An 'Intermetallic' Molecular Nanomagnet with the Lanthanide Coordinated Only by Transition Metals

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Abstract

Magnetic molecules known as molecular nanomagnets (MNM; or single molecule magnets SMMs) may be the key to ultra-high density data storage. A single sub-nanometer MNM is capable of storing a single bit of information while being 2-3 orders of magnitude smaller than the magnetic domains in the current HDD technology. The best performing molecular nanomagnets are designed by carefully arranging *p*-element donor atoms (C, N or O) around the central magnetic ion. This strategy, however, seems to be reaching its limit as the magnetic memory effect disappears above 80 K for this class of compounds. Inspired by the structure of the hardest intermetallic magnet SmCo₅, we have synthesized a nanomagnetic molecule where the central lanthanide (Ln) ion Er^{III} is coordinated solely by three transition metal (TM) ions in a perfectly trigonal planar fashion. The molecule [Er^{III}(Re^ICp₂)₃] (**ErRe₃**) constitutes the first example of a molecular nanomagnet (MNM; or single molecule magnet SMM) with unsupported Ln-TM bonds and paves the way towards molecular intermetallics with strong direct magnetic exchange interactions. Such interactions are believed to be crucial for quenching the quantum tunneling of magnetization which limits the application of Ln-SMMs as sub-nanometer magnetic memory units.

Introduction

Rare-earth intermetallic magnets – samarium-cobalt (SmCo)¹ and neodymium (NdFeB)^{2,3} – are the strongest permanent magnets known to date with multiple applications in modern technology ranging from hard disk drives to electric vehicles and wind turbines.⁴ Their commercial success results from the combination of the strong magnetic anisotropy of rare earths and their direct magnetic coupling with transition metal ions. At the other far end of the current search for novel magnetic materials are magnetic molecules, called molecular nanomagnets⁵ (MNM) or single molecule magnets (SMMs). MNMs are molecule-sized objects with magnetic memory effects governed by quantum mechanics.^{6–10} They are strongly believed to revolutionize magnetic information storage, but at the moment do not have any real-world applications, as their performance is limited by low blocking temperatures and quantum tunneling of magnetization (QTM).¹¹ Current trends in the design of MNMs^{12,13} were ignited by the discovery of terbium double-decker [TbPc₂][–] (Pc = phthalocyanine dianion)¹⁴ and were fueled by the seminal perspective of Rinehart and Long.¹⁵ Design principles focus on the precise control of the coordination sphere of a single lanthanide center in order to maximize the easy-axis magnetic anisotropy of the complex and to limit the spin-lattice relaxation rates.^{16–19} While this approach led to several breakthroughs, including the observation of the magnetic hysteresis loop of molecular origin above the liquid nitrogen barrier for dysprosocenium^{6,7} and magnetic field control of the magnetization blocking barrier,²⁰ it appears to be reaching its limit as the proposed modifications were not as successful as expected.^{21,22}

The original approach to MNMs was based on designing multinuclear systems with strong magnetic superexchange, where several paramagnetic centers are "glued" together by bridging ligands to form a

high-spin molecule. If magnetic anisotropy is present in such a system, it shows MNM properties.^{23,24} An MNM of this type stands behind the success story of the whole field as it was indeed started by the discovery of a dodecanuclear carboxylate-bridged cluster Mn_{12} – a high-spin molecule ($S = 10$) comprising eight Mn^{III} and four Mn^{IV} ions interacting magnetically via the bridging carboxylate ligands.^{25–27} However, the indirect character of these magnetic interactions, based on weak superexchange coupling mechanism, limits the performance of Mn_{12} to very low temperatures, below the boiling point of liquid helium. Attempts to adapt this particular strategy to dysprosocenium complexes suffer from a similar problem – weak superexchange interactions of the lanthanides with other metal centers through diamagnetic bridging ligands limit their influence on the slow magnetic relaxation.^{28–30} Therefore, the route towards the high-performance MNMs based on superexchange interactions has been largely abandoned.

Overall, despite the huge progress in the field initiated by Mn_{12} , its ultimate goal – the room-temperature molecular nanomagnet (RT-MNM) – remains elusive. However, the aforementioned examples of the rare-earth intermetallics: SmCo_5 ¹ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ ² provide clues for the possible direction in the design of RT-MNMs. Focusing the efforts on molecules comprising a rare-earth metal center coordinated solely by transition metal ions,^{31–34} mimicking the first coordination sphere of the Sm center in the SmCo_5 magnet (Figure 1A-1C) could enable the appearance of the direct exchange coupling between the highly anisotropic lanthanide central ion and the coordinated transition metals. This approach was recently predicted to efficiently suppress QTM in MNMs³⁵ and demonstrated for the ultra-hard MNM $(\text{Cp}^*\text{Pr}_5)_2\text{Dy}_2\text{I}_3$ where direct f - f exchange is operational.³⁶ Interestingly, even much weaker indirect interactions were reported to be quite efficient in this matter.³⁷

The concept of unsupported bonds between the lanthanide and the transition metal was first introduced and explored by Kempe et al.^{32,34} Later, it was proposed by Rinehart and Long¹⁵ as a possible strategy towards molecular nanomagnets and put to use by Nippe et al. reporting MNMs with unsupported direct bonds between the dysprosium ion and $4d$ (Fe) or $4d$ (Ru) transition metal ions.³⁸ However, the magnetic memory effect (magnetic hysteresis) has not been observed, most probably due to the unfavorable ligand field geometry³⁸ or the unfortunate choice of the rare-earth metal.³² Noteworthy, the introduction of p -block heavy metals directly into the coordination sphere of the lanthanide was also pursued resulting in interesting examples of MNMs.^{39,40}

Here, we apply the principles of easy-axis magnetic anisotropy design with the methodology of Kempe et al. that led previously to rare-earth metal complexes coordinated solely by transition metals.³² Herein, we demonstrate the first step toward molecular "intermetallic" nanomagnets, a perfectly trigonal planar $[\text{Er}^{\text{III}}(\text{Re}^{\text{I}}\text{Cp}_2)_3]$ complex (**ErRe₃**; Cp = cyclopentadienyl anion) with magnetic hysteresis up to 7.2 K (at 22 Oe/s magnetic sweep rate) where Er^{III} is solely coordinated by three Re^{I} ions.

Results And Discussion

Synthetic strategy

ErRe₃ is obtained following the literature procedure for [Sm^{III}(Re^ICp₂)₃].³² The starting material [Er^{III}(btmsm)₃] (obtained according to literature procedures^{41 42}; btmsm = bis(trimethylsilyl)methyl anion) reacts with [Cp₂ReH]⁴³ in benzene (Figure 1D). The btmsm⁻ ligand coordinated to Er^{III} acts as a strong base capable of deprotonating [Cp₂ReH] – a weak acid. Deprotonation of [Cp₂ReH] leads to the elimination of the by-product bis(trimethylsilyl)methane ('alkane elimination'³⁴) and the formation of the anionic [Cp₂Re]⁻ species that readily coordinate to Er^{III} resulting in the formation of a trigonal planar complex [Er^{III}(Re^ICp₂)₃].

Crystal structure

ErRe₃ crystallizes slowly from benzene in the form of small yellow prism crystals which were characterized structurally by single-crystal X-ray diffraction (SCXRD; trigonal *R*-3; Table S1). The SCXRD structural analysis confirmed the coordination of three Re^I ions to the Er^{III} center with the formation of a nearly perfect trigonal planar neutral complex [Er^{III}(Re^ICp₂)₃] (Figure 1C) with the Re-Er-Re angles very close to 120° (121.22(2), 119.15(2) and 119.62(2)°) and the Er atom lying only 0.013(1) Å above the Re₃ plane. The cyclopentadienyl ligands are coordinated solely to Re^I and arranged in a slightly tilted manner below and above the equatorial plane of the **ErRe₃** molecule (Figure 1C). There are no other coordination bonds to Er^{III}. Other intramolecular contacts of Er^{III} involve Cp ligands with the shortest Er×××C distances in the 2.829(8)-3.056(13) Å range – well beyond typical coordination bonds of lanthanide complexes. The Er-Re distances in **ErRe₃** (2.9004(5), 2.9124(5) and 2.9172(5) Å) are similar to those reported for [Sm^{III}(Re^ICp₂)₃], [La^{III}(Re^ICp₂)₃] and [Lu^{III}(Re^ICp₂)₃]³² as well as other molecular compounds with unsupported rare earth - transition metal bonds^{34,38} and the intermetallic SmCo₅ with Sm-Co distances of 2.888 Å.¹ The comparison of the Re-Cp distances in **ErRe₃** and the [Cp₂ReH] starting material (SCXRD structural analysis of [Cp₂ReH] was performed as part of this study Table S1; CCDC 2027573) confirms the change of the valence state of the Re centers upon coordination to Er^{III}. The slightly unsymmetrical and tilted [Cp₂ReH] with the average Re-Cp_{centroid} distance of 1.877(44) Å is similar to other compounds of this type⁴⁴⁻⁴⁶ and shows slight shortening of these contacts in **ErRe₃** to av. 1.864(8) Å (Figure S1). The [Er^{III}(Re^ICp₂)₃] molecules are stacked on top of each other in a hexagonal fashion along the *c* crystallographic direction, leading to the formation of channels filled with disordered benzene molecules (Figure S2). The shortest intermolecular distances between the Er^{III} centers can be found within the aforementioned stacks and amount to 7.6318(6) Å. There are six more nearest Er^{III} neighbors within the 10 Å radius with distances larger than 9 Å (Figure S3). This ensures sufficient magnetic isolation of the individual [Er^{III}(Re^ICp₂)₃] molecules taking into account that all intermolecular contacts are van der Waals in nature and do not transmit magnetic interactions efficiently. Before attempting the magnetic characterization **ErRe₃** was subjected to a rigorous purity verification by performing powder X-ray diffraction (PXRD) experiment for a sample loaded into a 0.3 mm glass capillary immersed in benzene

and sealed using high vacuum grease (identical conditions were applied during the magnetic measurements discussed below). The experimental PXRD pattern shows very narrow peaks and matches almost perfectly the simulated one using 270 K SCXRD data (Figure S4).

Magnetic properties

The unusual coordination environment of Er^{III} in **ErRe₃** may cast doubts on the nature of its electronic ground state. However, magnetic measurements for **ErRe₃** confirm the valence states of the central Er^{III} ion and the Re^I donor atoms. The χT (χ – molar magnetic susceptibility) value of 11.3 cm³×K×mol⁻¹ at 260 K is close to 11.48 cm³×K×mol⁻¹ expected for Er^{III} ⁴I_{15/2} ground multiplet (Figure S5). Similar agreement between the experiment and the expected χT was reported for [Sm^{III}(Re^ICp₂)₃] (⁶H_{5/2} multiplet).³² This is further confirmed by a very good agreement of the experimental χT and the *ab initio* calculations (red solid line in Figure S5 and supplemental information) using Molcas.^{47,48} The $\chi T(T)$ dependence shows an abrupt increase below 18 K, which can be ascribed to ferromagnetic intermolecular interactions and blocking of magnetization.

The $M(H)$ (M – molar magnetization, H – magnetic field) measurements (magnetic field sweep rate of 2.2 mT×s⁻¹) revealed the presence of waist-restricted (pinched) magnetic hysteresis loops up to 7.2 K (Figure 2A), originating from the slow relaxation of the magnetization of the trigonal **ErRe₃**. This temperature matches Er^{III} sandwich and metallocene complexes.⁴⁹ Furthermore, the hysteresis loop in **ErRe₃** opens in the 0.05 – 1.5 T range at 1.8 K and is the widest among trigonal Er^{III} MNMs.

The slow magnetization dynamics were studied and confirmed by the alternating current (AC) magnetic susceptibility measurements performed in the 1-10000 Hz frequency range up to 27 K in the absence of the external magnetic field (Figure 2C and Table S2). However, the resulting temperature dependence of the magnetic relaxation rate $\tau^{-1}(T)$ (Figure 2D) contains contributions from three processes: quantum tunneling of magnetization (QTM), Raman and Orbach described by five parameters included in Equation 1:

$$\tau^{-1} = A + CT^n + \tau_0^{-1} \exp\left(\frac{-U_{eff}}{k_B T}\right) \quad \text{Eq. 1}$$

hence, all relevant parameters: A , C , n , t_0 and, most importantly, the effective energy barrier for the magnetization reversal arising from the Orbach relaxation can be extracted only with limited confidence from AC data collected at zero DC field (best fit parameters $A = 179(4) \text{ s}^{-1}$, $C = 0.137(9) \text{ K}^{-n} \times \text{s}^{-1}$, $n = 3.60(2)$, $\tau_0 = 8.3(8) \cdot 10^{-10} \text{ s}$ and $U_{eff} = 285(3) \text{ K}$ with $R^2 = 0.99994$; Figure 2D). To mitigate this issue, the AC magnetic studies were repeated under an applied DC magnetic field of 0.15 T (Figure S6 and Table S3). The presence of a small applied magnetic field quenches the QTM with only negligible direct process, which was accurately determined from the magnetic field dependence of the relaxation time (Figure S7

and Table S4). Thus, the temperature dependence of the relaxation rate under $H_{DC} = 0.15$ T could be reliably fitted including only the Raman and Orbach relaxation mechanisms using Equation 2:

$$\tau^{-1} = CT^n + \tau_0^{-1} \exp\left(\frac{-U_{eff}}{k_B T}\right) \quad \text{Eq. 2}$$

where τ^{-1} is the magnetic relaxation rate, C and n parameters describe the Raman-like process, and τ_0 and U_{eff} are related to the Orbach process. The satisfactory fit could be obtained with $C = 0.0035(4) \text{ K}^{-n} \times \text{s}^{-1}$, $n = 4.74(3)$, $\tau_0 = 3.0(5) \cdot 10^{-10} \text{ s}$ and $U_{eff} = 314(5) \text{ K}$ with $R^2 = 0.99987$ (Figure 2E).

The obtained effective energy barrier for the magnetization reversal $U_{eff} = 314(5) \text{ K}$ is significantly smaller than expected from the theoretical calculations (CASSCF-RASSI; OpenMolcas 19.11⁴⁷; for details see Supplemental Information including Tables S5 and S6 with the information on basis sets, spin-orbit energies and g -tensors of the lowest Kramers Doublets, respectively), predicting the fastest relaxation between the $5\pm$ Kramers Doublet lying 576 K above the highly axial ground state (Figure 2B and Table S6). The value 314(5) K is therefore underestimated. Additional fittings of the Raman and Orbach processes with fixed U_{eff} values corresponding to the calculated energies of the lower KDs were performed: $2\pm$ of 224 K, $3\pm$ of 363 K and $4\pm$ of 475 K. The best fits (Figures S8A-S8C) are characterized by the following R^2 values: 0.99702 for $U_{eff\ 2\pm} = 224 \text{ K}$, 0.99960 for $U_{eff\ 3\pm} = 363 \text{ K}$ and 0.99808 for $U_{eff\ 4\pm} = 475 \text{ K}$. The best agreement is clearly observed for $U_{eff\ 3\pm} = 363 \text{ K}$, which corresponds to the energy of the third KD. This is also closest to the value obtained from the free fitting of the relaxation processes presented in Figure 2E. An attempt to describe the magnetic relaxation of **ErRe₃** using only the Raman-like process leads to a very poor fit as depicted in Figure S8D. Thus we conclude, that the observed Orbach relaxation for **ErRe₃** proceeds predominantly through the third Kramers Doublet, characterized by the estimated energy barrier U_{eff} approaching 363 K. This value is three times higher than that observed for the best trigonal^{42,50} or low-coordinate^{51,52} Er^{III} molecules and is comparable to the Er^{III} sandwich and metallocene complexes.^{37,49,53-57} Interestingly, **ErRe₃** shows significantly slower relaxation as compared to $[\text{Er}(\text{N}(\text{SiMe}_3)_2)_3]$ characterized by $U_{eff} = 122 \text{ K}$ ⁵⁰ and surpasses the theoretical limit of 306 K (212.6 cm^{-1}) for any trigonal planar molecule based on the theoretical analysis of a hypothetical $\text{Er}^{\text{III}}(\text{NH}_2)_3$ compound.⁵⁸ **ErRe₃** is a clear demonstration that direct bonding of transition metals to lanthanides might be one of the most promising directions towards room temperature MNMs, especially if paramagnetic donor atoms could be used.

Conclusions

The reported triangular molecule $[\text{Er}^{\text{III}}(\text{Re}^{\text{I}}\text{Cp}_2)_3]$ constitutes the first molecular nanomagnet that mimics structurally the hardest commercial rare-earth magnet known SmCo_5 and creates a connection between two incompatible fields: the rare-earth intermetallics and molecule-based compounds. **ErRe₃** is the first example of a lanthanide single molecule magnets coordinated solely by transition metals which enables

the formulation of a new strategy towards molecular intermetallic nanomagnets, where the lanthanide – the source of strong magnetic anisotropy – is directly coupled to the spins of softer transition metal ions playing the role of ligands.

Methods

Preparation of $[\text{Er}^{\text{III}}(\text{Re}^{\text{I}}\text{Cp}_2)_3]\cdot 0.5\text{C}_6\text{H}_6$ (ErRe_3)

All manipulations were performed in an argon-filled glovebox (Inert PureLab HE). $[\text{Cp}_2\text{ReH}]$ (242 mg; 0.76 mmol) was dissolved in anhydrous benzene (3.5 ml) and added to the benzene solution (2.5 ml) of $[\text{Er}^{\text{III}}(\text{btmsm})_3]$ (160 mg; 0.25 mmol). The resulting orange solution was stirred using a glass rod for 5 min and then stored in a 20 ml scintillation vial that was left open for 5 h inside the glovebox. After this time yellow-orange crystals appeared which were collected by vacuum filtration using a 1 μm Teflon membrane. Yield: 70 mg (0.061 mmol; 24%). The purity of the compound was checked by powder X-ray diffraction with the experimental pattern (Figure S4) matching nearly perfectly the simulated one from the SCXRD structural model obtained at 270 K (CCDC 2065531). IR, neat (cm^{-1}): 796s, 808s, 816s, 832m, 850m, 987s, 1000s, 1059m, 1087s, 1095vs, 1154vw, 1188vw, 1201vw, 1255m, 1273m, 1342m, 1358m, 1394s, 1419s, 1462m, 1479m, 1558s, 1657s, 2001vw, 2034vw, 2854s, 2929vs, 3036m, 3063s, 3089s, 3550b (Figure S9).

Declarations

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Author contributions

M.M. prepared the starting material $[\text{Cp}_2\text{ReH}]$, participated in the preparation of the target compound, performed and analysed the magnetic measurements and wrote the relevant fragment of the manuscript; M.B. prepared the starting material $[\text{Er}^{\text{III}}(\text{btmsm})_3]$, participated in the preparation of the target compound, analysed its structure and wrote a relevant fragment of the manuscript; S.B. participated in the AC magnetic measurements and their analysis. V.V. performed and analysed the *ab initio* calculations and wrote the relevant fragment of the manuscript. D.P. acquired funding, designed the experiments, performed the synthesis of the target compound, coordinated and supervised the research and wrote the manuscript. All authors reviewed and agreed to the final version of the paper.

Competing interests

The authors declare no competing interests.

Materials and correspondence

Further information and requests for resources/materials should be directed to the corresponding author: Dawid Pinkowicz (dawid.pinkowicz@uj.edu.pl).

Crystallographic data

Crystallographic data for this paper (**ErRe₃** at 100 K: CCDC 2065530, **ErRe₃** at 270 K: CCDC 2065531 and [Cp₂ReH] at 100 K: CCDC 2027573) were deposited with the Cambridge Structural Database and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All other data are available from the lead contact without restriction.

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Supplementary Information

Additional experimental and methods details as well as supplementary Figures and Tables can be found in the supplementary information. Below is the complete list of items that can be found in the relevant

file:

Description of the experimental and computational details including general synthetic considerations, details of single crystal X-ray diffraction, details of powder X-ray diffraction, details of infrared spectroscopy, description of magnetic measurements and details of *ab initio* calculation.

Table S1. Selected crystallographic parameters for **ErRe₃** at 100 and 270 K and the starting material [Cp₂Re^{III}H] at 100 K.

Figure S1. Structural diagrams showing the asymmetric units (ASUs) of the starting material [Cp₂Re^{III}H] (A) and the target compound **ErRe₃** (B). The red numbers indicate the distances (Å) between the Re atoms and the centroids of the cyclopentadienyl rings. C – grey, H – light grey, Re – blue, Er – green, centroids – white; ellipsoids at the 40 % probability level for A and 30% for B.

Figure S2. Structural diagram of **ErRe₃** as viewed along the *c* crystallographic direction showing the hexagonal packing pattern of the [Er^{III}(Re^ICp₂)₃] molecules highlighted by red dotted hexagons. This type of packing leads to the formation of channels along the *c* axis filled with benzene molecules (crystallization solvent). Cyclopentadienyl ligands and benzene molecules are represented by black sticks and H-atoms are omitted for clarity.

Figure S3. Structural diagram demonstrating and listing Er×××Er distances between all **ErRe₃** nearest neighbours. The shortest distance is 7.6318(6) Å along the *c* crystallographic direction.

Figure S4. Experimental (red line) and simulated (black line) powder X-ray diffraction experiments for **ErRe₃**. The simulated pattern is calculated based on the 270 K single crystal X-ray diffraction structural model and includes the contribution of the Cu K β which is observed in the experimental pattern.

Figure S5. Temperature dependence of the molar magnetic susceptibility and temperature product $\chi T(T)$ for **ErRe₃** recorded at $\mu_0 H = 0.1$ T (black points). The solid red line presents the $\chi T(T)$ obtained from the *ab initio* calculations (see text for details). The observed anomaly below 20 K is caused by the magnetization blocking and the ferromagnetic interactions between the neighbouring **ErRe₃** molecules.

Table S2. Results of the generalized Debye model fitting of the frequency dependence of the AC magnetic susceptibility χ' and χ'' for **ErRe₃** recorded at zero magnetic field in the 5.5 – 27 K range presented in Figure 2C (main text).

Figure S6. Frequency dependence of the AC magnetic susceptibility χ' and χ'' for **ErRe₃** recorded at $H_{DC} = 0.15$ T in the 5.5 – 27 K range using Quantum Design MPMS3 and PPMS instruments. Solid lines are the best fits to the generalized Debye model. The relevant fitting parameters can be found in Table S3 below.

Table S3. Results of the generalized Debye model fitting of the frequency dependence of the AC magnetic susceptibility χ' and χ'' for **ErRe₃** recorded at $H_{DC} = 0.15$ T in the 5.5 – 27 K range presented in Figure S6.

Figure S7. Frequency dependence of the AC magnetic susceptibility χ' and χ'' for **ErRe₃** recorded at $T = 7$ K in the 0.01 – 2 T range using Quantum Design MPMS3 and PPMS instruments. Solid lines are the best fits to the generalized Debye model. The relevant fitting parameters can be found in Table S4 below.

Table S4. Results of the generalized Debye model fitting of the frequency dependence of the AC magnetic susceptibility χ' and χ'' for **ErRe₃** recorded at $T = 7$ K in the 0.01 – 2 T range presented in Figure S6.

Table S5. The employed basis sets for *ab initio* calculations.

Table S6. Spin-orbit energies (cm^{-1}) and the g -tensors of the four lowest in energy Kramers doublets.

Figure S8. Temperature dependence of the magnetic relaxation rate $\tau^{-1}(T)$ for **ErRe₃** under applied 0.15 T DC magnetic field (circles). Solid lines represent the best fits assuming Raman-like and Orbach relaxation processes with C , n , τ_0 as free parameters and U_{eff} fixed at 224 K (A), 363 K (B), 475 K (C) or Raman-like relaxation process only (D). Fitting presented in B shows highest R^2 and is assumed to provide the most accurate value of the energy barrier for magnetization reversal. Fitting assuming Raman-like relaxation only (D) shows the lowest R^2 which sanctions the need for including the Orbach mechanism.

Figure S9. IR spectra of crushed crystals of **ErRe₃** (red solid line) with the overlaid IR spectrum of **SmRe₃** recorded as KBr pellet (black solid line) reproduced from ref. S13 in the $675\text{--}4000\text{ cm}^{-1}$ range (the IR spectrum from Fig. S6 from the Supplementary Information of ref. S13 was traced using CorelDRAW 2019 software). Both spectra are very similar. Weak Re-H stretching modes at 2001 and 2034 cm^{-1} observed for **ErRe₃** are due to the slight decomposition of this extremely sensitive compound. Note, that these stretches are also present in the IR spectrum of **SmRe₃**, but are largely obstructed by a significant background reaching 40% transmittance at 2000 cm^{-1} and nearly 15% transmittance at 4000 cm^{-1} .

List of references in the supplemental information

Figures

Figure 1

The synthetic strategy towards ErRe_3 and its structure.

Graphical representation of the structural design transfer from the intermetallic magnet SmCo_5 (A and B) to the molecular nanomagnet $[\text{Er}^{\text{III}}(\text{Re}^{\text{I}}\text{Cp}_2)_3]$ (C). The hexagonal planar SmCo_6 coordination with unsupported coordination bonds between the center of the rare earth and six transition metals in SmCo_5 (A and B) is mimicked by the trigonal planar coordination in ErRe_3 (C). All three panels A-C are based on single-crystal structural models of SmCo_5 ¹ and ErRe_3 . Sm-Co bonds in SmCo_5 : 2.888 Å; Er-Re bonds in ErRe_3 : 2.9004(5), 2.9124(5), 2.9172(5) Å. Panel D presents the synthesis of ErRe_3 based on the work of Kempe et al.³² This approach utilizes the reaction of the weak Brønsted acid $[\text{Cp}_2\text{ReH}]$ with the strong Brønsted base btmsm^- in $[\text{Er}^{\text{III}}(\text{btmsm})_3]$ resulting in $(\text{Me}_3\text{Si})_2\text{CH}_2$ "elimination" and the formation of $[\text{Er}^{\text{III}}(\text{Re}^{\text{I}}\text{Cp}_2)_3]$.

Figure 2

Magnetic properties of ErRe_3 .

Magnetic hysteresis loops recorded with the $2.2 \text{ mT} \times \text{s}^{-1}$ magnetic field sweep rate in the -2 to 2 T range (A). Energy of the calculated Kramers Doublets (KD) arising from the splitting of the $^4\text{I}_{15/2}$ multiplet of Er^{III} in ErRe_3 with the most probable relaxation pathway represented by the red arrows (B). AC magnetic susceptibility recorded at zero magnetic field in the 2.4 – 27 K range, demonstrating the slow magnetization dynamics of ErRe_3 , solid lines are the best fits to the generalized Debye model with parameters presented in Table S2 (C). Temperature dependence of the magnetization relaxation rate $\tau^{-1}(T)$ at zero (D) and 0.15 mT (E) magnetic field obtained from the generalized Debye fitting of the respective AC magnetic susceptibility measurements (circles – experimental points, red line – best fits using Eq. 1 (D) and Eq. 2 (E), blue dashed line – Orbach relaxation, green dashed line – Raman relaxation, magenta dashed line – QTM relaxation).

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