The first trigonal bipyramidal Fe(II) complex to display slow relaxation of magnetisation has been isolated, with this behaviour found to arise through a combination of a large magnetic anisotropy \((D = -27.5 \text{ cm}^{-1})\) and a pseudo-\(D_{3h}\) symmetry at the Fe(II) centre, as investigated through \textit{ab initio} and magnetic studies.

The continuing demand for the miniaturisation of technology to maximise data storage density drives research into molecular magnetic materials. One class of such materials are single-molecule magnets (SMMs), which show slow relaxation of the magnetisation.\(^{1,2}\) Engineering SMM properties to maximise the retention of magnetisation has led to molecular magnetic hysteresis up to 80 K.\(^{3-5}\) Initially increasing the spin ground state \(S\) was the focus, however maximising the axial magnetic anisotropy has become more extensively investigated.\(^{6,7}\) For example in cases where an uneven number of electrons reside in degenerate orbitals, as is the case with Ni(II) or Fe(II) in a trigonal example in cases where an uneven number of electrons reside in metallic Fe(II) complexes,\(^{13-17}\) we report the synthesis of \([\text{FeCl}_3(\text{MDABCO})_2][\text{ClO}_4]\) (1) and a pseudo-\(D_{3h}\) symmetry at the Fe(II) centre, with this behaviour found to yield good numerical estimates of zero-field splitting (ZFS) parameters for transition metal complexes.\(^{21,22}\) These calculations give an axial ZFS \((D)\) of \(-27.5 \text{ cm}^{-1}\) with a minimal transverse, or rhombic, \(E/D\) value of 0.02. This is in sharp contrast to a recently reported Fe(II) trigonal bipyramidal...
complex where a small positive $D$ value resulted, which can be attributed to the differences in geometric distortion (CShM value of 0.057 for 1 vs. 1.050 for [Fe(MST)(OH)₂]⁻ where [H₂MST] = $N_2N'N''_22',2',2''$-nitrilotris(ethane-2,1-diyl)tris(2,4,6-trimethylbenzenesulfonamide)).¹³ The computed $D_{zz}$ or $g_{zz}$ anisotropy axes for 1 lie very close to the N–Fe–N axis of the complex (see Fig. 2). The large negative $D$ value is primarily due to mixing with the 1st excited state ($^5E''_0$), which corresponds to the same $M_s$ level $d_{zz} \rightarrow d_{zz}$ electronic transition (see Table S4, ESI† and Fig. 2). In ideal $D_{10h}$ symmetry the $^5E''_0$ and $^5E''_1$ states are degenerate, but a small Jahn–Teller distortion results in the 1st excited state in 1 lying 137 cm⁻¹ above the ground state (see Table S4, ESI†). While this 1st excited state provides the largest contribution to the overall $D$ value, mixing with other quintet excited states also provide small (positive) contributions to $D$ (see Table S4, ESI†). As was observed with the Ni(II) analogue, the significant steric bulk of the axial ligands prevents the Jahn–Teller distortion modes. This retains a high-order pseudo-$D_{16h}$ symmetry around Fe(II) centre, which is reflected in the negligible $E/D$ value.¹¹,¹² The spin-orbit coupling analysis reveals a very small tunnel splitting (0.08 cm⁻¹) for the $M_s = ±2$ levels but the reduced weightage in the spin–orbit states ($|±2|$) suggests strong ground state quantum tunnelling (see Table S5, ESI†), which rationalises the observation of field-induced (rather than zero field) slow magnetic relaxation (vide supra), despite the favourable $D$ and $E/D$ parameters.

The variable-temperature magnetic susceptibility data for 1 were collected between 290 K and 2 K under an applied direct-current (dc) field of 1000 Oe (Fig. 3). At 290 K, the $\chi_M T$ value of 4.10 cm³ mol⁻¹ K is substantially higher than that expected for a spin-only model ($S = 2, g = 2, \chi_M T = 3.0$ cm³ mol⁻¹ K) indicating a significant residual orbital moment. $\chi_M T$ remains almost constant until approximately 50 K after which a sharp decrease is observed, reaching a minimum value of 3.08 cm³ mol⁻¹ K at 2 K. The magnetisation measurements ($M$ vs. $H$) were carried out between 0 and 5 T at 2, 4 and 6 K (Fig. 3 inset) and in each case did not reach saturation.

$$\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + \mu_B \vec{B} \cdot \hat{g} \cdot \vec{S}$$

(1)

The $\chi_M T$ vs. $T$ and $M$ vs. $H$ data were fitted simultaneously using the program Phi²⁵ using the Hamiltonian presented in eqn (1). Some parameters were fixed based on the results obtained from the ab initio calculations (vide supra): the axial and rhombic ZFS parameters, $D$ and $E$, were fixed at values of $-27.5$ cm⁻¹ and $0.58$ cm⁻¹, respectively as well as $g_x = 1.90$ and $g_y = 1.98$. The $g_z$ value however was fixed at 2.61 considering the local minimum in the residual determined via a survey of the $\chi_M T$ vs. $T$ data, although it should be noted that this is close to the ab initio determined $g_z$ value of 2.53. TIP and $\Omega T$ terms were determined from the fit (further details can be found in the ESI† along with additional fits and survey plots (see Fig. S2 and S3)).

Initial investigations of the dynamic susceptibility were carried out as a function of field with $H_{dc}$ ranging between 0 and 5000 Oe at a fixed temperature of 2 K (see Fig. 4 and Fig. S4, ESI†).

**Fig. 2** $D$ and $g_{zz}$ tensor directions (left), NEVPT2-LFT computed $d$-orbital energies in 1 (right).

**Fig. 3** Temperature dependence of $\chi_M T$ for 1 from 290 K to 2 K in a dc field of 1000 Oe (magnetization vs. field shown inset). The solid lines correspond to the fit (see text for details).

**Fig. 4** Frequency-dependence of the $\chi'$ response in $H_{dc}$ ranging between 500 and 5000 Oe at 2 K (upper) and in $H_{ac} = 600$ Oe between 1.9 and 9 K (lower).
No out-of-phase ac $\chi''$ response was observed in zero applied dc field, as is common for monometallic 3d complexes where spin-phonon relaxation and quantum tunnelling of magnetisation (QTM) can be particularly efficient,\textsuperscript{24–26} but on applying dc fields of above 500 Oe a frequency dependence was observed.\textsuperscript{8} At $H_{dc} \leq 1500$ Oe, a single high frequency (HF) relaxation pathway is apparent. On increasing $H_{dc}$ above 1500 Oe, a second low frequency (LF) relaxation path emerges (see Fig. 4). The co-existence of two relaxation regimes has been previously attributed to relaxation originating from the individual complexes for the HF pathway, with the LF pathway arising due to intermolecular interactions.\textsuperscript{27–31} This leads to a difference in behaviour as a function of temperature, with the signal arising from the HF pathway exhibiting a temperature dependence and that from the LF path remaining temperature independent. We therefore chose to investigate the variable temperature ac susceptibility at two fields; 600 Oe where only the HF relaxation mode is observable, and 2500 Oe where the LF pathway emerges, and the HF mode is under an optimal field (see Fig. S6 and relaxation mode is observable, and 2500 Oe where the LF pathway remaining temperature independence. This is more apparent on (QTM) can be particularly efficient,\textsuperscript{24–26} but on applying dc fields of above 500 Oe a frequency dependence was observed.\textsuperscript{8} At (QTM) can be particularly efficient,\textsuperscript{24–26} but on applying dc fields of above 500 Oe a frequency dependence was observed.\textsuperscript{8} At \begin{equation} \tau^{-1} = \tau_{0}^{-1} \exp \left( \frac{-DE}{k_{B}T} \right) + AH^{2}T + CT'' + \frac{B_{1}}{1 + B_{2}H^{2}} \tag{2} \end{equation}

and Raman processes, given by the second and third terms in eqn (2), respectively, as well as a QTM contribution denoted by the fourth term in eqn (2) (see Fig. S11, ESI\textsuperscript{†}).

To avoid over-parameterisation, the field dependence of the relaxation rate was initially fitted using the field-dependent processes (see Fig. S10, ESI\textsuperscript{†}). This allowed us to extract parameters relating to both direct relaxation and QTM ($A, B_{1}$ and $B_{2}$) giving $A = 182.35 \pm 0.05 \times 10^{-2}\ s^{-1}\ \text{kOe}^{-2}$, $B_{1} = 109.60 \pm 0.04 \times 10^{-2}\ s^{-1}$ and $B_{2} = 355.57 \pm 2.56 \times 10^{-2}\ \text{kOe}^{-2}$. Once obtained, these parameters were fixed in the fits of the temperature dependence of the relaxation rates at both 600 Oe and 2500 Oe. For data collected at $H_{dc} = 600$ Oe, the fit fixing $A$, $B_{1}$ and $B_{2}$ and $n = 7$ for an integer spin ion is shown in Fig. S11 (ESI\textsuperscript{†}) where $C = 5.64 \pm 0.06\ s^{-1}\ \text{K}^{-n}$. The fit can be improved by including an Orbach term but as discussed earlier it is not appropriate to include this term based on the estimated energy gap between ‘real’ states. For relaxation rates obtained under 2500 Oe the data could be fitted by fixing $A$ but it was not possible to do this for the QTM terms $B_{1}$ and $B_{2}$. The Raman parameters obtained were $C = 1.31 \pm 0.01\ s^{-1}\ \text{K}^{-n}$, $n = 6.39 \pm 0.01$. The general QTM term obtained from the fit (1.34 $\pm 0.01\) $\times 10^{-5}\ s^{-1}$) is close to that obtained based on the field dependent relaxation rates ($\langle B_{1}/(1 + B_{2}H_{dc}) \rangle \sim 9 \times 10^{-5}\ s^{-1}$).

[FeCl$_{3}$(MDABCO)$_{3}$][ClO$_{4}$] (1) is the first monometallic trigonal bipyramidal Fe(II) complex to show slow relaxation of the magnetisation. Rigorous control of the coordination environment produces a large axial magnetic anisotropy as confirmed by dc magnetic measurements and supported \textit{via} \textit{ab initio} calculations. Due to the rarity of slow magnetic relaxation in TBP Fe(II), even under an applied dc field, we stress the importance of minimising the geometric distortion in order to generate a large axial magnetic anisotropy while also minimising the rhombic magnetic anisotropy.

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Conflicts of interest

There are no conflicts to declare.

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