

Cite this: *Chem. Sci.*, 2019, 10, 1626

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Rare “Janus”-faced $\{\text{Fe}^{\text{II}}\}$ single-molecule magnet exhibiting intramolecular ferromagnetic interactions†

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A rare $[\text{Fe}^{\text{II}}(\text{N}_3)_{12}(\text{MeCN})_{12}](\text{ClO}_4)_2$ disk-like single-molecule magnet (SMM) exclusively bridged by end-on azides with a spin ground state of $S = 14$ was prepared by the reaction of a divalent Fe^{II} precursor with Me_3SiN_3 under basic conditions. AC magnetic susceptibility studies revealed unusual, “Janus”-faced SMM behavior for the dried and pristine forms of the $\{\text{Fe}^{\text{II}}\}$ compound attributed to solvation/de-solvation effects of the coordinated MeCN ligands which leads to alterations in the crystal field and symmetry of the metal ions. DFT calculations confirmed the ferromagnetic nature of the interactions between the Fe^{II} spin carriers with the zero-field splitting parameters $D = -0.2323 \text{ cm}^{-1}$ and $E/D = 0.027$. The results have important implications for the future study of single-molecule magnets incorporating volatile solvent molecules in the first coordination sphere of the metal ions and their effect on the relaxation dynamics.

Received 3rd October 2018
Accepted 3rd November 2018

DOI: 10.1039/c8sc04384a

rsc.li/chemical-science

Introduction

Single-molecule magnets (SMMs) are coordination compounds that exhibit slow relaxation of their magnetization at the molecular level,¹ a property that renders them suitable candidates for emerging technologies including high density data storage,² molecular electronic devices,³ and quantum computation.⁴ In the quest for strongly-coupled polynuclear SMMs with enhanced properties, one of the most difficult challenges to overcome is the combination of a large spin ground state (S) with a large and negative zero-field splitting parameter, as defined by the axial parameter, D .¹ To this end, bridging ligands have played a special role in not only fostering ferromagnetic exchange interactions between the metal ions they bridge, through either a superexchange⁵ or direct mechanism,⁶ but also in controlling the orientation of the magnetic anisotropy axes⁷ and stabilizing microstates with the largest spin and orbital angular momenta.⁸

In recent years 4f metal containing molecules have attracted considerable interest in the SMM field vis-à-vis enhancing the magnetization dynamics (*i.e.*, large energy barriers and

blocking temperatures).⁹ The progress in this area notwithstanding, there are limitations including effective quantum tunneling of the magnetization at zero field and weak-to-negligible magnetic exchange interactions due to the efficient shielding of the 4f orbitals by the outer 5s and 5p-orbitals.¹⁰ Given these issues, 3d metal based SMMs of oligo- and polynuclear complexes are still worth pursuing.¹¹

The syntheses of transition metal molecules with interesting magnetic properties often relies on self-assembly reactions between 3d-metal precursors and organic chelating/bridging ligands.^{11b} This strategy has afforded a plethora of SMMs with modest barriers but also some of the most spectacular and well-known SMMs to date including the ubiquitous $\{\text{Mn}_{12}\}$ -carboxylate¹² and $\{\text{Mn}_6\}$ -oximate complexes,¹³ and, recently, a nano-sized $\{\text{Mn}_{31}\}$ cluster¹⁴ and a low-coordinate $\{\text{Co}_4\}$ compound,¹⁵ all with high energy barriers and blocking temperatures. Unlike Mn compounds, Fe-based SMMs are scarce in the literature. Only a few trivalent Fe^{III} SMMs¹⁶ have been reported to date and divalent Fe^{II} examples are limited to three examples, *viz.*, an $\{\text{Fe}_2^{\text{II}}\}$,¹⁷ a family of $\{\text{Fe}_4^{\text{II}}\}$ cubanes,¹⁸ and a nonanuclear $\{\text{Fe}_9^{\text{II}}\}$ compound.¹⁹ Although organic bridging ligands assist in the thermodynamic stability, solubility, and crystallinity of 0-D compounds, their presence as neutral linkers often limits the magnetic properties and dynamics of SMMs, leading to competing magnetic interactions, moderate-to-weak magnetic couplings, and low-lying excited states, among others.^{11-14,16-19} A potential solution to these obstacles in preparing molecules with large S values and enhanced SMM properties is the discovery of new synthetic avenues to 3d compounds with exclusively ferromagnetic couplers.

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† Electronic supplementary information (ESI) available: Spectroscopy data, crystallographic data and tables, and magnetism details. CCDC 1850963. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc04384a



The IR spectra of both **1-w** and **1-d** are depicted in Fig. S1† as a single superimposed image illustrating: (i) the presence of end-on bridging N_3^- groups (IR bands $\sim 2100\text{ cm}^{-1}$),²⁷ and (ii) the de-solvation of **1** as evidenced by the disappearance of the IR bands attributed to MeCN molecules of the wet-sample ($2280\text{--}2310\text{ cm}^{-1}$).²⁸ Unfortunately, the potentially explosive nature of **1** owing to the presence of a large number of azido groups as well as ClO_4^- anions, renders the use of the TGA technique impossible as an additional tool for the study of the solvation/de-solvation effects of **1**.

Structural determination

The centrosymmetric heptanuclear cation in compound **1** (Fig. 1, top) consists of a nearly ideal planar hexagon of alternating Fe^{II} ions surrounding a central Fe^{II} atom, reminiscent of the known Anderson-type structure.²⁹ The oxidation states of the metal ions and the formula of **1** were determined by inspection of the metrical parameters (Table S2†), bond valence sum (BVS) calculations (Table S3†), and charge balance considerations. The $\{\text{Fe}_7\}$ disk-like unit possesses virtual S_6 symmetry and is stitched together by twelve nitrogen atoms of six $\mu_3\text{-}1,1,1$ and six $\mu\text{-}1,1$ end-on bridging azido ligands. The $\mu_3\text{-}1,1,1$ azides bridge the $\{\text{Fe}_6\}$ hexagon with the central Fe^{II} ion, while the $\mu\text{-}1,1$ azides link the Fe centers in the outer ring to form the hexagon. Peripheral ligation is completed by twelve terminal MeCN molecules, two on each of the external Fe^{II} ions. All Fe^{II} ions are six-coordinate with nearly octahedral geometries. All of the Fe–N bond distances fall into the expected range for compounds of high-spin Fe^{II} ions with N-donor atoms.³⁰

The $[\text{Fe}_7(\mu_3\text{-N}_3)_6(\mu\text{-N}_3)_6]^{2+}$ inorganic core of **1** (Fig. S2†) can also be described as consisting of six $\{\text{Fe}_3(\text{N}_3)_4\}$ partial-cubane units, each double face-sharing and which share six vertices with the central Fe^{II} ion. Complex **1** exhibits a layered structure, with layers of N atoms from azide and MeCN ligands situated above and below the $\{\text{Fe}_7\}$ plane (Fig. 1, middle). The intra-molecular Fe...Fe separations and Fe–($\mu\text{-N}_3$)–Fe angles span the range 3.336–3.354 Å and 95.6–104.9°, respectively. Several magnetostructural correlations for azido-bridged systems, especially for Cu^{II} , Ni^{II} and Mn^{II} complexes, have been developed and discussed in terms of the exchange interactions between non-orthogonal magnetic orbitals.^{20,21} Importantly, the $\text{M}^{\text{II}}\text{-N}_3(\text{EO})\text{-M}^{\text{II}}$ angles affect the nature and strength of the superexchange interactions. For divalent 3d metal complexes with EO bridging N_3^- ligands, the angle for switching from ferro- to antiferromagnetic coupling is typically $>104^\circ$. Exchange interactions between the Fe^{II} ions in **1** (av. Fe–N–Fe angle = 99.2°) are therefore expected to be ferromagnetic on the basis of the structural parameters.^{19–21} The packing of the $\{\text{Fe}_7\}$ cations in the crystal (Fig. 1, bottom) lead to large separations between Fe^{II} ions of neighboring molecules, with the closest intermolecular Fe...Fe contact being ~ 8 Å owing to the coordinated MeCN molecules.

Magnetic susceptibility data for 1-d

Variable-temperature direct-current (DC) magnetic susceptibility measurements were initially performed on a sample of **1-**



Fig. 1 Labelled representation of the cation in complex **1** (top), a side view of the $\{\text{Fe}_7\}$ cluster (middle), and a packing diagram of the cations, viewed along the crystallographic c -axis (bottom). Color scheme: Fe^{II} yellow, N blue, C dark gray, H light gray. Symmetry operation for the primed atoms: $1 - x, -y, 1 - z$.

d in the temperature range 2–300 K under an applied field of 1 kG (0.1 T). The $\chi_{\text{M}}T$ versus T plot is depicted in Fig. 2. The value of $\chi_{\text{M}}T$ at 300 K is $26.43\text{ cm}^3\text{ mol}^{-1}\text{ K}$, higher than the value of $21\text{ cm}^3\text{ mol}^{-1}\text{ K}$ (calculated with $g = 2$) expected for seven high-spin Fe^{II} ($S = 2$) non-interacting ions. The $\chi_{\text{M}}T$ value rapidly increases in the 300–22 K region, reaching a maximum of $104.61\text{ cm}^3\text{ mol}^{-1}\text{ K}$, and then decreases to a value of $72.16\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 2 K. The shape of the curve suggests an overall ferromagnetic system; the low- T decrease is attributed to the



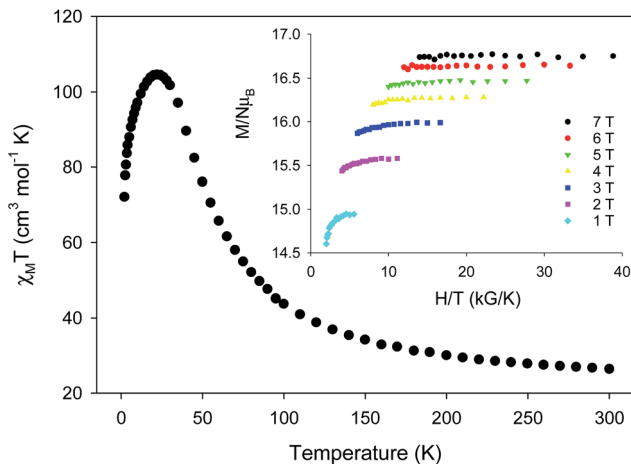


Fig. 2 Temperature dependence of $\chi_M T$ for **1-d** at 0.1 T. (inset) Magnetization (M) versus field (H) and temperature (T) data, plotted as reduced magnetization ($M/N\mu_B$) versus H/T , for **1-d** at applied fields of 1–7 T and in the 1.8–5 K temperature range.

presence of significant zero-field splitting in the ground state and/or antiferromagnetic intermolecular exchange interactions between neighboring cations. The $\chi_M T$ maximum value of $104.61 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 22 K indicates an $S = 14$ ground state, the maximum possible value for a ferromagnetically-coupled $\{\text{Fe}_7^{\text{II}}\}$ complex; the spin-only ($g = 2$) value for a state with $S = 14$ is $105 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Reduced magnetization studies performed on **1-d** at different fields and low temperatures (Fig. 2, inset) clearly indicate the presence of magnetic anisotropy as the various isofield lines do not superimpose onto a master curve expected for a system with a well-isolated spin ground state and negligible anisotropy. The magnetization curves fall substantially short of reaching the magnetization saturation of $28 \mu_B$ expected for an $S = 14$ ground state with $g = 2$, also an indication of magnetic anisotropy.

To probe the magnetization dynamics of **1-d**, alternating-current (AC) magnetic susceptibility measurements, as a function of both temperature (Fig. 3, top) and frequency (Fig. 3, middle and S3†), were performed under a zero applied dc field. Interestingly, the dried form of the $\{\text{Fe}_7^{\text{II}}\}$ compound displays frequency dependent in-phase (χ'_M) and out-of-phase (χ''_M) signals, which are entirely resolved, at two different temperature regions. The peak maxima for **1-d** in the low- T (1.8–2.6 K) and high- T (2.7–5 K) regimes exhibit similar intensities (Fig. 3, inset) and they do not overlap with each other. This is indicative of two individual relaxation processes, which both appear to be thermally assisted. The data were fit to obtain relaxation times (τ) for the respective ac frequencies (1–933 Hz; 37 frequencies in total) and the T_{max} of the peaks (Fig. 3, inset). The data were then fit to the Arrhenius law [$\ln \tau = \ln \tau_0 + U_{\text{eff}}/k_B T$], where U_{eff} is the effective energy barrier for the magnetization reversal and k_B is the Boltzmann constant, resulting in the parameters $U_{\text{eff}} = 43.7(1) \text{ K}$ and $\tau_0 = 4.2(1) \times 10^{-10} \text{ s}$, and $U_{\text{eff}} = 21.9(2) \text{ K}$ and $\tau_0 = 1.1(2) \times 10^{-8} \text{ s}$ for the high- and low temperature regimes, respectively (Fig. 3, bottom). The pre-exponential factor, τ_0 , is usually within the 10^{-6} to 10^{-10} s range for SMMs and it



Fig. 3 (top) Out-of-phase (χ''_M) ac magnetic susceptibility signals for **1-d** at zero dc field. (inset) χ''_M versus T plot at a representative ac frequency of 933 Hz showing the two separate relaxation processes at two different T regions; the solid blue lines represent fits of the data. (middle) Frequency dependence of the χ''_M component at different temperatures (2.5–5.0 K) for **1-d** at zero dc field; the solid lines are the best fits to the generalized Debye model. (bottom) Arrhenius plot of the relaxation times (τ) for **1-d**; the blue and red lines correspond to the fit of the high- and low- T regions, respectively.

provides a quantitative measure of the attempt time of relaxation from the thermal phonon bath.

The Cole–Cole plots (Fig. S4†) of **1-d** exhibit two sets of semicircular shapes at different temperatures; the data were fit using a generalized Debye model.³¹ The α -values for each set of low- and high-temperature data are in the range 0.26–0.38 and 0.13–0.39, respectively, suggesting the presence of multiple relaxation processes. The same magnetic results were reproduced three times from independent samples of **1** that were dried under the same conditions. The presence of two



thermally-assisted relaxation processes is a rare phenomenon in polynuclear 3d-metal SMMs and, to the best of our knowledge, has only been previously observed for a few members of the $\{\text{Mn}_{12}\}$ family of SMMs as a result of the 'Jahn-Teller isomerism' effect.³²

Magnetic susceptibility data for 1-w

The unusual emergence of two distinct relaxation processes in **1-d** prompted us to investigate the magnetic properties of the wet (as-prepared) crystalline form of **1-w** to measure a sample in which the coordinated and interstitial MeCN molecules are intact. The freshly prepared crystalline sample of **1-w** was immediately transferred and sealed in an NMR tube which was immediately used for the acquisition of the reported magnetic data. DC magnetic susceptibility studies for **1-w**, including $\chi_{\text{M}}T$ versus T (Fig. S5†) and reduced magnetization (Fig. S6†) studies, revealed a response similar to **1-d** and an $S = 14$ ground state. The only noticeable difference is the decrease of the $\chi_{\text{M}}T$ product at a lower temperature of 10 K as compared to **1-d**.

AC magnetic susceptibility studies as a function of both temperature (Fig. 4, top) and frequency (Fig. 4, middle) carried out for **1-w** led to the observation of a single slow relaxation of the magnetization below ~ 3 K. The χ_{M}'' versus frequency data were fit to a generalized Debye model to extract the corresponding relaxation times. The data were then fit to the Arrhenius law (Fig. 4, bottom), yielding the parameters: $U_{\text{eff}} = 14.1(2)$ K and $\tau_0 = 3.3(2) \times 10^{-7}$ s. Cole-Cole plots of **1-w** exhibit semicircular shapes at different temperatures below 3 K and the fit of the data gave α -values in the 0.12–0.37 range, indicating a wide distribution of relaxation times (Fig. S7†). The magnetic results of **1-w** are also reproducible, and the measurements were performed with two different wet samples of **1**. In addition, the AC magnetic dynamics of both **1-d** and **1-w** were also studied under an applied DC field of 0.1 T, but no noticeable differences were observed regarding the number of relaxation processes and magnitude of energy barriers.

Computational studies

The experimental magnetic susceptibility data for **1** were not fit due to the large size and low symmetry of the complex. Thus, the exchange interactions and magnetic anisotropy of **1** were determined using DFT calculations in order to evaluate the observed magnetic behavior. This strategy has been previously employed in a family of $\{\text{Mn}_7\}$ disk-like complexes, where the metal ions were bridged by organic groups, and it was able to reproduce very accurately the experimental findings.^{35c} The exchange topology used for the computational calculations for **1** is shown in Fig. 5 (left). The following exchange Hamiltonian was employed to evaluate the magnetic exchange interactions (J) in **1**.

$$\begin{aligned} \hat{H} = & -[2J_1(S_{\text{Fe}1}S_{\text{Fe}2} + S_{\text{Fe}1}S_{\text{Fe}3} + S_{\text{Fe}1}S_{\text{Fe}4} + S_{\text{Fe}1}S_{\text{Fe}5} \\ & + S_{\text{Fe}1}S_{\text{Fe}6} + S_{\text{Fe}1}S_{\text{Fe}7}) + 2J_2(S_{\text{Fe}2}S_{\text{Fe}3} + S_{\text{Fe}3}S_{\text{Fe}4} \\ & + S_{\text{Fe}4}S_{\text{Fe}5} + S_{\text{Fe}5}S_{\text{Fe}6} + S_{\text{Fe}6}S_{\text{Fe}7} + S_{\text{Fe}2}S_{\text{Fe}7})] \end{aligned} \quad (1)$$



Fig. 4 (top) Out-of-phase (χ_{M}'') ac magnetic susceptibility signals for **1-w** at zero dc field; the solid lines are guides for the eye. (middle) Frequency dependence of χ_{M}'' at different temperatures for **1-w** at zero dc field; the solid lines are best fits to the generalized Debye model. (bottom) Arrhenius plot of τ versus $1/T$ for **1-w**; the solid line is the best fit as described in the text.

To extract the exchange interactions on the full structure of **1**, the energies of three different spin configurations were used (Table S4†).³³ The exchange coupling constants were calculated using the broken symmetry (BS) approach developed by Noodleman.³⁴ This method has been employed extensively to compute good numerical estimates of exchange interactions in numerous polynuclear complexes.³⁵ DFT calculations were performed using the B3LYP basis functional³⁶ and Aldrich's triple- ζ -quality basis set³⁷ with the Gaussian 09 program.³⁸

Apart from the magnetic coupling, the ZFS (D) has also been computed for complex **1** using the Orca 3.0 programme suite.³⁹ In our DFT calculations, the spin-orbit coupling operators are represented by an effective one electron, using the spin-orbit mean field (SOMF) method as implemented in Orca.³⁹ We have





Fig. 5 (left) Magnetic exchange pathways in complex **1**; see the text for the DFT computed values. (right) DFT-computed spin-density plots for **1** for which all spins are up, rationalizing the experimental $S = 14$ ground state. The pink and blue colours represent positive and negative spin densities, respectively.

used the coupled perturbed (CP) SOC approach to evaluate the spin-orbit contribution to D (D_{SOC}). The spin-spin contribution (D_{SS}) was estimated by using the unrestricted natural orbital⁴⁰ approach. Furthermore, to improve the accuracy of the estimated D values, relativistic corrections are performed using the DKH method.³⁹

The coupling between the central and the outer Fe^{II} ions is designated as the J_1 interaction and the coupling between the two outer ring Fe^{II} ions is described as J_2 interaction. The DFT computed values predict that both the J_1 and J_2 interactions are ferromagnetic with values of $+3.0$ and $+3.3 \text{ cm}^{-1}$, respectively. Ferromagnetic coupling is consistent with the observation of ferromagnetic interactions in dinuclear $\text{Ni}(\text{II})$, $\text{Fe}(\text{III})$ and $\text{Mn}(\text{II})$ complexes with one or more μ -bridging azido ligands⁴¹ and in the azido-bridged $\{\text{Ni}_7\}$ and $\{\text{Co}_7\}$ disk-like complexes.²¹ Given that both J_1 and J_2 interactions are ferromagnetic, the ground state is $S = 14$. The computed spin density plots (Fig. 5, right) reveal a dominant spin delocalization mechanism. Calculations were performed also by using the diamagnetic substitution method (DSM), where, except for the desired pair of Fe^{II} centres, the remaining ions are substituted by diamagnetic Zn^{II} ions.^{35c,42} Such calculations are essential for validating the J values computed from the full structure and to realize the influence of other paramagnetic centres on a particular J value. This method also yields ferromagnetic coupling constants for both interactions ($J_1 = +3.1$ and $J_2 = +4.5 \text{ cm}^{-1}$) which are in excellent agreement with the full cluster coupling values.

Given the large ground state spin value and the observed slow relaxation of the magnetization for **1** at zero DC field, one would expect a negative D value for the molecule, thus the value of D was computed to further probe the SMM behavior. Although *ab initio* CASSCF/NEVPT2 calculations have proven to yield accurate estimates of D values,⁴³ this method cannot be employed for such large molecules.⁴⁴ The full cluster anisotropy was therefore computed using DFT methods which yielded the parameters $D = -0.2323 \text{ cm}^{-1}$ and $E/D = 0.027$, where E is the rhombic zero-field splitting parameter. The D_{SOC} plays a key role with a value of -0.191 cm^{-1} . The major contributions to D_{SOC} arise from DOMO (doubly-occupied molecular orbital) to SOMO (singly-occupied MO) $\beta \rightarrow \beta$ excitations (-0.127 cm^{-1}) and

SOMO to SOMO $\alpha \rightarrow \beta$ excitations (-0.072 cm^{-1}). The SOMO to VMO (Virtual Molecular Orbital) $\alpha \rightarrow \alpha$ excitations and DOMO to VMO $\beta \rightarrow \alpha$ excitations contribute to a small extent with values of 0.003 and 0.005 cm^{-1} , respectively.⁴⁵ Comparable behavior is observed for D_{SS} contributions of -0.04 cm^{-1} .

Magnetic properties of 1-d versus 1-w

The differences in the magnetic properties of **1-d** versus **1-w**, as indicated by the low temperature regimes of the $\chi_{\text{M}}T$ versus T plots and the AC magnetic susceptibility data, are due, in part, to the changes in intermolecular interactions between the individual $\{\text{Fe}_7^{\text{II}}\}$ molecules. The intermolecular distances in **1-w** are expected to be larger due to the presence of all of the MeCN ligands (Fig. 1, bottom). In the case of **1-d**, the drying process results in the removal of MeCN molecules and the $\{\text{Fe}_7^{\text{II}}\}$ cations are expected to be less well separated in the solid state. Moreover, the molecular magnetic anisotropy of **1** is expected to deviate from **1-w** to **1-d** due to the dissimilar coordination environment of the six peripheral Fe^{II} ions. In **1-w**, all of the Fe^{II} ions are six-coordinate with a distorted octahedral geometry. In **1-d**, however, drying leads to loss of coordinated MeCN molecules and the peripheral Fe^{II} ions will be primarily four-coordinate. These low-coordinate Fe^{II} ions are expected to exhibit larger single-ion magnetic anisotropies which, in turn, effects the global molecular anisotropy.⁴⁶ For example, complete removal of all twelve bound MeCN molecules in **1** would render the six external Fe^{II} ions four-coordinate with slightly distorted see-saw geometries (CShM values = 0.82 – 0.85 , C_{2v} point group; Fig. S8 and Table S5[†]). In support of this contention is the fact that large uniaxial magnetic anisotropy and slow magnetization relaxation with high energy barriers have been reported for a family of four-coordinate, trigonal pyramidal Fe^{II} -pyrrolide complexes with C_{3v} point group symmetry.⁴⁷ Therefore, the crystal field around four-coordinate Fe^{II} ions in **1-d** would induce increased molecular magnetic anisotropy for this system and consequently a larger energy barrier than for **1-w**. It is also possible that the two ClO_4^- anions found in the elemental analyses of **1-d** are bound to the Fe^{II} centers. Although rare,^{48a-c} terminally coordinated ClO_4^- ions are of precedence in Fe^{II} chemistry, and this is also expected to affect the crystal field and coordination geometries of some of the outer Fe^{II} ions in **1-d**. On a final note, the shift (ΔT_{max}) in the χ''_{M} peak maximum temperature (T_{max}) with AC frequency (f) was measured by a parameter $\phi = (\Delta T_{\text{max}}/T_{\text{max}})/\Delta(\log f)$. For the dried sample, **1-d**, we obtained $\phi = 0.11$ – 0.19 and 0.17 – 0.22 for the high- and low- T regions, which are both within the range of normal superparamagnets, thereby excluding the possibility of a spin glass state.^{48d}

Conclusions and outlook

In summary, the synthesis of a rare, ferromagnetically-coupled $\{\text{Fe}_7^{\text{II}}\}$ (**1**) disk-like cluster with an $S = 14$ ground state and unusual “Janus”-faced SMM behavior has been found to exhibit different AC magnetic dynamics in the dried (**1-d**) versus wet (**1-w**) forms of the crystals. Such a rare phenomenon in 3d-cluster



SMMs is primarily rationalized in terms of the loss or presence of coordinated/interstitial MeCN molecules in **1-d** or **1-w**, respectively. The $[\text{Fe}_7(\text{N}_3)_{12}]^{2+}$ core is present in both forms of **1**, as confirmed by X-ray diffraction studies (for **1-w**), elemental analyses (for **1-d**) and DC magnetic studies ($S = 14$ for both forms). The different number of relaxation processes (two for **1-d** and one for **1-w**) and values of energy barriers for the magnetization reversal are attributed to differences in intermolecular interactions⁴⁹ and the dissimilar molecular anisotropies emanating from different crystal fields around the peripheral Fe^{II} ions.

These results underscore the importance of solvation/desolvation effects on the structural and magnetic properties of polynuclear metal complexes and the sensitivity of magnetic dynamics upon altering the first coordination sphere of 3d-metal ions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

K. R. D. gratefully acknowledges support for this work by the National Science Foundation (CHE-1808779) and the Robert A. Welch Foundation (Grant A-1449). The SQUID magnetometer was purchased with funds provided by the Texas A&M University Vice President of Research. We are grateful to the HPRC at Texas A&M for the computing resources. Th. C. S. thanks NSERC-DG, ERA and Brock Chancellor's Chair for Research Excellence.

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