

Encapsulation of a Cr(III) Single-Ion Magnet within an Fe(II) Spin-Crossover Supramolecular Host.

Mohanad Darawsheh^[a], Leoní A. Barrios^[a,d], Olivier Roubeau,^{[b]*} Simon J. Teat,^[c] and Guillem Aromí.^{[a,d]*}

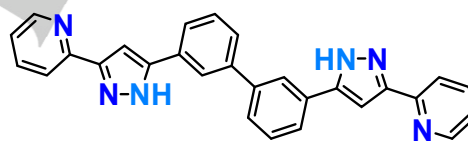
Abstract: Single functional molecules are regarded as future components of nanoscale spintronic devices. Supramolecular coordination chemistry provides unlimited resources to implement multiple functions to individual molecules. Here, we demonstrate that a novel coordination [Fe₂] helicate exhibiting spin-crossover is ideally suited to encapsulate a [Cr(ox)₃]³⁻ complex anion (ox=oxalate), unveiling for the first-time single ion slow relaxation of the magnetization for this metal. A possibility of tuning the dynamics of this relaxation as well as the performance of the Cr(III) center as qubit arises from the observation that metastable high spin Fe(II) centers from the host can be generated by irradiation with green light at low temperature.

One of the current goals in supramolecular chemistry is generating molecules as operative components of nanoscale devices.^[1-2] Such components must be capable of performing functions in response to the appropriate external stimuli. In this context, efforts are devoted to implement single-molecule memory units,^[3-5] quantum bits^[6-7] or switches.^[8-11] A promising strategy for incorporating useful properties into molecular objects is through encapsulation of responsive guests within functional hosts. In the area of coordination supramolecular chemistry, a few remarkable reports show the inclusion of complexes inside discrete coordination chemistry frameworks sometimes enhancing the properties of one or both components of the assembly.^[12-17]

This appears as a convenient approach for influencing the dynamic properties of the magnetization of single-ion magnets (SIMs). The latter are molecules constituted by one sole open-shell metal ion (3d,^[4, 18] 5d,^[19-20] 4f^[5] or 5f^[21-22]) that exhibit slow relaxation of the electronic spin magnetization. However, the only precedent of an encapsulated SIM did not result in any improvement of the slow relaxation dynamics.^[23] We present a

flexible ligand, L (Scheme 1), designed to interact with Fe(II) ions and form [Fe₂L₃]⁴⁺ helicates featuring a large cavity and, predictably,^[24] spin crossover (SCO) behavior.^[25-26] Combining Fe(II) salts and ligand L with chromium oxalate, the encapsulation of a [Cr(ox)₃]³⁻ (ox = oxalate) coordination complex (with S = 3/2) inside the [Fe₂L₃]⁴⁺ helicate was achieved. In this environment, this guest shows field induced slow relaxation of the magnetization, which has never been manifested for Cr(III).

The ligand 3,3'-bis(3-(pyridin-2-yl)-1H-pyrazol-5-yl)-1,1'-biphenyl (L, Scheme 1) was obtained by closing through nucleophilic attacks by hydrazine, the 1,3-dicarbonyl groups of the bis-β-diketone obtained after a double Claysen condensation between 3,3'-diacetylbiphenyl and ethylpicolinate (Fig. S1). The analogue to L with a phenylene spacer had furnished SCO [Fe₂] helical architectures capable of encapsulating halide anions as guests.^[27-28]



Scheme 1. Molecular structure of ligand L, 3,3'-bis(3-(pyridin-2-yl)-1H-pyrazol-5-yl)-1,1'-biphenyl.

Diffusing a solution of Fe(BF₄)₂ and L in methanol into a DMF solution of K₃[Cr(ox)₃] and 18-crown-ether produces crystals of the supramolecular assembly [Cr(ox)₃]@[Fe₂L₃]BF₄ (**1**) after four weeks. Compound **1** crystallizes in the *P*2₁/*c* space group with an asymmetric unit containing one [Fe₂L₃]⁴⁺ helicate encapsulating a [Cr(ox)₃]³⁻ complex anion (Fig. 1, Table S1). The overall positive charge is compensated by a BF₄⁻ anion, which is accompanied, in the asymmetric unit at 100 K, by two (sometimes partially occupied) molecules of MeOH and six of water, the unit cell enclosing four such ensembles.

The helical architecture of [Fe₂L₃]⁴⁺ is reached after three L ligands chelate two Fe(II) ions, one at each end, providing them with their conventional octahedral coordination, and thanks to their flexibility. The latter is ensured by rotations around the five C–C bonds that connect pairwise a total of six aromatic rings. Thus, the dihedral angles between pairs of adjacent rings in the assembly average 39.28° (phen-phen), 19.76° (phen-pz) 11.37° (pz-py), with phen, pz and py being phenylene, pyrazolyl and pyridyl, respectively. The central [Cr(ox)₃]³⁻ complex exhibits the expected octahedral geometry with conventional Cr–O bonds ranging 1.964 to 1.991 Å of length. The slight dispersion in bond distances is because the guest does not contain any

[a] Dr. M. Darawsheh, Dr. L. A. Barrios, Dr. G. Aromí
Departament de Química Inorgànica i Orgànica
Universitat de Barcelona
Diagonal 645, 08038 Barcelona (Spain)
E-mail: guillem.aromi@qi.ub.es

[b] Dr. O. Roubeau
Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC and
Universidad de Zaragoza
Plaza San Francisco s/n, 50009 Zaragoza (Spain)
E-mail: roubeau@unizar.es

[c] Dr. S. J. Teat
Advanced Light Source, Berkeley Laboratory
Cyclotron Road, Berkeley, CA 94720 (USA)

[d] Dr. L. A. Barrios, Dr. G. Aromí
Institute of Nanoscience and Nanotechnology (IN2UB)
Universitat de Barcelona

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crystallographic symmetry element. Likewise, the crystal lattice causes both Fe centers of the host to be inequivalent. Thus, both supramolecular Cr...Fe separations within the helical entity differ slightly (5.426 and 5.281, for Fe1 and Fe2, respectively). The host-guest recognition takes place through six strong O...H-N hydrogen bonds between the inner set of oxygen atoms of the Cr(III) complex and perfectly disposed pyrazolyl moieties of the L ligands (Table S2). These interactions are stronger near Fe2 than on the opposite site, as inferred from the values shown in Table S2. The oxalate groups reach radially the exterior of the cage through the three lateral crevices and establish O...H-O hydrogen bonds with MeOH or H₂O molecules (Fig. S2). These contacts contribute to establish 2D networks of interactions connecting the [Cr(ox)₃]³⁻ moieties to each other (Fig. S3). The [Fe₂L₃]⁴⁺ hosts establish mutual and weak C-H...π interactions. Mass spectrometry experiments demonstrate the persistence of the host-guest complex in DMF/acetonitrile solution, as indicated by the presence prominent signals for ([Cr(ox)₃][Fe₂L₃])⁺ (m/z=1749.27), ([Cr(ox)₃][Fe₂L₃]⁺ + Na⁺)²⁺ (m/z=886.13), and ([Cr(ox)₃][Fe₂L₃]⁺ + H⁺)²⁺ (m/z=875.14) consistent with the expected isotopic distribution (Figs. S4 and S5).

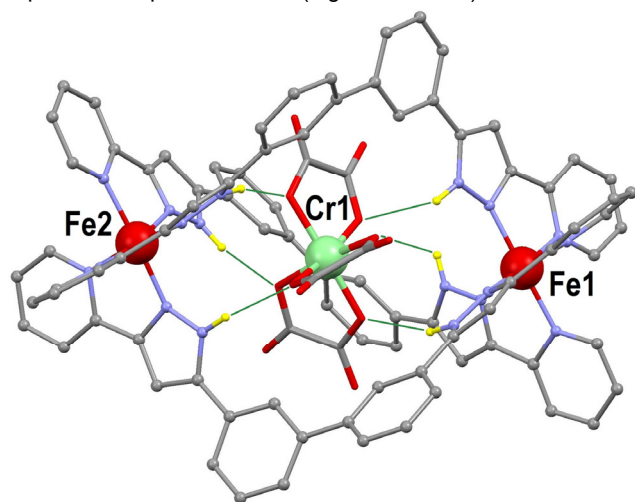


Figure 1. Representation of the supramolecular ([Cr(ox)₃][Fe₂L₃])⁺ cationic moiety of **1**. Only metal atoms are labelled. Color code: gray, C; red sticks, O; purple, N; yellow, H. Only H atoms from N-H groups shown. Green lines are hydrogen bonds.

The chirality of the octahedral coordination moieties within each Cr@Fe₂ assembly defines the handedness of the helical ensemble. Both possibilities are present within the lattice (ie. $\Lambda\Lambda\Lambda$ and $\Delta\Delta\Delta$), which is racemic. At 100 K, the average Fe-N bond distances ($\langle d_{\text{Fe-N}} \rangle$) are 1.96 and 1.98 Å for Fe1 and Fe2, respectively, which shows that at this temperature both metal centers lie in the LS state in agreement with bulk magnetization data (*vide infra*).²⁷ The molecular structure of **1** was determined at eight different temperatures in between 90 and 280 K (SI), revealing that near 280 K a process of desorption of solvate molecules occurs not affecting the single crystal integrity (SI). The data show that Fe2 gradually increases $\langle d_{\text{Fe-N}} \rangle$ with temperature from 1.98 Å below 160 K to 2.13 Å at 280 K, revealing a process of SCO, whereas the other Fe center maintains the average Fe-

N distances near 1.96 Å, thus staying in the LS state (Fig. 2). Different SCO behavior is expected from small variations in the secondary coordination sphere around Fe sites, here in particular leading to H-bonds of varying strengths involving the pyrazole rings. This has been proven in solution studies, to cause slightly differing ligand-field strengths and a shift to SCO temperatures.^[29] In the solid state, however, packing effects become important. For example, differences on the degree of distortion of the octahedral coordination sphere can also be relevant.^[8]

Both components of **1** are magnetically active, and their performance was investigated. The bulk magnetization behavior in the 2-320 K range is represented as a χT vs T curve (Fig. 2). A plateau of χT below near 100 K (at approximately 1.9 cm³Kmol⁻¹) is the result of the Curie-like behavior of an isolated Cr(III), $S = 3/2$ center (expected to yield 1.875 cm³Kmol⁻¹ if $g = 2$), while both Fe(II) centers remain in the diamagnetic LS state. This is consistent with the M vs. H data at 1.8 K, which agree well with a Brillouin function for an $S = 3/2$ spin and $g = 1.97$ (Fig. S6). The slight decrease of χT below 10 K (down to ca. 1.624 cm³Kmol⁻¹) is likely due to the zero-field splitting (ZFS) of Cr(III).^[30-32] Above approximately 120 K, the χT product gradually increases to reach the value of 4.89 cm³Kmol⁻¹ at 300 K, which confirms the SCO of 50% of the Fe(II) centers (the calculated spin-only value of **1** with one Fe(II) in the HS state is 4.875 cm³Kmol⁻¹), with $T_{1/2}$ near 200 K. The curve recorded subsequently, upon cooling, is superimposable to the warming branch over the whole temperature range indicating that the process of solvent desorption does not affect the SCO (see above).

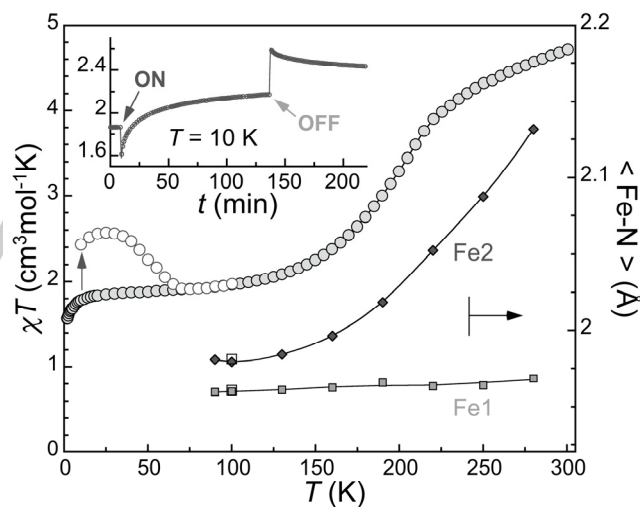


Figure 2. Plot of χT vs. T per mole (full circles) of [Cr(ox)₃][Fe₂L₃]BF₄ (**1**) and temperature dependence of the average Fe-N bond lengths at both Fe sites (full squares). The empty green circles represent χT vs. T upon warming after having irradiated the sample with continuous green light at 10 K. The inset shows a characteristic χT isotherm at 10 K during an obscurity-irradiation-obscurity sequence, as indicated.

Many SCO Fe(II) complexes may be brought to a metastable HS state at low temperature through irradiation. This phenomenon is called light induced excited spin state trapping (LIESST) effect.^[33] In this case, illumination of **1** with green-light at 10 K results in a significant increase of χT by 0.6 cm³Kmol⁻¹ (inset in Fig. 2). The

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latter is reverted upon increasing the temperature, with a T_{LIESST} of ca. 50 K (calculated as the maximum of the derivative of χT with respect to T).^[34] Here, this light-induced transformation, most likely occurring on Fe2, remains incomplete, namely in the order of only 20 % after irradiation for over 2 hours. The lack of completeness may be due to any of the following two effects, *i*) insufficient light penetration due to its absorption by the colored sample and *ii*) competition between excitation and relaxation back to the ground LS state, apparently already significant at 10 K (inset in Fig. 2).

Differential scanning calorimetry measurements (Fig. 3 and SI) show a very broad anomaly associated with the SCO and consistent with the results from magnetometry. Extraction of the lattice heat capacity from the total specific heat provides the energy associated to the SCO, which furnishes reasonable thermodynamic values of $\Delta H_{\text{SCO}} = 5.66 \text{ kJmol}^{-1}$ and $\Delta S_{\text{SCO}} = 30.5 \text{ Jmol}^{-1}\text{K}^{-1}$. An increase in heat capacity above 280K is associated to the solvent desorption observed crystallographically. Subsequent DSC experiments on dried samples confirm that the SCO is independent on the solvation state of the sample.

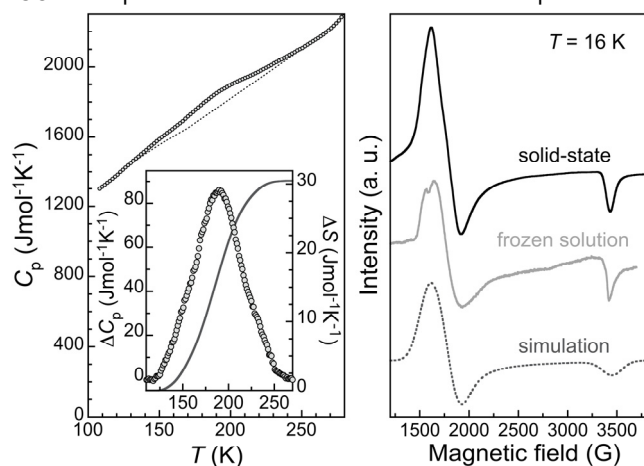


Figure 3. (left) Molar heat capacity at constant pressure of **1** obtained from DSC measurements, with the estimated lattice component shown as a dashed line. The inset shows the derived excess heat capacity (circles) and entropy variation (solid line) associated to the SCO derived from these measurements. (right) Solid state and frozen solution X-band cw-EPR of **1** at 16 K, together with the simulated spectra for $S = 3/2$, $g_x^{\text{eff}} = 4.24$, $g_y^{\text{eff}} = 3.71$, $g_z^{\text{eff}} = 1.94$, $A_x = 157$, $A_y = 283$ and $A_z = 301 \text{ MHz}$, obtained using Easyspin.^[35]

X-band cw-EPR measurements of **1** in the solid state and in frozen solution served to confirm that the low temperature magnetic response of the system (*vide supra*) is solely due to the encapsulated $[\text{Cr}(\text{ox})_3]^{3-}$ guest. Very similar spectra were obtained in both cases, with signals at $g \approx 1.93$ - 1.95 and $g \approx 3.6$ - 4.2 , fully consistent with a Cr(III) ion in a distorted octahedral environment,^[36] and supporting the persistence of the supramolecular assembly ($[\text{Cr}(\text{ox})_3]@[\text{Fe}_2\text{L}_3]^+$) in solution (Fig. 3). The solid-state experiments were performed at variable temperature (4-299 K), the spectra showing almost no variation other than to the intensity (Fig. S7). The lack of contribution from Fe(II) at $T > 120 \text{ K}$ (when a fraction of $S = 2$ centers starts to appear) is expected due to the ZFS, which renders this paramagnetic center EPR silent at the X-band. The spectra at 16

K were simulated (Fig. 3) with Easyspin^[35] ($S = 3/2$ and linewidth of 16 MHz) with the following parameters (in the solid/solution format); $g_x^{\text{eff}} = 4.23/4.24$, $g_y^{\text{eff}} = 3.72/3.71$, $g_z^{\text{eff}} = 1.94/1.94$, $A_x = 155/157$, $A_y = 280/283$ and $A_z = 362/301 \text{ MHz}$, in line with these obtained previously for the $[\text{Cr}(\text{ox})_3]^{3-}$ anion.^[31, 36]

Recent reports have described the performance of the transitions within the $S = 3/2$ manifold of Cr(III) mononuclear complexes as potential qubits for quantum computing.^[30, 37] We thus examined here the relaxation dynamics of the magnetization associated to the spin of the $[\text{Cr}(\text{ox})_3]^{3-}$ guest in **1**. *ac* magnetic susceptibility measurements under zero applied *dc* field showed only hints of the onset of an out-of-phase component of the susceptibility, χ'' , indicating fast zero-field relaxation of the orientation of the molecular magnetic moment. Consequently, frequency-dependent experiments in the 100-10000 Hz frequency range were performed at 1.8 K and various applied *dc* fields in order to determine an optimal field maximizing the spin-lattice relaxation (Fig. S8), which was established in the range of 0.1–0.5 T. Similar experiments were then performed at 1000 Oe and temperatures between 1.9 and 10 K. In the whole range of *dc* fields and temperatures studied, a frequency-dependent response characteristic of a slow relaxation of magnetization is observed, indicative of so-called single-ion magnet behavior. χ''_{max} is always close to twice $\Delta\chi'$ (χ' is the in-phase magnetic susceptibility) as expected, but χ' does not reach zero. This indicates the presence of a much faster relaxation mode for a fraction of the Cr(III) ions. Possibly, this could be a consequence of slight variations of the environment due to differences in the lattice solvent, which does interact directly with the $[\text{Cr}(\text{ox})_3]^{3-}$ moiety through H-bonding. The sensitivity of the zero-field splitting of the $[\text{Cr}(\text{ox})_3]^{3-}$ ion to variations in lattice solvent environment is documented.^[38-39] To extract the characteristic relaxation time τ of the slow relaxation mode, a generalized Debye model was fitted to the χ'' isotherms (Fig 4 and S9). Similar values for τ were obtained by fitting the χ' vs. χ'' data to a Cole-Cole model. Various acoustic phonon processes can participate to the spin-lattice relaxation of non-interacting paramagnetic centers, usually involving direct one-phonon and two-phonon Raman processes, or excitations to energy orbital levels or Orbach process.^[2] The field dependence of τ at 1.8 K is non-monotonous (Fig. 4, top right), with a significant increase up to 0.5 T and a rapid decrease above. This rapid decrease at high fields can reasonably be ascribed to the direct process, which has a H^{-4} field dependence and is dominant at high fields for a Kramers ion, while the low-field increase is likely a consequence of the cancellation of fast relaxation through quantum tunneling or spin-spin interactions. In fact, the data below 0.3 T is close to a H^2 dependence, which has been related to magnetic interactions.^[3] A reasonable simulation of the data (full line in Fig. 4, see SI for details) can be obtained through a phenomenological model used and described previously.^[5]

The temperature dependence of τ at 0.1 T is dominated by the direct mechanism of relaxation, although a temperature-induced process is clearly participating above 5 K (Fig. 4 bottom right). Considering that the zero-field splitting of the m_s levels of the $S = 3/2$ state of the $[\text{Cr}(\text{ox})_3]^{3-}$ ion is too small to give rise to the latter through an Orbach process,^[30] the data were satisfactorily reproduced using the expression

$$\tau^{-1} = aT + bT^n + c$$

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with $a = 1.68 \cdot 10^4 \text{ s}^{-1}$, $b = 109 \text{ s}^{-1}$, $n = 3.1$ and $c = 1.0 \cdot 10^4 \text{ s}^{-1}$. The inclusion of the latter temperature independent term, typically corresponding to a tunneling relaxation path, is necessary to properly reproduce the lower temperature range.

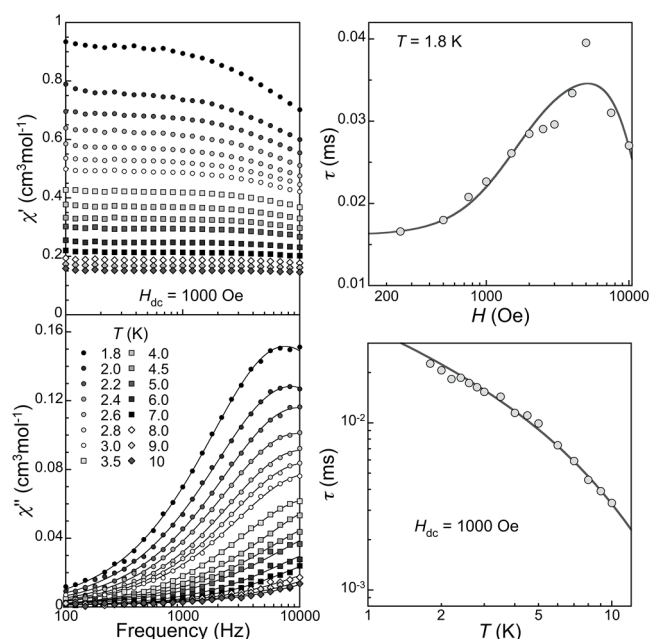


Figure 4. (left) Frequency dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibility of **1** at 0.1 T dc field. The solid lines are fits to the generalized Debye model expression of the imaginary susceptibility data at the indicated temperatures. (right) Field (top, $T = 1.8$ K) and temperature (bottom, $H_{dc} = 0.1$ T) dependence of the characteristic relaxation time τ . Solid lines are fits to respective phenomenological models (see text and SI).

To our knowledge, the observation of slow magnetization dynamics using magnetic susceptibility measurements is unprecedented for an isolated Cr(III) ion. In this respect, we note that the same $[\text{Cr}(\text{ox})_3]^{3-}$ ion in the form of its potassium salt, which is used here as reagent, does not present any signs of slow relaxation of magnetization in the same range of applied dc fields and temperatures studied for **1** (Fig. S9). The observation here of field-induced single-ion magnet behavior of the $[\text{Cr}(\text{ox})_3]^{3-}$ species could therefore be related to steric and electronic effects caused by the $[\text{Fe}_2]$ helicate host. Interestingly, a significant quantum coherence time was demonstrated for this ion in frozen solution through pulsed-EPR spectroscopy, demonstrating its potential as spin qubit.^[30] Determining the performance of encapsulated $[\text{Cr}(\text{ox})_3]^{3-}$ as qubit and the ability of tuning its properties via the LIESST effect of its $[\text{Fe}_2\text{L}_3]^{4+}$ host are two crucial aspects that shall be investigated on this new supramolecular system.

Acknowledgements

G.A. thanks the Generalitat de Catalunya for the prize ICREA Academia 2008 and 2013 and the ERC for a Starting Grant (258060 FuncMolQIP). The authors thank the Spanish MINECO for funding through MAT2014-53961-R (OR) and CTQ2015-

68370-P (GA and LB). MD thanks Avempace II Erasmus Mundus Action 2 program for a PhD scholarship. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

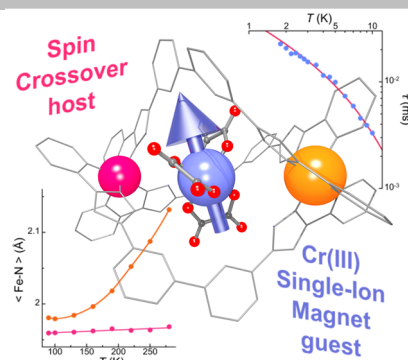
Keywords: Host-guest chemistry, single ion magnet, spin crossover, spintronic devices.

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A spin crossover supramolecular $[\text{Fe}_2\text{L}_3]^{4+}$ helicate (L is a bis-pyridylpyrazolyl ligand) encapsulates a $[\text{Cr}(\text{ox})_3]^{3-}$ (ox=oxalate) complex anion, conferring unprecedented single ion magnet properties to it. The host may be placed in a metastable high spin state using irradiation, suggesting the possibility of externally tuning the functional properties of the guest, via stimulation of the host.



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