

Tuning the spin crossover behavior of the polyanion $[(\text{H}_2\text{O})_6\text{Fe}_3(\mu\text{-L})_6]^{6-}$: the case of the cesium salt

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The magnetic behavior of the polyanion $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$ ($\text{L}^{2-} = (1,2,4\text{-triazol-4-yl})\text{ethanedisulfonate}$) as the corresponding dimethylammonium salt shows memory effect above room temperature, with a dynamic thermal hysteresis cycle over 90 K and temperature-induced excited spin state trapping (TIESST) phenomena at the highest temperatures reported. Taking advantage of the polyanionic nature of this trimetallic complex, we were able to substitute the dimethylammonium cations by the monovalent heavy alkali metal cesium. This metathesis yielded the salt $\text{Cs}_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$, with different molecular packing that increases the number and strength of cation–anion interactions, including a more robust H-bonded network. In this phase, the spin transition still occurs above room temperature, but it is more abrupt and narrow (≈ 50 K wide hysteresis). Despite these differences, TIESST is observed with almost identical characteristic temperature ($T_{\text{TIESST}} = 240$ K) than in the parent compound, which is an additional experimental evidence supporting the molecular origin of the TIESST behavior in these materials.

Introduction

In the last few decades, molecular materials have been proposed as plausible alternatives for the miniaturization of components for information storage devices.^{1–5} Molecules represent the well-defined minimum size limit,^{6–10} along with additional advantages when compared with the more common top-down approach: solid state materials typically lose their bulk properties at the nanoscale.^{11–13} Molecule-based alternatives to optical,^{14,15} electric^{16,17} or magnetic^{18,19} materials have been studied with excellent perspectives, including multifunctional materials exhibiting tailor-made combinations of the abovementioned materials.^{20–23} This trend is particularly true in magnetic materials, which are able to mimic and even surpass the performance of solid state materials. Some unique

examples include light-weight room temperature magnets,^{24,25} single molecule magnets^{26–33} and photoactive magnets.^{34–37} Successful attempts to incorporate such materials into single-molecule based nanostructured devices have been already reported following this trend.^{38–45}

In this field, spin crossover (SCO) compounds^{46,47} are some of the most extraordinary magnetic materials.^{48–52} They exhibit switching between the low spin (LS) and the high spin (HS) metastable excited state controlled by external stimuli. Additionally, in the solid state, a thermal hysteresis cycle may appear, conferring on them true memory effect that can be tuned at and well above room temperature via preparation and/or processing.^{53–57} Because of these reasons, SCO materials are promising candidates for the actual implementation of molecules into molecular electronics, display devices, data storage, etc.^{58–64}

Although several transition metal centers are prone to exhibiting SCO phenomena,^{65,66} most studies have been focused on Fe(II) compounds, where the switching between LS and HS states brings some additional changes including spectroscopic properties and even molecular volume/chemical pressure.^{67,68} Fe(II) complexes, including coordination polymers, have shown wide thermal hysteresis,⁶⁹ ultrafast switching,^{70–72} and electromechanical features,^{73,74} bridging them closer to practical applications. In the miniaturization

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† Dedicated to Prof. Kim R. Dunbar on occasion of her 60th birthday, with deep gratitude.

‡ Electronic supplementary information (ESI) available: TGA, and crystallographic data. CCDC 1832927. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt01339j

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trend, SCO materials have also shown to retain the memory effect down to the nanoscale.^{75–82} However, since the spin transition is governed by lattice dynamics,^{83–85} it is still uncertain if memory effect (hysteretic behavior) exists at the single molecule level.⁸⁶

Our group is interested in anionic SCO complexes, which are less common than the cationic or neutral counterparts.⁸⁷ One example is the polyanion $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$ (1, L = 4-(1,2,4-triazol-4-yl)ethanedisulfonate).^{88,89} Its molecular structure consists of a linear array of three octahedral Fe(II) centers, which are bridged by two triple 1,2,4-triazole bridges. The two terminal Fe(II) centers complete their octahedral coordination with three water molecules. In the solid state, as the corresponding dimethylammonium (Me_2NH_2) salt, a thermally induced spin transition above room temperature was found for the central Fe(II), with a hysteresis cycle of 85 K and notably slow dynamics. In addition, the excited state (HS) of this compound can be easily quenched in a temperature-induced excited spin-state trapping (TIESST) phenomena^{90–93} when it is cooled at a rate of at least 5 K min^{-1} or faster. A characteristic T_{TIESST} of 250 K was determined, which is still the highest T_{TIESST} reported up to date.

Since spin transition phenomenon is very sensitive to changes in crystal structure and packing, we realized that substitution of the dimethylammonium cations by other cationic types could influence the bistability and switchability of these trimeric units. By analogy, in the most common case of cationic SCO complexes, changes in anionic content and solvation may drastically change the magnetic features from complete and cooperative transition to stabilization of the LS or HS states.^{94–99} Herein, we describe how simple metathesis in aqueous solution of 1 with excess Cs salt yields single crystals of the corresponding Cs^+ salt, displaying distinct magnetic features. Indeed, the nature of the cation induces a different crystal structure and packing, severely affecting the SCO behavior. These results show an easy strategy to tune the magnetic features of this intriguing SCO complex.

Experimental

Materials and instrumentation

All reagents were obtained from commercial sources and used without further purification. The ligand 4-(1,2,4-triazol-4-yl)ethanedisulfonate (L) and the dimethylammonium salt $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]$ (1) were prepared according to the literature procedures.^{88,100} Thermogravimetric analyses were performed using a TGA/SDTA851 Mettler Toledo with a MT1 microbalance. Differential Scanning Calorimetry analyses (DSC) were performed using a Mettler Toledo/DSC822e instrument with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$ in a nitrogen stream. Magnetic measurements were carried out on grained single crystals with a Quantum Design MPMS-XL SQUID magnetometer (Quantum Design, Inc., San Diego, CA, USA). Magnetic measurements were carried out under an applied field of 1000 Oe at different temperature scan rates.

Synthesis

$\text{Cs}_6[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6] \cdot 13\text{H}_2\text{O}$ (2). This compound was obtained by metathesis. Initially, 180 mg (0.082 mmol, 1 eq.) of 1 and 275.6 mg (1.64 mmol, 20 eq.) of CsCl were separately dissolved in 5 mL of distilled water. Ascorbic acid ($\approx 2 \text{ mg}$) was added to both solutions to avoid the oxidation of Fe(II) to Fe(III). Both solutions were mixed for 10 minutes under stirring. Subsequently, the solution was filtered off and ethanol vapor was slowly diffused into the solution to promote the growth of single crystals. After two days, single crystals of 2 were collected, filtered, washed with ethanol and dried in air. No proper yield was estimated since only single crystals were used for further characterization to assure complete purity of the samples.

Single crystal X-ray diffraction

Single crystal X-ray diffraction measurements were performed on a Bruker-Nonius diffractometer with an APEX 2 4 K CCD area detector at 100 K. Crystal structure solution and refinement were performed using SHELXTL Version 6.10. Data collection and refinement parameters are shown in Table 1.

Results and discussion

Synthesis and structure

Single crystals of 2 were obtained by ethanol slow vapor diffusion into an aqueous solution of 1 with 20-fold excess of cesium chloride. These single crystals contain the same trinuclear polyanion, $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$ (Fig. 1), where all dimethylammonium cations have been substituted by Cs^+ cations. The molecular structure of the trimer is analogous to that described before.⁸⁷ The iron ions occupy two crystallographic

Table 1 Crystallographic data for compound 2

Chemical formula	$\text{C}_{24}\text{H}_{68}\text{Cs}_6\text{Fe}_3\text{N}_{18}\text{O}_{55}\text{S}_{12}$
Formula weight	2838.69
T (K)	100(2)
Crystal system	Monoclinic
Space group	C2/c
Crystal size	$0.01 \times 0.02 \times 0.4$
a (Å)	34.4273(12)
b (Å)	11.4107(4)
c (Å)	26.1316(9)
α (°)	90
β (°)	128.2290(8)
γ (°)	90
V (Å ³)	8064.0(5)
Z	4
ρ_{calcd} (g cm ⁻³)	2.338
μ (mm ⁻¹)	3.631
F (000)	5512
θ range (°)	1.583–28.010
Index ranges	$-45 \leq h \leq 44$ $-14 \leq k \leq 12$ $-32 \leq l \leq 34$
Data/restr/parameters	9659/921/585
Goodness-of-fit on F^2	1.028
R_1 ($I > 2\sigma(I)$)	0.0684
wR_2 ($I > 2\sigma(I)$)	0.1988

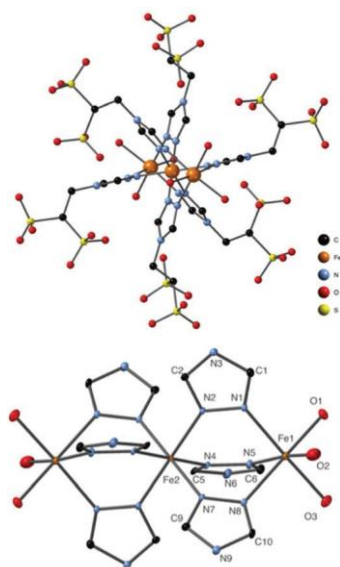


Fig. 1 Molecular structure of $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_6]^{6-}$ (top) and labelled ORTEP representation of the core trimer (bottom), showing the triple triazole-bridges and terminal water molecules. (H atoms have been omitted for clarity.)

positions (Fe1 and Fe2), forming a linear array of octahedral $\text{Fe}(\text{II})$ linked by triazole bridge. The outer irons (Fe1) complete their hexacoordination with three water molecules in *fac* conformation. The metal to ligand distances obtained at 100 K reveal the spin state of the SCO centers to be high spin (HS) for Fe1 (average Fe1–N distance: 2.19 Å) and low spin (LS) for Fe2 (average Fe2–N distance: 1.97 Å).

Regarding the crystallographic packing, cations and anions form segregated layers along the *a* axis, following ABAB stacking pattern (Fig. 2). The structure of the anionic layers is pseudo-hexagonal, with each trimer surrounded by six nearest neighbors (Fig. 3a). There are multiple intermolecular H-bond intralayer interactions, with very short H-bond contacts in the range $\text{O}_w \cdots \text{OSO}_2 = 2.69\text{--}2.95$ Å between oxygen atoms from the

sulfonate groups and from coordinated water molecules of adjacent trimers. The sulfonate groups that do not participate in this intralayer H-bonded network point towards the cationic layers.

The cationic layers are formed by two planes of Cs^+ cations, separated by 2.1 ± 0.1 Å (Fig. 3b and c). Each Cs^+ center has short contacts with both adjacent anionic layers, connecting them with $\text{Cs}^+ \cdots \text{O}_3\text{S}$ distances in the 2.9–3.4 Å range. The three different Cs^+ crystallographic positions exhibit different coordination modes. Cs1 is heptacoordinated, surrounded by three SO_3 groups in monodentate coordination mode and four water molecules. Cs2 is octacoordinated by six SO_3 groups (one acting as bidentate ligand) and one water molecule. Finally, Cs3 is heptacoordinated to four SO_3 groups (one acting as bidentate ligand) and two water molecules. This complex H-bonded network connects crystallographic trimers between layers with direct $\text{O} \cdots \text{Cs}^+ \cdots \text{O}$ contacts.

Magnetic measurements

The magnetic properties of grained single crystals of 2 were studied in the 200–400 K range. At room temperature, the $\chi_m T$ product is $6.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which corresponds to two high spin iron centers per trimer, suggesting a HS–LS–HS configuration for the ground state as in the parent compound 1. At very slow temperature scan (Fig. 4), this value remains constant in the 200–350 K range. Above 350 K, $\chi_m T$ shows a sharp increase, indicating the onset of the spin transition. This transition to the HS–HS–HS state shows two different regimes: first a sharp increase reaching $8.1 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 354 K with $T_{1/2}(\uparrow) = 352$ K and second, a gradual increase reaching $9.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 400 K. This second regime shows slow kinetics, and at 400 K (the highest T available in our set-up), about 140 min are needed for $\chi_m T$ to saturate (see Fig. 4 inset). According to these values, about 2/3 of the centers participate in the abrupt process, but all anions reach the thermally induced HS–HS–HS state after the gradual transition is over. When temperature is decreased at the same scan rate (0.3 K min^{-1}), a thermal hysteresis cycle opens for both regimes. The gradual transition

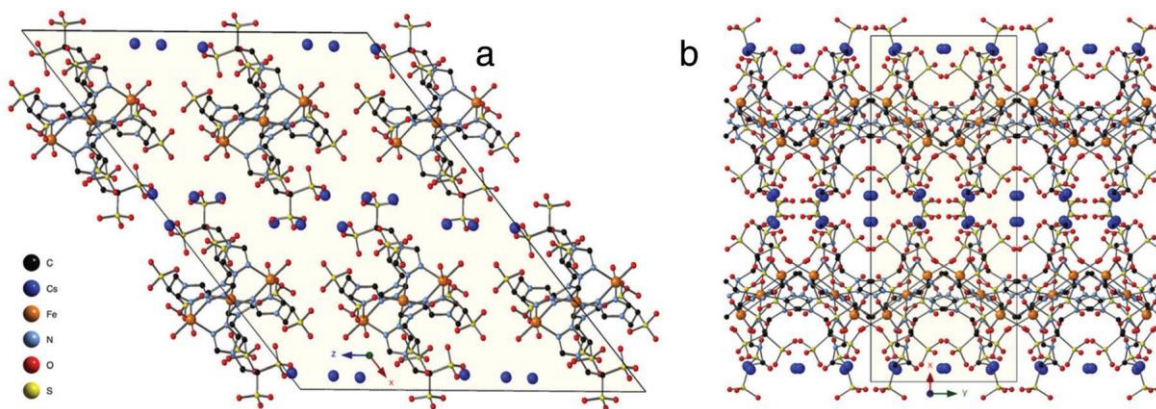


Fig. 2 Projection of the crystal structure of 2 on the *ac* (a) and the *ab* (b) planes, showing the stacking of alternating layers along the *a* axis. (Solvation water molecules and H atoms have been omitted for clarity.)

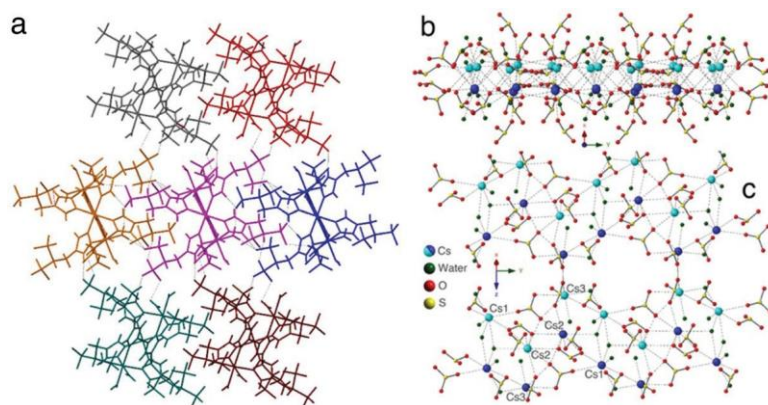


Fig. 3 Representation of the H-bonded networks in the crystal structure of 2. (a) Top view of the anionic layer, showing the pseudo-hexagonal arrangement of the trinuclear complexes and their closest contacts as dotted lines. (b, c) Side and top views of the cationic layer, showing the contacts between cations, anions and water molecules as dotted lines. Cs atoms are represented in two colors to highlight the two planes in the cationic layers. (H atoms omitted for clarity.)

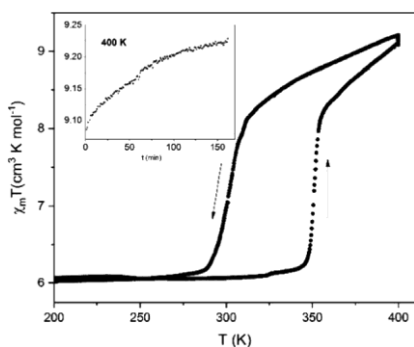


Fig. 4 $\chi_m T$ vs. T plot for 2 during the heating and cooling processes, at a 0.3 K min^{-1} scan rate. Inset: The sample was kept at 400 K for 140 minutes to reach saturation.

closes just below 300 K, where the abrupt transition drives the compound back to the ground state with $T_{1/2}(\downarrow) = 305 \text{ K}$. This creates a thermal hysteresis cycle of 47 K for the abrupt regime.

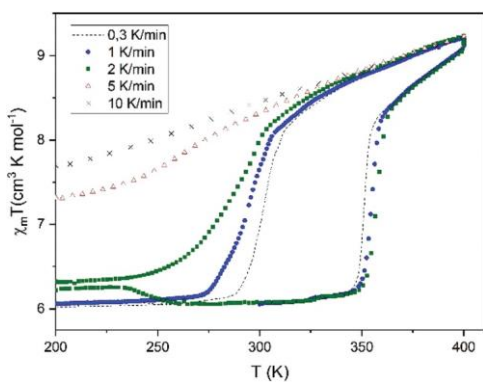


Fig. 5 Thermal hysteresis cycles for compound 2 at different scan rates.

We studied the effect of the scan rate in the thermal hysteresis cycle of 2 (Fig. 5). The hysteresis loop is indeed very sensitive to scan rate.¹⁰¹ Dynamic hysteresis cycles observed at 1 and 2 K min^{-1} are wider, with loops of 57 and 65 K, respectively. The effect upon the cooling branch is particularly significant, and the signature of temperature induced excited spin state trapping (TIESST) is already apparent at 2 K min^{-1} . The compound is not able to relax to the ground state, reaching a minimum low temperature value of $6.25 \text{ cm}^3 \text{ K mol}^{-1}$. This indicates that about 8% of the molecules are trapped in the HS–HS–HS state. In the heating branch, these molecules are able to relax to the ground state above 230 K. At faster cooling rates, the fraction of HS–HS–HS trapped molecules is also higher, reaching 40% at 5 K min^{-1} , and 52% at 10 K min^{-1} (Fig. 5). A characteristic $T_{\text{TIESST}} = 240 \text{ K}$ was estimated following the method established by Letard et al.¹⁰² (Fig. 6). This value is very close to that reported for 1 (250 K).

It is important to note that all these cycles were robust and reproducible since they correspond to the second and succes-

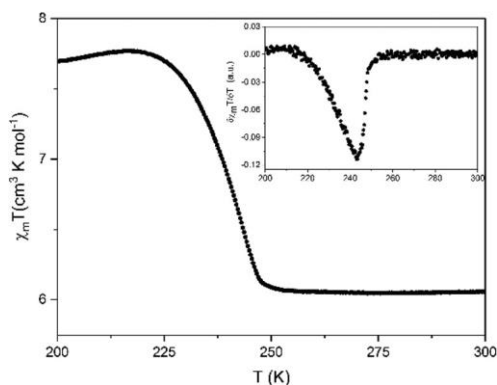


Fig. 6 $\chi_m T$ vs. T plot for the heating branch (at 0.3 K min^{-1}) after trapping the metastable HS–HS–HS of a sample of 2 via fast cooling at 10 K min^{-1} . (Inset: The derivate of the heating data, defining T_{TIESST}).

sive cycles once the sample was dehydrated in situ during the first heating process. We are not reporting the magnetic data from the very first cycle, where dehydration may also play a role, as confirmed by thermogravimetric analyses (TGA). Interstitial solvent molecules are lost upon heating below 130 °C, and the bound water molecules begin to release above 160 °C (Fig. S1†). The gravimetric plateau above 220 °C, which is stable at least up to 300 °C, corresponds to a total weight loss of 8.5%, indicating that not all water molecules are lost even at such high temperatures. Thus, this material shows very high thermal stability, with no decomposition of the organic matter in this temperature range. Differential Scanning Calorimetry (DSC) detected two dehydration processes during the first heating cycle (see Fig. S2†). However, successive cycles did not show any feature that could be assigned to a phase transition associated with the spin transition. In the same direction, powder XRD data from the same sample used for multiple thermal hysteresis measurements (four cycles in the 200–400 K range) confirms that the crystal structure is robust and preserved after the thermal treatment (Fig. S3†) and after partial dehydration, supporting that no major structural change occurs.

Discussion

When compared with the parent dimethylammonium salt (1), we can highlight some significant differences in the crystal packing. The crystal structure of 1 showed high crystallographic disorder in the position of cations and solvent water molecules even when having lower solvent content (5 vs. 13 crystallization water molecules). The disorder affects the intermolecular interactions network. In particular, the connectivity among trimers increases from four $O_w \cdots OSO_2$ contacts in 1 up to six nearest neighbors in 2. Additionally, the strong and directional interlayer interactions mediated by the Cs^+ cations were also absent in 1. In general, the crystal structure of 2 increases the connectivity between trimers in all crystallographic directions.

This phenomenon is expected to increase the cooperativity of the spin transition in this new salt, which is indeed confirmed from the magnetic data, with the appearance of an abrupt transition. In addition, the transition moves to lower temperatures and is complete at 400 K. Apart from this observation, the increase in cooperativity is typically associated with wider thermal hysteresis. However, the thermal hysteresis shrinks from 90 K (1) down to 50 K (2). Even more surprisingly, the higher cooperativity does not affect the TIESST effect, showing freezing of the metastable state at slower cooling rates (just above 2 K min^{-1}). In case of the parent compound, these combinations are counterintuitive to the common magneto-structural correlations established for spin crossover materials. The completeness of the spin transition in this new compound below 400 K, as confirmed by magnetic measurements, has also allowed us to study the DCS data. No features indicative of a phase transition were

found after the first cycle showed some events due to dehydration. The second and successive cycles were featureless. This result supports the primarily molecular origin of the magnetic features and switching kinetics of this polyanion.

Conclusions

A cesium salt of the polyanionic trimer $[Fe_3(\mu-L_6)(H_2O)_6]^{6-}$ was isolated by completely substituting the dimethylammonium cations of its soluble salt by excess Cs^+ salt and its crystal structure was determined. This compound displays SCO behavior, showing a two-step spin transition of the central $Fe(II)$ atom in each trimer from the combination of an abrupt step above 350 K and a gradual transition up to completeness at 400 K. The difference between heating and cooling branches showed a quasi-static 47 K wide hysteresis cycle. This finding is in contrast with that for the parent compound, which showed wider hysteresis ($>85 \text{ K}$) but a gradual transition. Furthermore, cooperativity increases while hysteresis decreases, which is a counterintuitive observation. The appearance of SCO hysteresis should be associated with crystallographic transition, that is, cooperativity. In addition to the abrupt hysteresis, there is a second regime that still showed gradual transition. We assign this non-cooperative contribution to defects in the crystal and surface effects, arising from molecules loosely participating in the H-bonded network.

These results show that simple cation exchange can modify the SCO behavior of this complex since substitution of dimethylammonium by the heavy cesium monocation has changed the gradual SCO transition into an abrupt process, which we related to stronger intermolecular connectivity. Nevertheless, the almost identical TIESST phenomenon suggests that single-molecule events may be at the origin of the slow dynamics and features of the compounds containing this polyanionic trimer. Further studies to confirm if memory-like effects may arise in this polyanionic complex at the single molecule level are under way.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

We would like to acknowledge financial support from the Spanish Ministerio de Economía y Competitividad (MINECO) through project CTQ2015-71287-R and the Severo Ochoa Excellence Accreditation 2014–2018 SEV-2013-0319 and the Generalitat de Catalunya (2017-SGR-1406 and the CERCA Programme). AMC thanks MINECO for a pre-doctoral FPI fellowship.

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