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A Diferrous Single-Molecule Magnet

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The diferrous complex [Fe_2(acpypentO)$(NCO)_3$] (**1**), (acpypentO^- = the anion of 1,5-bis[2-pyridyl(1-ethylimino)]pentane-3-ol) was studied by spectroscopic (dual-mode X-band EPR and ^{57}Fe-Mössbauer) and magnetic (AC magnetic susceptibility) techniques. Complex **1** (A. K. Boudalis et al., *Inorg. Chem.* **2004**, *43*, 1574) was previously shown to exhibit an intramolecular ferromagnetic coupling with important single-ion anisotropies with marked differences in the single-ion electronic parameters of the two iron sites. In this contribution, additional studies are carried out to probe its dynamic magnetic properties. Mössbauer spectra recorded at liquid helium temperatures indicate slow paramagnetic relaxation and a ground state of the system characterized by a non-Kramers doublet with an Ising-type anisotropy, a condition which favours single-molecule magnet (SMM) behaviour. A frequency-dependent out-of-phase signal observed below 3 K in AC susceptibility measurements is in line with such a picture. The out-of-phase signal, however, is relatively weak in comparison with the in-phase signal. Dual mode X-band EPR spectroscopy revealed characteristic signals, the analysis of which suggests inhomogeneities in the system. For some molecules, the splitting Δ_0 of the non-Kramers ground doublet is vanishingly small, which gives rise to out-of-phase signals in AC susceptibility measurements and magnetically split Mössbauer spectra in the absence of external magnetic fields. Other molecules, however, are characterized by a non-negligible Δ_0, which gives rise to the dual mode X-band EPR signals. For these molecules the magnetic relaxation is fast.

Introduction

Molecule-based magnetic materials have been a field of intense scientific research during the past decades. A reason for their increasing interest both to chemists and physicists is that molecular objects like complexes (0D) or chains (1D), which otherwise are best described by quantum mechanics, display phenomena like slow magnetic relaxation, usually seen in classical magnetic materials. These classical phenomena are observed alongside purely quantum phenomena like quantum tunnelling of the magnetization (QTM) thus bridging the classical (macroscopic) and the quantum (microscopic) worlds. In this field, single-molecule magnets (SMMs) and single-chain magnets (SCMs) are classes of molecules that have generated much excitement because they exhibit both slow magnetic relaxation and Arrhenius kinetics due to strong uniaxial anisotropy, without experiencing 3D magnetic ordering.

Since the first observation of the SMM phenomenon for the dodecanuclear manganese cluster [$Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4$], many other clusters have been shown to exhibit the same phenomenon, with nuclearities reaching 84, as observed in the giant $\{Mn_{84}\}$[1] torus reported by Christou et al. The maximum ground spin-state ever attained is 83/2 reported for a $\{Mn_{19}\}$ complex by Powell et al.[2] However, smaller molecules have been reported to exhibit slow relaxation of their magnetization, like mononuclear Co^{II}[3,4] and Ln^{III} (Ln = Tb, Dy) complexes[5] or dinuclear Fe^{III},[6] Mn^{III},[7] Tb^{III}–Cu^{II}[8] and Fe^{III}–Dy^{III}[9] clusters. These species are particularly interesting as their small size allows us to study their electronic properties with exact methods, and fewer approximations. It is thus possible to correlate their observable behaviour with more fundamental parameters and to subsequently gain insight into the behaviour of larger systems. Moreover, they allow us to envisage applications concerning memory recording at the smallest scale.[10]

Dinuclear complexes comprising high-spin ferrous ions have been synthesized and studied as synthetic models for the active sites of metalloenzymes.[11] In a number of cases, ferromagnetic interactions have been observed that result in magnetic ground states.[12] Moreover, electron paramagnetic resonance (EPR) and Mössbauer spectroscopy indicate that the ground state is characterized by a non-Kramers doublet with an Ising-type magnetic anisotropy. This special feature, in combination with the relatively large spin, is one of the requirements for a molecule to exhibit single-molecule magnetic behaviour.

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Recently, we reported the synthesis and physical characterization of a series of polynuclear Fe^{II} complexes including the dinuclear species $[Fe_2(acpypentO)(NCO)_3]$ (**1**),[13] where acpypentO$^-$ is the anion of 1,5-bis[2-pyridyl(1-ethylimino)]pentane-3-ol (Figure 1). This complex was found to contain two pentacoordinate Fe^{II} ions bridged by one alkoxido oxygen belonging to the ligand, and one end-on cyanato anion. Analysis of the thermal variation of the $\chi_M T$ product of **1** indicated that the two $S = 2$ spins are ferromagnetically coupled with $J = 3\,cm^{-1}$. In addition, the analysis of the magnetic susceptibility measurements indicated the critical involvement of zero-field splitting interactions. Under appropriate conditions, these interactions might eventually lead to an important anisotropy of the ground state. Indeed, the two Fe^{II} ions showed important differences in their axial and rhombic single-ion anisotropies with $D_1 = 1.6\,cm^{-1}$, $E_1 = -0.35\,cm^{-1}$ ($\lambda_1 = 0.22\,cm^{-1}$) and $D_2 = -12.2\,cm^{-1}$, $E_2 = 1.1\,cm^{-1}$ ($\lambda_2 = 0.09\,cm^{-1}$).

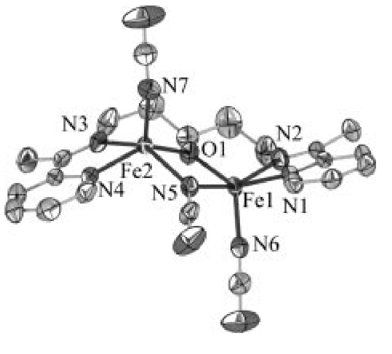

Figure 1. Molecular structure of complex **1**.

With these in mind, we considered it worthy to examine the properties of the ground state of this system in more detail and to monitor its dynamic magnetic properties at low temperatures. Taking into account the ferrous nature and the high reactivity of this dinuclear complex with dioxygen, we considered Mössbauer and X-band EPR (⊥ and ∥ modes) spectroscopy to be the most appropriate techniques for elucidating the properties of its ground state.

Mössbauer Spectroscopy

The Mössbauer spectra at temperatures above liquid nitrogen consist of two quadrupole-split doublets attributed to the two different irons sites of the molecule. At 78 K, the two ferrous sites are characterized by $\delta_1 = 1.01\,mm\,s^{-1}$, $\Delta E_{Q1} = 2.27\,mm\,s^{-1}$ and $\delta_2 = 1.01\,mm\,s^{-1}$, $\Delta E_{Q2} = 3.38\,mm\,s^{-1}$.[13] The temperature dependence of the isomer shifts above 78 K is attributed to the second-order Doppler effect whereas the dependence of the quadrupole splitting values is typical for high-spin ferrous ions.

In the present work, we study spectra recorded at temperatures below 78 K. Representative spectra are shown in Figure 2. In the temperature range 10–78 K, there is no significant variation of the doublets: the two sites exhibit almost temperature-independent isomer shifts and quadrupole splittings. For temperatures below 10 K, the spectra exhibit line-broadening and a spectrum with magnetic features is observed at 4.2 K. These spectra look slightly different from those recorded previously[13] *essentially* because of a remarkable sensitivity related to a strong dependence of the relaxation times on temperature below 7 K.

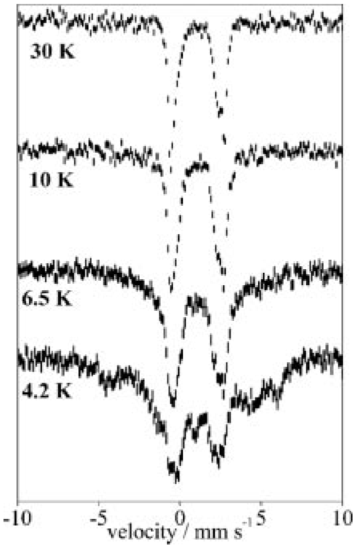

Figure 2. Zero-field Mössbauer spectra from a powdered sample of **1** at liquid helium temperatures.

From DC magnetic susceptibility measurements, no evidence for long-range effects were observed, which suggests that the magnetically split spectrum at 4.2 K is due to slow paramagnetic relaxation. The Mössbauer spectra are in line with the magnetic susceptibility measurements, which indicate ferromagnetic coupling between the ferrous ions. In the case of antiferromagnetic coupling, the ground state would be diamagnetic ($S_T = 0$) and quadrupole-split doublets would be observed in zero-field at liquid helium temperatures. The magnetic ground state of **1** is further supported by spectra recorded in the presence of applied magnetic fields.

Figure 3 shows the Mössbauer spectra of a powdered sample of **1** in the presence of external magnetic fields up to 5.0 T applied perpendicularly to the γ-rays. Clearly, the magnetically perturbed spectra are incompatible with an $S_T = 0$ ground state.[12d] Useful information may be derived by considering the dependence of the spectra on the strength of the applied magnetic field. This can be visualized by following the shift of the absorption peak at ca. $-4.5\,mm\,s^{-1}$ in the zero-field spectrum. This peak does not shift further to more negative velocities under a 0.55 T field, but its intensity increases. For higher magnetic fields, this peak shifts *inwards*, which indicates that the external magnetic field opposes the intrinsic one. This indicates that the internal magnetic field has reached saturation for a relatively small external magnetic field (vide infra). This overall behaviour implies a number of properties regarding the nature of the electronic ground state of the system as commented next.

The ^{57}Fe Mössbauer spectra of high-spin ferrous compounds usually exhibit fast spin relaxation even at liquid helium temperatures and in such a case quadrupole-split

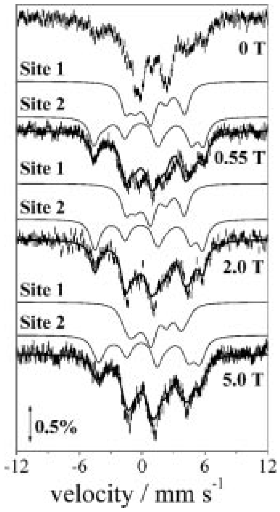

Figure 3. Mössbauer spectra of a powdered sample of **1** at 4.2 K in the absence and in the presence of external magnetic fields applied perpendicular to the γ-rays. Continuous lines are theoretical simulations obtained by assuming two different ferrous sites as described in the text. The contribution of each site is shown separately.

doublets are observed. However, slow paramagnetic relaxation effects were observed in the spectra of a number of high-spin ferrous compounds.[14] The magnetic spectra resulting from paramagnetic relaxation are related with non-Kramers doublets exhibiting a significant Ising-type anisotropy. The magnetically split spectra at zero external magnetic field are due to mixing between the electronic and nuclear spin states.[15] On the contrary, the Mössbauer spectra associated with singlets from such systems consist of quadrupole-split doublets.[16] The non-Kramers character of the ground state with an Ising-type anisotropy is further supported by simulations of the Mössbauer spectra described in a subsequent section.

Dynamic Magnetic Properties

The Mössbauer spectroscopic results presented above indicate that the ground state of complex **1** is characterized by a uniaxial doublet. This, in combination with the nominally high spin of the system, encouraged us to investigate the possibility of slow magnetic relaxation phenomena in **1**, using AC magnetic susceptibility (Figure 4). Indeed, the out-of-phase data clearly show a frequency-dependent signal below ca. 3 K, which indicates the occurrence of slow relaxation phenomena. The maximum of the signal was not observed down to 2 K, which was the lower limit of our SQUID facility. This hampered us from carrying out a quantitative analysis of the relaxation phenomena, but it was clear evidence for the onset of slow magnetic relaxation. Rough estimations may be obtained by considering the following.[17,18h] From the temperature dependence of the zero-field spectra, we may assume that at 4.2 K the spin relaxation time $\tau \approx 10^{-7}$–10^{-8} s, the characteristic time of the Mössbauer spectroscopy.[17d] From the AC susceptibility data we may estimate that at 2 K, $\tau \approx 10^{-3}$ s. Assuming an Arrhenius dependence of τ ($\tau = \tau_0 e^{\Delta E/kT}$), we estimate $\tau_0 \approx 10^{-11}$–10^{-13} s and $\Delta E < 40$ K (28 cm^{-1}). Under a zero applied static field, and for a 250 Hz oscillating field, the $\chi_M{}'T$ product at 2 K was 9.72 cm^{3}mol^{-1} K, which is close to the expected value on the basis of the analysis of the DC susceptibility data.[13] Upon raising the static magnetic field, there is a decrease in the $\chi_M{}'T$ product that is due to the increased splitting of the Zeeman states. This is similar to the sudden drop of the $\chi_M T$ product at low temperatures, as evidenced in the DC data.[13]

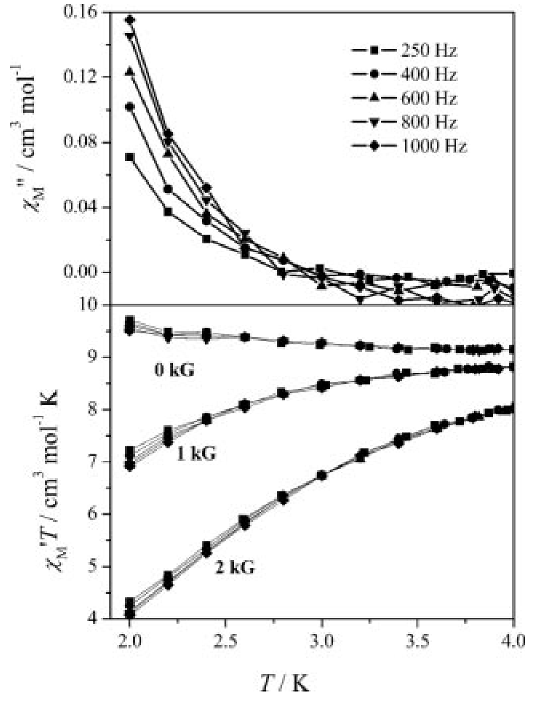

Figure 4. Out-of-phase, $\chi_M{}''$ vs. T, AC magnetic susceptibility data for complex **1** (top) under a zero static magnetic field and with oscillating frequencies of 250, 400, 600, 800 and 1000 Hz. The effect of the static magnetic field on the in-phase signals is depicted in the $\chi_M{}'T$ vs. T curves (bottom), for fields of 1 and 2 kG.

The imaginary component of the ac susceptibility signal is rather small (≈3.5% of the real part). This is not unprecedented as many molecules exhibiting SMM behaviour have a similarly weak χ''/χ' ratio.[18] A possible origin for this behaviour might be the existence of heterogeneities concerning the relaxation properties of the molecules. Namely, a fraction of the molecules is characterized by slow relaxation whereas another fraction is relaxing fast, as further commented below.

The pertinent spin Hamiltonian that describes the magnetic properties of **1** is depicted in Equation (1).[19]

$$\hat{H}_1 = -2J\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 + \sum_{i=1}^{2}\left[D_i\left(\hat{S}_{z,i}^2 - 2\right) + E_i\left(\hat{S}_{x,i}^2 - \hat{S}_{y,i}^2\right) + \beta\hat{\mathbf{S}}_i\mathbf{g}_i\mathbf{H}\right] \quad (1)$$

In the case of axial symmetry ($E = 0$), the ground state of the system is characterized by a non-Kramers doublet with an Ising-type anisotropy. In this case, slow relaxation might be favoured. If, however, rhombic distortions ($E \neq 0$) are present, the degeneracy of the non-Kramers doublet splits by an amount Δ_0[20] and in this case, fast relaxation may occur through quantum tunnelling effects.[21] The existence of molecules for which Δ_0 is nonzero can be monitored by dual-mode X-band EPR spectroscopy (vide infra).

Dual-Mode EPR Studies

For an isolated non-Kramers doublet, intradoublet transition is expected provided that the transition probability $P \neq 0$. Because $P \approx \Delta_0^2$, no signals are observed in the case of $\Delta_0 \approx 0$, whereas signals are observed for $0 < \Delta_0 < h\nu$ ($h\nu \approx 0.3$ cm^{-1} at X-band). In Figure 5, we show X-band EPR spectra of a powdered sample of **1** recorded at 4.2 K. Strong signals are observed in the low-field region in both the parallel and perpendicular modes. No signals attributable to half-integer spin systems are observed (i.e. a "$g \approx 4.3$" signal at ≈1500 G), which indicates that the samples are not oxidized. The signals exhibit saturation effects at 4.2 K and decrease as the temperature increases. The latter indicates that the signals arise from the ground state.

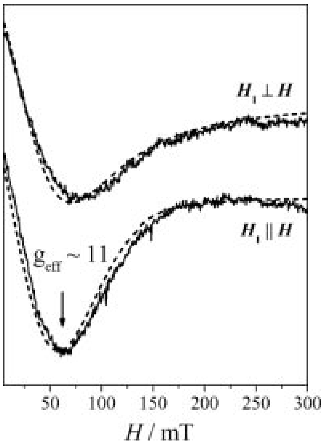

Figure 5. Dual-mode X-band EPR spectra for a powdered sample of **1** at 4.2 K under nonsaturating conditions. Dashed lines are theoretical simulations obtained as described in the text. EPR conditions: Microwave power: 0.13 mW, modulation amplitude: 1.0 mT, microwave frequency: 9.60 (perpendicular mode), 9.36 GHz (parallel mode).

The line-shape of the EPR signals is consistent with an integer spin system[22] as expected for **1**. The EPR properties of diferrous complexes have been extensively studied by Hendrich et al.[11,23] The dashed lines superimposed above the experimental spectra are simulated spectra considering an effective $S = 4$ spin Hamiltonian [Equation (2)].[24]

$$\hat{H}_2 = D\left(\hat{S}_z^2 - 20/3\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) + \beta\hat{\mathbf{S}}\mathbf{g}\mathbf{H} \qquad (2)$$

Satisfactory simulations were obtained with different sets of parameters [from Equation (1)] that is, there is not a unique set of parameters for simulating the spectra. However, these different sets result in a unique description regarding the magnetic properties of the doublet giving rise to the signal.[24] The signal arises from transitions within a non-Kramers doublet with uniaxial magnetic properties which is split by an amount $\Delta_0 \approx 0.3$ cm^{-1} at zero field.[23a,20] To account properly for the line shape of the EPR spectra, a Gaussian distribution of Δ_0 with an apparent width $\sigma\Delta_0 = 0.06$ cm^{-1} must be incorporated. The Δ_0 distribution is due to a distribution of parameters such as D, E and J. Alternatively, solid-state effects may effectively lead to line broadening. As a conclusion, the results from dual mode X-band EPR spectroscopy indicate that the system contains molecules for which Δ_0 is nonnegligible.

Simulations of the Mössbauer spectra

It was noticed that the analysis of Mössbauer spectra from diferrous complexes is not trivial when the zero-field splitting terms and the exchange coupling constant are of comparable magnitude[12a,12d,25] because the number of parameters involved is large. Therefore, a unique set of parameters cannot be obtained unambiguously. A complete analysis of the spectra was not pursued; however, we checked whether the behaviour of the magnetically perturbed Mössbauer spectra is consistent with the results from X-band EPR spectroscopy discussed above. The EPR spectra were analyzed within the framework of Hamiltonian in Equation (2) and it was found that the ground non-Kramers doublet of the system is characterized by a distributed Δ_0, centred at 0.3 cm^{-1}.

For the magnetically perturbed Mössbauer spectra we assumed two sites at a 1:1 ratio and we used the effective spin Hamiltonian $\hat{H}_3$ for $S = 4$ (strong exchange limit) [Equation (3)]:

$$\hat{H}_3 = \hat{H}_2 + \sum_{i=1,2}\left[\hat{\mathbf{S}}\tilde{\mathbf{A}}_i\hat{\mathbf{I}}_i - g_n\beta_n\hat{\mathbf{I}}_i\mathbf{H} + \hat{H}_{Q,i}\right] \qquad (3)$$

with [Equation (4)]:

$$\hat{H}_{Qi} = \frac{eQV_{\zeta\zeta}}{12}\left[3\hat{I}_{\zeta i}^2 - \frac{15}{4} + \eta_i\left(\hat{I}_{\xi i}^2 - \hat{I}_{\eta i}^2\right)\right] \qquad (4)$$

where (ξ, η, ζ) designates the principal axis system of the electric field gradient (EFG) tensor and where $\eta_i = (V_{\xi\xi i} - V_{\eta\eta i})/V_{\xi\xi i}$ is the asymmetry parameter. Equation (3) is written in the coupled representation.

For the isomer shift and quadrupole splittings we used the values obtained from the zero-field spectra recorded at 78 K (δ_1 = 1.01 mm s^{-1}, ΔE_{Q1} = 2.27 mm s^{-1} and δ_2 = 1.01 mm s^{-1}, ΔE_{Q2} = 3.38 mm s^{-1}). For the parameters involved in the electronic part of Hamiltonian $\hat{H}_2$ we used the values from the analysis of the EPR spectra.[24] The splittings observed in the magnetically perturbed spectra reflect a total magnetic field acting on the ^{57}Fe nucleus, $\mathbf{H} = \mathbf{H}_{\text{appl}} + \mathbf{H}_{\text{int}}$ where the internal field is given by Equation (5).

$$\mathbf{H}_{\text{int}} = -\frac{\langle \hat{\mathbf{S}}_i \rangle \tilde{\mathbf{A}}_i}{g_n \beta_n} \tag{5}$$

For the given zero-field splitting values *D*, *E*/*D*, the easy axis of magnetization is *y* for the ground non-Kramers doublet, and the magnetically perturbed Mössbauer spectra at liquid helium temperature are sensitive only on $\langle \hat{S}_{yi} \rangle$. Therefore, as far as the hyperfine tensor of the ferrous ions is concerned, only the A_{yi} components may be estimated. The spectra recorded at different magnetic fields can be reasonably reproduced with a common set of parameters (Figure 3) with A_{y1} = –6.2 MHz and A_{y2} = –10.2 MHz. With this model, the characteristic feature at –4.5 mm s^{-1} observed in the low-field spectra belongs to the spectrum from site 2.

It is inferred that the magnetically perturbed spectra are consistent with the dual-mode X-band EPR results. For non-Kramers systems, saturation of the internal magnetic field, $\mathbf{H}_{\text{int}}$, requires the application of an external magnetic field, $\mathbf{H}_{\text{ext}}$, the value of which depends on Δ_0 (Figure 6). For $\Delta_0 = 0$, a very small magnetic field suffices to saturate H_{int}. In that case, a characteristic magnetic Mössbauer spectrum is observed. In the present case, a magnetic spectrum is already observed in the absence of external magnetic fields. We assume that this spectrum arises from a fraction of molecules for which Δ_0 is vanishingly small. Application of a moderate magnetic field (0.55 T) induces an intensity increase in the ca. –4.5 mm s^{-1} peak. We suggest that this increase arises from molecules that require an external magnetic field to induce saturation of $\mathbf{H}_{\text{int}}$ and therefore for these molecules $\Delta_0 \neq 0$.

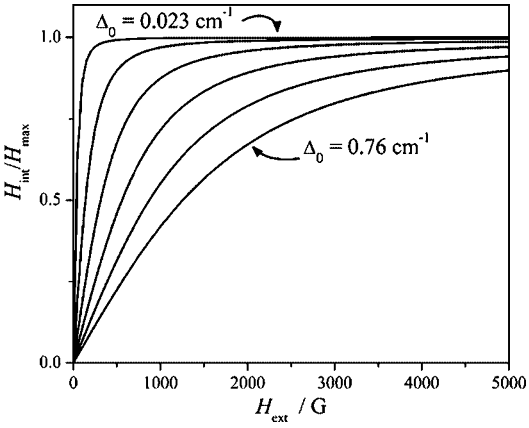

Figure 6. Dependence of the $H_{\text{int}}/H_{\text{sat}}$ ratio on the externally applied magnetic field along the easy axis (H_{ext}) for a non-Kramers doublet with various Δ_0 values (0.023, 0.090, 0.200, 0.352, 0.540 and 0.760 cm^{-1}).

Discussion and Conclusions

In the present work we study the dynamic magnetic behaviour of differous compound **1** by applying AC susceptibility measurements and dual mode X-band EPR and Mössbauer spectroscopic techniques. The incentive for this study stems from the bulk DC magnetic measurements which revealed ferromagnetic interactions between the two ferrous ions leading to a ground state with a relatively large nominal spin.[13] AC susceptibility measurements presented herein indicate slow relaxation effects at liquid helium temperatures.

The combined results from the present studies offer an explanation for the relaxation behaviour of **1**. We suggest that the molecules are characterized by inhomogeneities which eventually affect the splitting of the non-Kramers ground doublet. For a fraction of molecules, Δ_0 is negligible (ideally 0), which gives rise to the magnetically split Mössbauer spectrum at zero-field. Because the quantum tunnelling rate is proportional to Δ_0, these molecules are expected to have slow relaxation properties and cause an out-of-phase AC signal. On the contrary, a fraction of the molecules appears to be characterized by significant Δ_0 as deduced by the dual mode X-band EPR measurements. For these molecules, quantum tunnelling is expected to be favoured, which results in fast relaxation. We should stress that as a result of the molecular nature of **1**, these inhomogeneities must be at the molecular level, that is, not discernible by X-ray crystallography.

In assessing the origin of the slow magnetic relaxation in **1**, one might readily argue that the relatively high effective spin of the ground state in combination with a high uniaxial magnetic anisotropy established by spectroscopic techniques leads to an SMM behaviour. However, we explored the possibility that slow relaxation might stem from an SCM behaviour due to weak intermolecular interactions.[26] The packing diagram of **1** (Figure S1) revealed weak π–π interactions between pyridyl rings of the ligand in adjacent molecules (2 – *x*, 1 – *y*, 1 – *z*), but not the presence of 1D chains.[27] This finding excludes to possibly attribute the observed slow relaxation to single-chain magnetism; thus, the slow relaxation must be related to superparamagnetism. From this point of view, **1** can be viewed as a rare example of an iron(II) single-molecule magnet, with the only other examples being three {Fe$_4$} cubanes prepared by Oshio et al.[28] and the enneanuclear complex [Fe$_9$(O$_2$CMe)$_8${(py)$_2$CO$_2$}$_4$(N$_3$)$_2$].[29] Further originality of this compound stems from the fact that the two Fe$^{\text{II}}$ centres have different ligand field symmetries.

In the literature, several examples of diferrous complexes exhibiting ferromagnetic interactions yielding a magnetic ground state exist. To the best of our knowledge, **1** is the first for which the spin dynamics has been monitored directly by AC susceptibility and slow relaxation was observed. It would be interesting to explore the possibility of slow magnetic relaxation in other similar diferrous complexes as well. A majority of these complexes, apart from DC susceptibility measurements, were studied by spectroscopic techniques, which give additional information regarding the nature of the ground state. We showed here that Mössbauer spectroscopy is a useful technique, which can probe whether the ground state satisfies the conditions for slow relaxation. We suggest that observation of a magnetically split spectrum in the absence of applied magnetic field (not arising from long-range magnetic ordering) indicates that these complexes may be suitable SMM candidates. On the contrary, quadrupole-split doublets are related either to singlets, fast relaxation ($<10^{-7}$ s), or non-Kramers doublets with relatively large zero-field splitting, Δ_0. For the cases found in the literature, quadrupole-split doublets have been observed at liquid helium temperatures: these complexes are thus unlikely candidates for slow magnetic relaxation.

The above discussion may be extended to ferrous complexes of higher nuclearity. We have recently observed single-molecule magnet behaviour for enneanuclear ferrous compounds.[29] In these cases, magnetically split Mössbauer spectra are observed in the absence of an applied magnetic field as a result of slow paramagnetic relaxation in the temperature range 4.2–10 K. At present, we are not aware of relevant studies for the cubanes reported by Oshio et al.[28]

In the present work we report the first example of a diferrous single-molecule magnet and a rare example of ferrous SMM. In addition, we probe the relaxation mechanism through various techniques and show that owing to molecular-level inhomogeneities, slow relaxation requirements are fulfilled for a fraction of the molecules only. This realization is particularly important for molecular species, which are generally considered as "monodisperse". Although it is reasonable to assume that this situation may occur in other SMMs as well, its verification in the present system was possible mainly due to the probing of its ground state and relaxation mechanism through techniques like AC susceptibility and Mössbauer and dual-mode X-band EPR spectroscopy.

Experimental Section

Complex **1** was synthesized as described previously.[13] Mössbauer measurements were recorded with a constant-acceleration conventional spectrometer with a 50 mCi source of ^{57}Co (Rh matrix). The absorber was a powdered sample enclosed in a 20-mm diameter cylindrical plastic sample holder, the size of which was determined to optimize the absorption. To avoid oxidation of the sample, the sample holder was sealed with Araldite and stored in liquid nitrogen. Variable-temperature spectra were obtained in the 4.2–300 K range, by using Oxford cryostats, operating at 4.2–300 K. One cryostat was equipped with a superconducting magnet that allowed application of external magnetic fields up to 5.0 T perpendicular to the γ-rays. Isomer shift values (δ) are relative to iron foil at 293 K. The magnetically perturbed spectra were analyzed with the WMOSS software package (WEB Research, Edina, MN). Variable-temperature (2.0–5.0 K) AC magnetic susceptibility data were collected from a powdered microcrystalline sample with a Quantum Design MPMS SQUID susceptometer. The sample was moulded into a pellet inside the glove box to avoid orientation in the magnetic field. Data were corrected with the standard procedure for the contribution of the sample holder and diamagnetism of the sample. X-band EPR measurements were carried out with a Bruker ER-200D spectrometer equipped with a Bruker Dual Mode cavity, an Anritsu frequency counter, an NMR Gaussmeter and an Oxford ESR-9 cryostat. EPR tubes were flame-sealed under vacuum to avoid air-oxidation of the sample. ***Caution:*** *Molten quartz generates large amounts of harmful UV radiation, thus proper eye-protection should be worn.* Simulations of the spectra were carried out with SpinCount software kindly provided to us by Prof. M. Hendrich, Dept. of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA.

Supporting Information (see footnote on the first page of this article): Packing diagram of **1**, which shows the intermolecular π–π interactions.

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[1] A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2004**, *43*, 2117–2121.

[2] A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem. Int. Ed.* **2006**, *45*, 4926–4929.

[3] S. Karasawa, G. Zhou, H. Morikawa, N. Koga, *J. Am. Chem. Soc.* **2003**, *125*, 13676–13677.

[4] S. Kanegawa, S. Karasawa, M. Nakano, N. Koga, *Chem. Commun.* **2004**, 1750–1751.

[5] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694–8695.

[6] R. Schenker, M. L. Leuenberger, G. Chaboussant, H. U. Güdel, D. Loss, *Chem. Phys. Lett.* **2002**, *358*, 413–418.

[7] a) H. Miyasaka, R. Clérac, W. Wernsdorfer, L. Lecren, C. Bonhomme, K.-I. Sugiura, M. Yamashita, *Angew. Chem. Int. Ed.* **2004**, *43*, 2801–2805; b) Z. Lü, M. Yuan, F. Pan, S. Gao, D. Zhang, D. Zhu, *Inorg. Chem.* **2006**, *45*, 3538–3548; c) C. Kachi-Tarajima, H. Miyasaka, K. Sugiura, R. Clérac, H. Nojiri, *Inorg. Chem.* **2006**, *45*, 4381–4390; d) C.-H. Ge, A.-L. Cui, Z.-H. Ni, Y.-B. Jiang, L.-F. Zhang, J. Ribas, H. Z. Kou, *Inorg. Chem.* **2006**, *45*, 4883–4885.

[8] J.-P. Costes, F. Dahan, W. Wernsdorfer, *Inorg. Chem.* **2006**, *45*, 5–7.

[9] M. Ferbinteanu, T. Kajiwara, K.-Y. Choi, H. Nojiri, A. Nakamoto, N. Kojima, F. Cimpoesu, Y. Fujimara, S. Takaishi, M. Yamashita, *J. Am. Chem. Soc.* **2006**, *128*, 9008–9009.

[10] M. Cavallini, J. Gomez-Segura, D. Ruiz-Molina, M. Massi, C. Albonetti, C. Rovira, J. Veciana, F. Biscarini, *Angew. Chem. Int. Ed.* **2005**, *44*, 888–892.

[11] E. Tshuva, S. Lippard, *Chem. Rev.* **2004**, *104*, 987–1012.

[12] a) A. S. Borovik, M. P. Hendrich, T. R. Holman, E. Münck, V. Papaefthymiou, L. Que Jr, *J. Am. Chem. Soc.* **1990**, *112*, 6031–6038; b) A. Stassinopoulos, G. Schulte, G. C. Papaefthymiou, J. P. Caradonna, *J. Am. Chem. Soc.* **1991**, *113*, 8686–8697; c) Y. Zang, H. G. Jang, Y.-M. Chiou, M. P. Hendrich, L. Que Jr, *Inorg. Chim. Acta* **1993**, *213*, 41–48; d) A. Stubna, A. D.-H. Jo, M. Costas, W. W. Brenessel, H. Andres, E. L. Bominaar, E. Münck, L. Que Jr, *Inorg. Chem.* **2004**, *43*, 3067–3079.

[13] A. K. Boudalis, J. M. Clemente-Juan, F. Dahan, J.-P. Tuchagues, *Inorg. Chem.* **2004**, *43*, 1574–1586.

[14] a) H. N. Ok, *Phys. Rev.* **1969**, *185*, 472–476; b) V. Petrouleas, A. Simopoulos, A. Kostikas, *Phys. Rev. B* **1975**, *12*, 4675–4681; c) D. C. Price, C. E. Johnson, I. Maartense, *J. Phys. C: Solid State Phys.* **1977**, *10*, 4843–4853; d) C. Nicolini, W. M. Reiff, *Inorg. Chem.* **1980**, *19*, 2676–2679; e) K. K. P. Srivastava, *J. Phys. C: Solid State Phys.* **1983**, *16*, L53–L55; f) F. F. Charron, W. M. Reiff, *Inorg. Chem.* **1986**, *25*, 2786–2790; g) B. D. Howes, D. Creagh, D. C. Price, *J. Phys. C: Solid State Phys.* **1988**, *21*, 2439–2451; h) P. Garge, R. Chikate, S. Padhye, J.-M. Savariault, P. de Loth, J.-P. Tuchagues, *Inorg. Chem.* **1990**, *29*, 3315–3320; i) M. A. Martinez-Lorente, F. Dahan, Y. Sanakis, V. Petrouleas, A. Bousseksou, J.-P. Tuchagues, *Inorg. Chem.* **1995**, *34*, 5346–5357; j) W. M. Reiff, A. M. LePointe, E. H. Witten, *J. Am. Chem. Soc.* **2004**, *126*, 10206–10207; k) K. L. Taft, A.

Caneschi, L. E. Pence, C. D. Delfs, G. C. Papaefthymiou, S. J. Lippard, *J. Am. Chem. Soc.* **1993**, *115*, 11753–11766.

[15] K. K. Surerus, M. P. Hendrich, P. D. Christie, D. Rottgardt, W. H. Orme-johnson, E. Münck, *J. Am. Chem. Soc.* **1992**, *114*, 8579–8590.

[16] a) J. Chappert, G. Jehanno, F. Varret, *J. Phys. Paris* **1977**, *38*, 411–418; b) Y. Sanakis, P. P. Power, A. Stubna, E. Münck, *Inorg. Chem.* **2002**, *41*, 2690–2696.

[17] a) A.-L. Barra, P. Debrunner, D. Gatteschi, C. E. Shulz, R. Sessoli, *Europhys. Lett.* **1996**, *35*, 133; b) A. Caneschi, L. Cianchi, F. Del Gallo, D. Gatteschi, P. Moretti, F. Pieralli, G. Spina, *J. Phys.: Condens. Matter* **1999**, *11*, 3395–3403; c) L. Cianchi, F. Del Giallo, G. Spina, W. M. Reiff, A. Caneschi, *Phys. Rev. B* **2002**, *65*, 064415; d) P. Gütlich, R. Link, A. Trautwein in *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer, Berlin, Heidelberg, New York, **1978**.

[18] a) C. Dendrinou-Samara, M. Alexiou, C. M. Zaleski, J. W. Kampf, M. L. Kirk, D. P. Kessissoglou, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2003**, *42*, 3763–3766; b) S. Wang, J.-L. Zuo, H.-C. Zhou, H. J. Choi, Y. Ke, J. R. Long, X.-Z. You, *Angew. Chem. Int. Ed.* **2004**, *43*, 5940–5943; c) H. J. Choi, J. J. Sokol, J. R. Long, *Inorg. Chem.* **2004**, *43*, 1606–1608; d) M. Murugescu, J. Raftery, W. Wernsdorfer, G. Christou, E. K. Brechin, *Inorg. Chem.* **2004**, *43*, 4203–4209; e) P. King, W. Wernsdorfer, K. A. Abboud, G. Christou, *Inorg. Chem.* **2004**, *43*, 7315–7323; f) E. M. Rumberger, S. J. Shah, C. C. Beedle, L. N. Zakharov, A. L. Rheingold, D. N. Hendrickson, *Inorg. Chem.* **2005**, *44*, 2742–2752; g) Y. Li, W. Wernsdorfer, R. Clérac, I. J. Hewitt, C. E. Anson, A. K. Powell, *Inorg. Chem.* **2006**, *45*, 2376–2378; h) J. van Slageren, P. Rosa, A. Caneschi, R. Sessoli, H. Casellas, Y. V. Rakitin, L. Cianchi, F. Del Giallo, G. Spina, A. Bino, A.-L. Barra, T. Guidi, S. Carretta, R. Caciuffo, *Phys. Rev. B* **2006**, *73*, 014422.

[19] a) R. C. Reem, E. I. Solomon, *J. Am. Chem. Soc.* **1987**, *109*, 1216–1226; b) A. Bencini A, D. Gatteschi, *EPR of Spin Coupled Systems*, Springer, New York, **1991**.

[20] In the strong exchange limit where we may assume that the ground state is characterized by $S = 4$, $\Delta_0 \approx (35/16)|D|(E/D)^4$ for $D < 0$. In the case of weak ferromagnetic coupling between two equivalent ferrous sites, $\Delta_0 \approx \Delta\iota^2/16|J|$ with $\Delta\iota = 3|D_i|(E_i/D_i)^2$ ($i = 1,2$).[18a]

[21] F. Hartmann-Boutron, *J. Phys. I* **1995**, *5*, 1281–1300.

[22] M. P. Hendrich, P. G. Debrunner, *Biophys. J.* **1989**, *56*, 489–506.

[23] a) M. P. Hendrich, L. L. Pearce, L. Que Jr, N. D. Chasteen, E. P. Day, *J. Am. Chem. Soc.* **1991**, *113*, 3039–3044; b) M. P. Hendrich, E. Münck, B. G. Fox, J. D. Lipscomb, *J. Am. Chem. Soc.* **1990**, *112*, 5861–5865; c) H. G. Jang, M. P. Hendrich, L. Que Jr, *Inorg. Chem.* **1993**, *32*, 911–918; d) M. P. Hendrich, E. D. Day, C.-P. Wang, B. S. Synder, R. H. Holm, E. Münck, *Inorg. Chem.* **1994**, *33*, 2848–2856.

[24] Although Equation (1) is more appropriate in the present case, Equation (2) suffices to describe the X-band EPR spectra from the ground-state non-Kramer's doublet of **1**. The simulations shown in Figure 5 were obtained with $D = +2.97\ \text{cm}^{-1}$, $E/D = 0.21$, $\sigma_{E/D} = 0.0241$, $g = 2.0$ and an intrinsic linewidth of 2.4 mT.

[25] B. G. Fox, M. P. Hendrich, K. K. Surereus, K. K. Andersson, W. A. Froland, J. D. Lipscomb, E. Münck, *J. Am. Chem. Soc.* **1993**, *115*, 3688–3701.

[26] N. Chakov, W. Wernsdorfer, K. A. Abboud, G. Christou, *Inorg. Chem.* **2004**, *43*, 5919–5930.

[27] In the original paper it was inadvertently noted that **1** forms pairs of 1D chains through π–π interactions in the crystal lattice. This was not detrimental to the discussion of its magnetic properties to that particular direction, but for the purposes of the present work a more careful structural analysis was carried out. This revealed that **1** actually forms pairs of molecules through π–π stacking.

[28] a) H. Oshio, N. Hoshino, T. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 12602–12603; b) H. Oshio, N. Hoshino, T. Ito, M. Nakano, *J. Am. Chem. Soc.* **2004**, *126*, 8805–8812.

[29] A. K. Boudalis, B. Donnadieu, V. Nastopoulos, J. M. Clemente-Juan, A. Mari, Y. Sanakis, J.-P. Tuchagues, S. P. Perlepes, *Angew. Chem. Int. Ed.* **2004**, *43*, 2266–2270, and manuscript in preparation.

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