An intermetallic molecular nanomagnet with the lanthanide coordinated only by transition metals

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Magnetic molecules known as molecular nanomagnets (MNMs) may be the key to ultra-high density data storage. Thus, novel strategies on how to design MNMs are desirable. Here, inspired by the hexagonal structure of the hardest intermetallic magnet SmCo5, we have synthesized a nanomagnetic molecule where the central lanthanide (Ln) ErIII is coordinated solely by three transition metal ions (TM) in a perfectly trigonal planar fashion. This intermetallic molecule [ErIII(ReICp2)3] (ErRe3) starts a family of molecular nanomagnets (MNM) with unsupported Ln-TM bonds and paves the way towards molecular intermetallics with strong direct magnetic exchange interactions—a promising route towards high-performance single-molecule magnets.

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Rare earth intermetallic magnets—samarium-cobalt (SmCo) and neodymium (NdFeB)—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. Their commercial success results from the combination of the strong magnetic anisotropy of rare-earth ions 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 nanomagnets (MNNs) or single-molecule magnets (SMMs). MNNs are molecule-sized objects with magnetic memory effects governed by quantum mechanics. They are strongly believed to revolutionize magnetic information storage, but at the moment do not have any real-world applications, as strongly believed to revolutionize magnetic information storage, but at the moment do not have any real-world applications. This approach was recently predicted to efficiently suppress QTM in MNMs and demonstrated for the ultra-hard metals. This approach was recently predicted to efficiently suppress QTM in MNMs and demonstrated for the ultra-hard metals. The concept of unsupported bonds between the lanthanide and the transition metal was first introduced and explored by Kempe et al. Later, it was proposed by Rinehart and Long as a possible strategy for molecular nanomagnets and put to use by Nippe et al. Reporting MNNs with unsupported direct bonds between the dysprosium ion and 4d (Fe) or 4d (Ru) transition metal ions. However, the magnetic memory effect (magnetic hysteresis) has not been observed, most probably due to the unfavorable ligand field geometry or the unfortunate choice of the rare-earth metal. The introduction of p-block heavy metals directly into the coordination sphere of the lanthanide was also pursued resulting in interesting examples of MNNs. Other systems involving direct bonds between actinides and d-metal elements were also reported, but slow magnetization dynamics were not studied. Noteworthy, the concept of placing transition metal ions in the proximity of Ln-based MNNMs employing suitable bridging ligands was pursued for tens of years with several examples showing enhancement of the slow relaxation of the magnetization due to the presence of the transition metal. However, this strategy, while providing very good control of the connectivity of the target multi-metallic compounds, cannot warrant strong coupling between the two metal ions due to the weak overlap of the relevant orbitals of the lanthanide and the bridging moiety. Only the direct bonding of the transition metal to the lanthanide center could result in strong electronic and magnetic interactions.

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. We demonstrate an important step toward molecular intermetallic nanomagnets—a perfectly trigonal planar [ErIII(R-eCp)3] complex (ErRe3) with magnetic hysteresis up to 7.2 K (at 2.2 mT s⁻¹ magnetic sweep rate) where ErIII is solely coordinated by three diamagnetic ReI ions.

**Results and discussion**

**Synthetic strategy.** ErRe3 is obtained following the literature procedure for [SmIII(Btmsm)]3. The starting material [ErIII(btmsm)] (obtained according to literature procedures) bis(trimethylsilyl)methyl anion reacts with [Cp2ReH] in benzene (Fig. 1D). The btmsm ligand coordinated to ErIII acts as a strong base capable of deprotonating [Cp2ReH]—a weak acid. Deprotonation of [Cp2ReH] leads to the elimination of the byproduct bis(trimethylsilylmethane)alkane elimination and the formation of the anionic [Cp-ReI] species that readily coordinate to ErIII resulting in the formation of a trigonal planar complex [ErIII(R-eCp)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; Supplementary Table 1). The SCXRD structural analysis confirmed the coordination of three ReI ions to the ErIII center with the formation of a nearly perfect trigonal planar neutral complex [ErIII(R-eCp)3] (Fig. 1C) with the Re-Re angles very close to 120° (121.22(2), 119.15(2), and 119.62(2)°) and the Er atom lying only 0.13(1) Å above the Re3 plane. The cyclopentadienyl ligands are coordinated solely to ReI and arranged in a slightly tilted manner below and above the equatorial plane of the ErRe3 molecule (Fig. 1C). There are no other coordination bonds to ErIII. Other intramolecular contacts of ErIII 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 Re–Re distances in ErRe3 (2.9004(5), 2.9124(5), and 2.9172(5) Å) are similar to those reported for [SmIII(R-eCp)3], [LaIII(R-eCp)3], and [LuIII(R-eCp)3] as well as other molecular compounds with unsupported rare earth—transition metal bonds.
The unusual coordination environment of Er\textsuperscript{III} in ErRe\textsubscript{3} may cast doubts on the nature of its electronic ground state. However, magnetic measurements for ErRe\textsubscript{3} confirm the valence states of the central Er\textsuperscript{III} ion and the diamagnetic Re\textsuperscript{I} donor atoms. The $\chi T$ ($\chi$—molar magnetic susceptibility) value of 11.3 cm\textsuperscript{3} K mol\textsuperscript{-1} at 260 K is close to 11.48 cm\textsuperscript{3} K mol\textsuperscript{-1} expected for a single Er\textsuperscript{III} $4I_{15/2}$ ground multiplet. A similar agreement between the experimental and the expected $\chi T$ was reported for [Sm\textsuperscript{III}(Re\textsubscript{2}Cp\textsubscript{2})\textsubscript{3}] ($^6I_{15/2}$ multiplet)\textsuperscript{32}. This is further confirmed by a very good agreement of the experimental $\chi T$ and the ab initio calculations (red solid line in Supplementary Fig. 5 and supplemental information) using Molcas\textsuperscript{53,54}. The $\chi(T)$ 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\textsuperscript{-1}) revealed the presence of waist-restricted (pinched) magnetic hysteresis loops up to 7.2 K (Fig. 2A), originating from the slow relaxation of the magnetization of the trigonal ErRe\textsubscript{3}. This temperature matches Er\textsuperscript{III} sandwich and metallocene complexes\textsuperscript{55}. Furthermore, the hysteresis loop in ErRe\textsubscript{3} opens in the 0.05–1.5 T range at 1.8 K and is the widest among trigonal Er\textsuperscript{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 (Fig. 2C and Supplementary Table 2). However, the resulting temperature dependence of the magnetic relaxation rate $\tau^{-1}(T)$ (Fig. 2D) contains contributions from three processes: quantum tunneling of magnetization (QTM), Raman and Orbach described by five parameters included in Eq. 1:

$$\tau^{-1} = A + CT^n + r_0^{-1} \exp \left( - \frac{U_{\text{eff}}}{k_B T} \right)$$



Fig. 1 The synthetic strategy towards ErRe3 and its structure. Graphical representation of the structural design transfer from the intermetallic magnet SmCo\textsubscript{5} (A, B) to the molecular nanomagnet [Er\textsuperscript{III}(Re\textsubscript{2}Cp\textsubscript{2})\textsubscript{3}] (C). The hexagonal planar SmCo\textsubscript{5} coordination with unsupported coordination bonds between the center of the rare earth and six transition metals in SmCo\textsubscript{5} (A, B) is mimicked by the trigonal planar coordination in ErRe\textsubscript{3} (C). All three panels A–C are based on single-crystal structural models of SmCo\textsubscript{5} and ErRe\textsubscript{3}. Sm-Co bonds in SmCo\textsubscript{5}: 2.888 Å; Er-Re bonds in ErRe\textsubscript{3}: 2.9004(5), 2.9124(5), 2.9172(5) Å. Panel D presents the synthesis of ErRe\textsubscript{3} based on the work of Kempe et al.\textsuperscript{52}. This approach utilizes the reaction of the weak Brønsted base btmsm\textsuperscript{-} in [Er\textsuperscript{III}(btmsm)\textsubscript{3}] in benzene at room temperature (RT) resulting in (Me\textsubscript{3}Si)\textsubscript{2}CH\textsubscript{2} elimination and the formation of [Er\textsuperscript{III}(Re\textsubscript{2}Cp\textsubscript{2})\textsubscript{3}].
Fig. 2 Magnetic properties of ErRe₃. Magnetization (M) hysteresis loops were recorded with the 2.2 mT s⁻¹ magnetic field (μₐH) sweep rate in the −2 to 2 T range (A). The energy of the calculated Kramers Doublets (KDs) arising from the splitting of the 4I₁₅/₂ multiplet of Er³⁺ in ErRe₃ with the most probable relaxation pathway represented by red arrows (B). In-phase (χ') and out-of-phase (χ'') AC molar magnetic susceptibility recorded at zero magnetic field in the 2.4–27 K temperature range, demonstrating the slow magnetization dynamics of ErRe₃, solid lines are the best fits to the generalized Debye model with parameters presented in Supplementary Table 2 (C). Temperature dependence of the magnetization relaxation rate τ⁻¹(T) at zero (D) and 0.15 mT (E) magnetic field obtained from the generalized Debye fitting of the respective AC molar 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). Standard deviations in A, C, D, and E are smaller than the size of the data points.

extracted only with limited confidence from AC data collected at zero DC field (best-fit parameters A = 179(4) s⁻¹, C = 0.137(9) K⁻¹ s⁻¹, n = 3.60(2), τ₀ = 8.3(8)·10⁻¹⁰ s, and U_eff = 285(3) K with R² = 0.99994; Fig. 2D). To mitigate this issue, the AC magnetic studies were repeated under an applied DC magnetic field of 0.15 T (Supplementary Fig. 6 and Supplementary Table 3). The presence of a small applied magnetic field quenches the QTM with only a negligible direct process, which was accurately determined from the magnetic field dependence of the relaxation time (Supplementary Fig. 7 and Supplementary Table 4). 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 Eq. 2:

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

where τ⁻¹ is the magnetic relaxation rate, C and n parameters describe the Raman-like process, and τ₀ and U_eff are related to the Orbach process. The satisfactory fit could be obtained with C = 0.0035(4) K⁻¹ s⁻¹, n = 4.74(3), τ₀ = 3.0(5)·10⁻¹⁰ s, and U_eff = 314(5) K with R² = 0.99997 (Fig. 2E). The relation between U_eff and τ₀ falls perfectly in the statistically expected range for prolate Ln MNMs as analyzed by Gaita-Arino et al. in their work covering 1405 examples of SIMs[12]. The observed low Raman exponent of 4.74 is most probably caused by spin-lattice coupling with optical phonons as summarized and discussed by Gu and Wu[56].

The obtained effective energy barrier for the magnetization reversal U_eff = 314(5) K is significantly smaller than expected from the theoretical calculations (CASSCF-RASSI; OpenMolcas 19.11 [52]; for details see Supplementary Information including Supplementary Tables 5 and 6 with the information on basis sets, spin-orbit energies and g-tensors of the lowest Kramers Doublets, respectively), predicting the fastest relaxation between the ± Kramers Doublet lying 576 K above the highly axial ground state (Fig. 2B and Supplementary Table 4). 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± of 224 K, 3± of 363 K, and 4± of 475 K. The best fits (Supplementary Fig. 8A–C) are characterized by the following R² values: 0.99702 for U_eff 2± = 224 K, 0.99960 for U_eff 3± = 363 K, and 0.99808 for U_eff 4± = 475 K. The best agreement is observed for U_eff 3± = 363 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 Fig. 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 Supplementary Fig. 8D. 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[58,59] or low-coordinate[58,59] Er³⁺ molecules and is comparable to the Er³⁺ sandwich and metallocene complexes[37,55,60–64]. Interestingly, ErRe₃ shows significantly slower relaxation as compared to [Er(N(SiMe₃)₂)₂]₃ characterized by U_eff = 122 K[57] 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 ErIII(NH2)3 compound. 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.

Our findings regarding the magnetic dynamics of ErRe3 are consistent with the recent data analysis by Gaita-Ariño et al.11. The analysis shows relatively high magnetic hysteresis temperatures for probe systems such as equatorial ErIII SIMs coordinated by rigid ligands accompanied by the maxima of the out-of-phase magnetic susceptibility (χ′) at relatively low temperatures. ErRe3 is a perfect demonstration of this trend with the Thyst of 7.2 K and Ueff = 314 K.

In conclusion, the reported triangular molecule [ErIII(ReCp2)] constitutes a molecular nanomagnet that mimics structurally the hardest commercial rare-earth magnet known SmCo5 and creates a connection between two incompatible fields: the rare-earth intermetallics and molecule-based compounds. ErRe3 is a rare example of a lanthanide single-molecule magnet coordinated solely by transition metals which enables the implementation of a promising 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

General considerations. All manipulations were performed under an argon gas atmosphere inside the Inert PureLab HE glovebox (O2 < 0.1 ppm and H2O < 0.5 ppm). All solvents used in this study (except benzene) were of HPLC grade and were additionally dried under argon using the Inert PureSolv E7 solvent purification system and stored over 3 Å molecular sieves for at least 24 h before use. Anhydrous benzene was purchased from commercial sources (Merck) and degassed by performing three freeze-pump-thaw cycles before use. Anhydrous ReCl5 (at least 99.9%) was purchased from Merck and used as received for the preparation of [Cp2ReH] according to the modified literature procedure described below. The obtained [Cp2ReH] was characterized by means of SCXRD and the purity was confirmed by performing PXRD measurements. [ErIII(btmsm)] was also prepared following the modified literature procedures described below for the description of the preparation procedure. The purity of the obtained product was checked by PXRD. See Supplementary Information file for measurement details and ab initio calculations. Warning! Benzene is recognized as carcinogenic to humans and should be handled with caution using a well-ventilated hood or glovebox.

Preparation of [ErIII(btmsm)] 0.5Cp2H2 (ErRe3). All manipulations were performed in an argon-filled glovebox (Inert PureLab HE). [Cp2ReH] (242 mg, 0.76 mmol) was dissolved in anhydrous benzene (3.5 ml) and added to the benzene solution (2.5 ml) of [ErIII(btmsm)] (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 0.2 μm Teflon membrane (Whatman). Yield: 70 mg (0.061 mmol; 24%). The purity of the compound was checked by powder X-ray diffraction, with the experimental pattern (Supplementary Fig. 4) matching perfectly the simulated one from the SCXRD structural model obtained at 270 K (CCDC 2065531). IR, neat (cm−1): 796, 808, 816, 832, 832, 850, 987, 1000, 1059, 1087, 1095vs, 1154wv, 1188wv, 1201wv, 1255, 1273, 1342, 1358, 1372, 1419, 1442, 1462, 1479, 1558, 1657s, 2011wv, 2034wv, 2545, 2929vs, 3036, 3063, 3068, 3089, 3550 (Supplementary Fig. 9).
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**Acknowledgements**

This work was financed by the Polish National Science Centre within the Sonata Bis 6 project no. 2016/22/ST5/00055 (D.P.). The research was partly carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Smart Growth Operational Program 2014-2020, contract no. POIR.01.02.00-0001/20-00 (D.P.). The open-access publication of this article was funded by the program “Excellence Initiative - Research University” at the Jagiellonian University in Krakow. The authors acknowledge Alejandro Gaita-Arrio for
pointing out and formulating an important observation regarding the slow magnetic dynamics of the reported compound ErRe$_3$, in comparison to known Ln-SIMs.

**Author contributions**
M.M. prepared the starting material [Cp$_2$ReH], participated in the preparation of the target compound, performed and analyzed the magnetic measurements, and wrote the relevant fragment of the manuscript; M.B. prepared the starting material [Er$^{III}$(btmsm)], participated in the preparation of the target compound, analyzed 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 analyzed 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.

**Additional information**
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-29624-7.

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Peer review information Nature Communications thanks Thomas Albrecht-Schoenzaert, Alejandro Gaita-Ariño and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

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