduction, structure solution and refinement were done with the SAINT^[52] and SADABS^[79,80] programs. The structure was solved with the SHELXS structure solution program, by using the Patterson method. The model was refined with version 2018/3 of SHELXL against F^2 on all data by full-matrix least squares techniques.^[81-83] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms of the ligand were set in calculated positions and refined isotropically by using the riding model. Hydrogen atoms on the coordinated water molecules were found and refined with restraints on bond lengths and angles. Chlorine and oxygen atoms of the perchlorate anions were found to be statistically disordered (for symmetry) on two positions. Accordingly atom O(5) has been refined with 0.5 occupancy factor. The final geometrical calculations and the graphical manipulations were carried out with the PLATON package^[84,85] and CRYSTAL MAKER.^[86] Crystallographic data for 1 are given in Table S1 of the Supporting Information. Deposition Number 1872265 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures. The comments for the main alerts A and B are described in the CIF validation report form (vrf).

Computational details

The parameters that determine the axial (*D*) and rhombic (*E*) components of the local ZFS of **1** were estimated from theoretical calculations based on DFT. Calculations were carried out on the experimental geometry with version 4.0 of the ORCA program^[87] by using the PBE and BP functionals,^[88–91] the resolution of the identity (RI) approximation^[92,93] and the auxiliary TZV/J Coulomb fitting basis sets.^[94–98] All calculations were done in solution, including electronic effects of the solvent (acetonitrile) by the conductor-like polarizable continuum model,^[99] in which the cavity that accommodates the molecule is built by sing the GEPOL algorithm.^[100–102] The spin–orbit and spin–spin coupling operators were based on the SOMF scheme.^[103,104] Coupled perturbed (CP) and Pederson–Khanna (PK) methods were used in the calculation of the spin–orbit contribution to the ZFS.^[105,106]

DFT calculations were carried out with the Gaussian 09 package to estimate the magnitude of the intermolecular magnetic couplings.^[107] These calculations were performed with the CAM-B3LYP hybrid functional,^[90,108–110] the quadratic convergence approach and a guess function generated with the fragment tool of the same program. The triple- ζ all-electron basis set proposed by Ahlrichs et al. with addition of an extra p polarisation function was employed for all atoms.^[95] The study was done with models includ-

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ing two neighbouring iron(III) complexes in their experimental geometries. The magnetic coupling states were obtained from the relative energies of the broken-symmetry (BS) singlet spin state from the high-spin state with parallel local spin moments. Details about the use of the BS approach to evaluate magnetic coupling constants can be found in the literature.^[111-113] A polarizable continuum model was introduced in the calculations with the parameters corresponding to acetonitrile.^[114] The optimisation of the molecular geometry of a mononuclear iron(III) complex was done starting from the experimental geometry of 1 and by using the PBE functional as implemented in Gaussian 09.^[88,91] To improve the goodness of the calculated analytical vibrational frequencies, the restricted conditions were imposed in the self-consistent convergence of the wavefunction and in the evaluation of the bielectronic integrals (very tight and ultrafine, respectively) for the geometry optimisation and evaluation of the vibrational modes. The calculated values of the D and E/D parameters shown in Table S5 of the Supporting Information were made on the last optimised geometry with the PBE functional.

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Conflict of interest

The authors declare no conflict of interest.

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