The nanosized self-assemblies \( \{[\text{Ln}^\text{III}\{\text{H}_2\text{O}\}_3\{\text{prop} \cdot \text{SMe}\}}_3\} \) \( \{\text{H}_2\text{O}\} \) (\( \text{Ln} = \text{Dy, 1 and Tb, 2} \)) based on new 3d–4f mixed-metal coordination topologies are formed via extensive intramolecular hydrogen bonding that is directed by enclosed water molecules. Compounds 1 and 2 show single-molecule magnet characteristics manifested by hysteresis loops up to 1.6 K \( (U_{\text{eff}} = 8.3 \text{ cm}^{-1}) \) and 1 K \( (U_{\text{eff}} = 3.4 \text{ cm}^{-1}) \), respectively.

Cooperative non-covalent interactions, in particular hydrogen bonds, are key to hierarchical self-assemblies (e.g., supramolecular polymeric structures). Hydrogen bonding has been shown to affect exchange coupling mechanisms, slow magnetization relaxation, electron tunneling, quantum phase interference, and superconductivity, which has far-reaching implications in the field of molecular electronics and spintronics. Specifically, magnetic compounds with single-molecule magnet (SMM) behavior stand in the focus of these cross-disciplinary efforts. To date, for a great number of SMMs intermolecular hydrogen bonds were related to their quantum coherence, Landau–Zener tunneling and exchange-biased quantum tunneling of magnetization, whereas discrete SMMs with structurally crucial intramolecular hydrogen-bond arrays have not yet been elaborated.

Herein we introduce two charge-neutral 3d–4f molecular magnets whose suprastructure with a metal skeleton dimension of ca. 17 × 12 Å are maintained by purely intramolecular hydrogen bonds between the self-assembled, nuclearity-distinct molecular entities: \( \{[\text{Dy}^\text{III}\{\text{H}_2\text{O}\}_3][\text{Dy}^\text{III}\{\text{prop-SMe}\}_3]_2[\text{H}_2\text{O}]_2\} \), \( \{[\text{H}_2\text{O}]_2[\text{H}_2\text{O}]_2[\text{prop-SMe}]_2\}_2\} \), \( \{[\text{H}_2\text{O}]_2[\text{H}_2\text{O}]_2[\text{prop-SMe}]_2\}_2\} \), \( \{[\text{H}_2\text{O}]_2[\text{H}_2\text{O}]_2[\text{prop-SMe}]_2\}_2\} \). The most prominent structural motifs in 1 and 2 are \( \{\text{H}_2\text{O}\} \{\text{Ln}^\text{III}\}_3 \) rings that are linked into supramolecular aggregates via a solely hydrogen-bonding \( \text{H}_2\text{O} \) bridge, resulting in linear triads, capped at their axial ends by additional \( \text{Ln} \) sites. The \( \{\text{H}_2\text{O}\} \{\text{Cr}^\text{III}\} \{\text{Ln}^\text{III}\}_6 \) entities are further decorated by terminal prop–SMe ligands. Both the ligand patterns of the \( \{\text{H}_2\text{O}\} \{\text{Cr}^\text{III}\} \{\text{Ln}^\text{III}\}_6 \) rings and the terminal ligand environment of the capping \( \text{Ln} \) sites differ and thus break the dimer-like symmetry of 1 and 2.

Compounds 1 and 2 form as octahedrally shaped crystals in one-pot aerobic reactions (see the ESI†) of basic chromium(III) acetate \( \text{[Cr}(\text{OH})_2\{\text{OAc}\}_3\} \) and lanthanide(III) acetate tetrahydrate \( \text{Ln(OAc)}_3 \cdot 4\text{H}_2\text{O} \) in a 1 : 1 metal ratio with 2.0 eq. of \( \text{H}_2\text{bda} \) in \( \text{MeCN} \) under reflux, followed by addition of 2.2 eq. of 3-(methylthio)propionic acid \( \text{Hprop-SMe} \). When \( \text{Hprop-SMe} \) is replaced by 4-(methylthio)phenol \( \text{Hphe-SMe} \) under otherwise identical conditions, slightly larger single crystals of the quasi-isotrostructural yet thioether-free compound \( \{[\text{H}_2\text{O}]_2[\text{H}_2\text{O}]_2[\text{H}_2\text{O}]_2[\text{OAc}]_3[\text{H}_2\text{bda}]_3[\text{glyc}]_3[\text{ox}]_3[\text{H}_2\text{O}]_2\} \) \( 10.5\text{H}_2\text{O} \cdot 1.5\text{MeCN} \) (3) can be obtained in low yields. Although not present in the product, \( \text{Hphe-SMe} \) here is required for isolation of the crystalline material. The presence of oxalates and glycrolates in 1–3 is likely linked to aerobic catalytic oxidation of the acetate ligands of the precursors – direct addition of small amounts of oxalic and glycolic acids to the reaction mixtures did not afford the crystalline product. Due to their low solubility, very few oxalate-containing lanthanoid compounds are known (29 CCDC entries; only 6 entries for oxalate-containing complexes of 3d–4f metal ions). Under hydrothermal oxidative conditions, in situ oxalate formation has been reported for the decomposition of 2,3-pyrazinedicarboxylic acid in the presence of lanthanoid salts,11,12 oxalate and glycrolate can also
be generated similarly in situ in the presence of uranium oxynitrates and 1,4-diazabicyclo[2.2.2]octane. In situ production of oxalato-bridged heterometallic compounds by crystallization at room temperature from solutions of 3d metal precursors, lanthanoid acetates and L-ascorbic acid is also known, but it remains unclear if oxalates here originate from the decomposition of L-ascorbic acid, from the oxidation of acetate, or impurities in the employed lanthanoid salts.

The isostructural compounds 1 and 2 crystallize in the trigonal space group P31c (Table S2, ESI†). The Cr3-symmetric supramolecular \{H2OCr3Ln6\}⋯\{H2O\}⋯\{H2OCCr3Ln6\}···Ln\] assemblies in these structures consist of two \{H2O\}⊂Cr3Ln6\} aggregates sandwiching a central water molecule (Fig. 1). In one of the aggregates a [Ln(OAc)3(H2O)3] moiety is situated above the mixed-metal \{H2O\}⊂Cr3Ln6\} ring (Ln⋯O1H2O: ca. 4.83 Å for Dy, 4.88 Å for Tb), while the other aggregate is capped by a [Ln(H2O)3(prop·SMe)] unit (Ln⋯O1H2O: ca. 4.69 Å for Dy, 4.70 Å for Tb). The capping Ln sites in the [Ln(H2O)3L6] moieties as well as the three central water guests reside on the C3 axis. While three acetate/thioether ligands of the [LnL6(H2O)3] moieties are directed outwards, the three aqua ligands form hydrogen bonds with oxalate and acetate ligands of the \{H2OCCr3Ln6\} rings.

Each \{H2OCCr3Ln6\} ring is composed of three oxalate-bridged \{CrLn2(OAc)4(H2bda)(glyc)(prop·SMe)\} triangles (Fig. 1c), with intra-triangle CrIII–LnIII distances of 3.339(4)–3.360(4) Å for 1 and 3.356(3)–3.374(3) Å for 2. Intra-triangle Ln–Ln distances are 4.100(2)–4.133(2) Å (1) and 4.117(1)–4.150(1) Å (2); inter-triangle oxalate-bridged Ln−Ln pairs range from 6.25–6.28 Å (1) and 6.27–6.31 Å (2). The Ln6 sub-structure is nearly flat, while the outer Cr sites are slightly displaced toward the equator of the entire assembly and each coordinates to one H2bda via its N and two OH sites, two carboxylates in an η1 mode (OAc− or prop-SMe−), and a glycolate O atom. The bridging OH groups of H2bda as well as the carboxylates and the glycolate ligands link the Cr to the Ln centers within the \{CrLn2\} triangles. One of the LnIII ions in \{CrLn2\} is eight-coordinated bearing the monodentate carboxylate ligand (OAc− or prop-SMe−), the OH group of H2bda, two oxygens of oxalate, alchoolate and one carboxylic oxygen of glycolate, an O atom of α-bridging the LnIII center with CrIII as well as an oxygen atom of the α,η1η2-acetate ligand connecting the two LnIII ions within the \{CrLn2\} triangle. The second LnIII center is nine-coordinated bearing the chelating acetate ligand instead of the monodentate carboxylate and coordinating two oxygens of the µ2,η1η2-OAc group instead of a carboxylic glycolate oxygen. The central oxalate oxygen of glyc2− in \{CrLn2\} units thus adopts a µ3-coordination mode, hitherto not observed for this ligand, to connect the three metal ions (see the ESI†). The prop-SMe− ligands occupy two positions within the \{H2O\}⊂Cr3Ln6\} rings that are disordered with acetates: (i) monodentate carboxylates coordinate to the LnIII centers with coordination number 8, and (ii) µ3-carboxylates connecting CrIII and eight-coordinated LnIII centers. 

Fig. 1 Side (a) and top (b) views of the solid-state \{Cr6Ln14\} assembly in 1 and 2. Ln: light blue, Cr: purple spheres; O: red, S: yellow. The central linear water triad is highlighted by red spheres representing the oxygen atoms. C is colored according to the ligand type: dark gray: H2bda, light gray: oxalate, green: acetate and prop-SMe−, dark gray spheres: glycolate. Hydrogen bonds are indicated as dashed black lines. (c) One of the \{Cr3Ln6\} rings, shown without the encapsulated water guest. For disordered acetate and prop-SMe− ligands, only their common O2C2 terminus is shown (green). Glyc ligands are highlighted in ball-and-stick mode (C: dark gray, O: orange). All hydrogen atoms are omitted for clarity.
and 3.64 Å (2), no direct hydrogen bonding within the \([\text{H}_2\text{O}]_3\) substructure is possible.\(^{16}\) The –CH$_2$–S–Me moieties of prop-SMe$^-$ ligands in 1 and 2 are heavily disordered and in part cannot be fully located in single crystal X-ray analyses, despite the fact that several crystals have been measured for every compound. The situation is even more complicated due to the afore-mentioned disorder of prop-SMe$^-$ and OAc$^-$ groups on the \([\text{H}_2\text{O} \text{Cr}_3\text{Ln}_6]\) rings. Therefore, the exact formulae determined by X-ray analyses (see the ESI\(^\dagger\)) differ from the disorder-corrected formulae used herein, in particular in a lower content of prop-SMe$^-$. Nevertheless, the sulfur content of 4.3–4.6% determined by elemental analysis in compounds 1 and 2 clearly corresponds to nine to ten S atoms per formula unit. Additional evidence for exactly nine prop-SMe$^-$ ligands in 1 and 2 was found by negative-ion electrospray mass spectrometry. As exemplified by compound 2 containing isotopically pure $^{159}$Tb, each \({\text{[CrLn}_3]\}) triangle bears one sulfur atom, as indicated by the 100% molecular ion peak assigned to \([\text{CrTb}_2\text{OAc}_3\text{(prop-SMe)(H}_2\text{bda)(glyc)}_3\])$^-$ (expt. 1062.989 Da, calcd 1063.007 Da; Fig. S3, ESI\(^\dagger\)).

The unusual structural arrangement of the H-bonded and water-templated \([\{\text{Ln} III\}{\text{H}_2\text{O}}\text{Cr}_3\text{Ln}_6]\) assemblies prompted us to investigate the magnetism of 1 and 2 by both direct current (dc) and alternating current (ac) magnetic susceptibility measurements down to 1.8 K and the low-temperature magnetization measured down to 30 mK using micro-SQUID magnetometry. For 1, the diamagnetism-corrected \(\chi_m T\) value of 190.45 cm$^3$ K mol$^{-1}$ at 290 K is slightly below the range of 192.41–208.12 cm$^3$ K mol$^{-1}$ expected$^{17}$ for six high-spin Cr$^{III}$ and 14 Dy$^{III}$ non-interacting centers. This low value hints at the presence of small intramolecular antiferromagnetic exchange interactions. Upon decreasing \(T\), \(\chi_m T\) gradually increases to a maximum at ca. 120 K, subsequently decreases to a minimum at ca. 20 K, and finally sharply increases to a maximum of 232.18 cm$^3$ K mol$^{-1}$ at 2.2 K (Fig. 2a). While both increases indicate ferromagnetic exchange interactions, the decrease may be due to antiferromagnetic interactions and/or due to the thermal depopulation of the \(m_i\) substates of the Dy$^{III}$ centers generated by the ligand field. Due to the observation of the low \(\chi_m T\) value at 290 K, the minimum and the maxima, the exchange interactions are potentially small and of comparable magnitude. The molar magnetization \(M_m\) at 2.0 K is a linear function of the applied field \(B\) up to ca. 0.3 T, and is almost linear for 2–5 T characterized by \(a\), however, distinct different slope reaching 70.8N$_{\mu_B}$ at 5 T. This value is considerably below the saturation value of ca. 158N$_{\mu_B}$ and may be thus due to antiferromagnetic exchange interactions. However, since the curve is still rising at 5 T, and the states of the Dy$^{III}$ centers are usually mixed \(m_i\) states whose compositions can depend on the applied magnetic field,\(^{17}\) the small magnetization values may be also due to single-ion effects of the Dy$^{III}$ centers. As such, the dc data reveal both antiferromagnetic and ferromagnetic exchange interactions within the compound besides single-ion effects. The ac magnetic susceptibility data at zero bias field show slow relaxation for temperatures below 7.0 K, within the frequency limits of the employed experimental set-up (Fig. 2b).

Analyzing the in-phase \(\chi_m\) and out-of-phase \(\chi''_m\) components as a function of the applied frequency \(f\) in terms of a generalized Debye expression\(^{18}\) yields least-squares fits which are depicted as solid lines in Fig. 2b and S5 (ESI\(^\dagger\)). The distribution of relaxation times \(\langle\alpha\rangle\) suggests the existence of multiple relaxation pathways \((\alpha = 0.09–0.46, \text{mean 0.25})\), and the
semi-logarithmic representation of τ vs. T⁻¹ indicates a mono-
 exponential perspective (Fig. 2c). From this phenomenological
 perspective, the mono-exponential behavior reveals that the
 Orbach relaxation process clearly dominates the ac behavior
 within this temperature range (2.0–7.0 K). We therefore fit the
data to a single Arrhenius expression \( \tau = \tau_0 \exp[U_{\text{eff}}(k_B T)] \) (\( k_B \):
 Boltzmann constant) in the range of 2.0–5.5 K yielding the at-
tem plate time \( \tau_0 = (3.7 \pm 0.3) \times 10^{-6} \) s and the effective en-
 ergy barrier \( U_{\text{eff}} = (8.3 \pm 0.2) \) cm⁻¹ representing a rather large
 Orbach relaxation time and a small effective energy barrier.¹⁹

The magnetic properties of 2 are discussed in detail in the
ESI. T The dc susceptibility data reveal antiferromagnetic and
ferromagnetic exchange interactions within the compound
besides single-ion effects. The magnetic ac data show slow
magnetization relaxation for \( T \lesssim 4.6 \) K characterized by an
attempt time \( \tau_0 = (7.5 \pm 0.8) \times 10^{-6} \) s and an effective en-
ergty barrier \( U_{\text{eff}} = (3.4 \pm 0.2) \) cm⁻¹.

A comparison of the magnetic properties of 1 and 2
revealed by measurements down to 2 K shows an overall
similar magnetic behavior although there are a few differences:
1 is characterized by more pronounced ferromagnetic
exchange interactions than 2. Both compounds show slow
relaxation at low temperatures, and both \( \tau_0 \) and \( U_{\text{eff}} \) differ by a
factor of roughly 2.

Low temperature magnetization measurements were
carried out on single crystals of 1 and 2 (see the ESI). The
magnetic field is applied parallel to the easy axis of magne-
tization using the transverse field method. Open hysteresis
loops were observed up to 1.6 K for 1 (Fig. 3) and 1 K for 2 at
a sweep rate of 0.14 T s⁻¹, suggesting that 1 has a slightly
higher energy barrier as manifested in the ac data. The coer-
civity fields of the hysteresis loops increase with decreasing
temperature and increasing field sweep rates, which is consist-
ent with the phenomenon of superparamagnetic behavior,
suggesting that both 1 and 2 behave as SMMs. No step-like
feature associated with the occurrence of quantum tunneling
of magnetization (QTM) was observed around zero field in the
loops for these compounds, indicative of a broadened effect
because of the presence of hyperfine coupling of the Tb³⁺
and Dy³⁺ ions and/or inter- and intramolecular interactions. The
width of the loops of around zero field is slightly broader
than that of 1. This can be explained by the nature of the two
different types of lanthanoid ions, Tb and Dy (integer spin vs.
half-integer spin – non-Kramers vs. Kramers theorem of spin
parity), providing that the direct relaxation process is faster
for Tb than for Dy. Similar features were also reported in the
hysteresis loops of DyPc₂ and TbPc₂ double-decker complexes
where Pc is a phthalocyaninato ligand.²⁰ We attempted to
take the relaxation time \( \tau \) at zero applied field from the
decay measurements of the dc magnetization in the tempera-
ture range of 1.3–0.03 K. Due to the wide distribution of relax-
ation processes operating at very low temperatures which
coexist with zero-field QTM, no reliable relaxation time could
be obtained for both complexes (see the ESI†). The quantum
relaxation time approaches toward about 10 s for 1 and 100 s
for 2, confirming the slower zero-field quantum tunneling
effect present in the Tb containing complex as indicated in the
ac data.

In summary, the formation of quasi-isostructural SMMs 1
and 2 with a layer-like motif is likely induced by templating
through cooperative hydrogen bonds of a central, linear triad
of water molecules. The \{Cr₃Ln₂(H₂O)₁₀\} aggregates feature
several unique structural aspects, from the μ₃-binding mode of
glycolate to an unprecedentedly low Cr : Ln²¹ ratio of 3 : 7
-reported in CCDC: 1 : 1, 1 : 2, 2 : 3, 3 : 1 and 3 : 2 for Ln = Dy
and Tb). The obtained 3d–4f SMMs are reminiscent of quantum-dot ‘artificial molecules’ exhibiting inter-dot coupling.²²
Moreover, the templating role of water resembles that in
polyoxovanadate chemistry (see e.g. the archetypal spin-fru-
strated molecular magnet \{H₂O@V⁵O₆(C₅H₄O₄)₉\}⁻.²³ Given that
the supramolecular aggregates are in principle susceptible to
temperatures of the component-dependent dynamic processes
inducing and controlling an exchange-biased quantum tunnel-
ing in such supramolecular SMM architectures.

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