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Chemical and magnetic tuneability in structurally defined hetero-trimetallic dendrimers

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The inaccessibility of magnetic dendrimers stems not only from the complexity of their synthesis but more critically from the challenge of crystallising dendritic structures. Magnetic architectures are difficult to decipher without X-ray data considering magneto-structural correlations for the rational design of molecular magnets and better understanding of the physical and magnetic properties. Here, we report the synthesis and characterisation of a tuneable magnetic hetero-trimetallic dendrimer family, MLn_3Co_6, with Ln^{3+} = La, Gd, Tb, Dy and M^{3+} = Cr or Co. We present, for the first time, a hetero-trimetallic dendrimer with a fully resolved X-ray structure and direct mass spectrometry evidence, providing unprecedented insight into the structural and magnetic properties of metallo-dendrimers. Furthermore, the chemical flexibility enables the synthesis of species with distinct magnetic behaviours depending on the incorporated metal ions. The choice of spin carriers determines whether the system exhibits a high-spin molecule behaviour or slow relaxation of magnetisation.

Introduction

Since their development in the 1980s, dendrimers have offered powerful platforms for applications across diverse fields, owing to their nanometric dimensions, starburst architectures and, crucially, their monodispersity.[1–3] There is now an abundant literature reporting examples of dendrimers that offer many additional possibilities for application as functional materials.[4–8] When it comes to magnetic materials, the radial topology of dendrimers, and particularly metallo-dendrimers, makes them attractive molecular analogues of magnetic nanoparticles for data storage, quantum computing and magnetocaloric applications.[9] Additionally, incorporating metal ions at various positions within the dendrimer can impart additional functionalities or synergistic properties.[10–12] Yet examples of magnetic dendrimers remain rare due to synthetic challenges and difficulties in characterisation, especially by single-crystal X-ray diffraction.[13–15] The few reported systems are mostly characterised spectroscopically, complicating the study of magnetostructural correlations.[16,17]

Metallo-dendrimers generally fall into two categories: (i) covalent dendrimers with organic backbones and (ii) supramolecular dendrimers built through coordination bonds.[18] Incorporating metals into organic dendrimers is more common and can involve using metal ions or clusters as polyfunctional cores,[19] functionalising peripheral groups,[20] or embedding metal ions into cavities or nodes.[21] However, dendrimers integrating metals at the core, nodes and periphery remain rare, especially heterometallic examples, and often require a combination of these strategies.[22–25] Notable examples include Le Pleux's hetero-trimetallic porphyrin dendrimers containing a gold core, magnesium nodes and zinc ions at the periphery,[26] and Yamamoto's fourth-generation phenylazomethine dendrimers coordinating up to four different metal ions (Fe, Ga, V, and Sn).[27,28] Nevertheless, none have been structurally confirmed by single-crystal X-ray diffraction.

Organic scaffolds often introduce flexibility that hinders the precise geometry needed for magnetic molecules.[29,30] Supramolecular dendrimers, based on metal–ligand coordination, offer greater rigidity and topological control, yet their synthesis remains challenging due to equilibria in solution. A promising route is the "complexes-as-ligands" approach, in which preorganised metal complexes act as functional building blocks in dendritic architectures. Pioneered by Balzani and Campagna, this method enables precise control over dendri-

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mer size, shape, and branching by careful selection of cores, nodes, and peripheral groups.[31,32] Despite the absence of crystallographic characterisation, this approach has enabled the synthesis of hetero-polymetallic dendrimers incorporating diverse metal centres and exhibiting intriguing photophysical and electrochemical properties relevant to light harvesting, energy transfer and molecular electronics.[33,34]

A similar building-block approach can be applied to the design of metallo-dendrimers exhibiting magnetic properties such as high-spin molecules (HSMs) and single-molecule magnets (SMMs). Central to this adaptation is the careful selection of metal centres that provide high spin states, essential for HSMs, or strong magnetic anisotropy, crucial for establishing energy barriers to magnetisation reversal in SMMs.[35] Concurrently, rigid and symmetrically arranged ligands act as dendritic scaffolds that not only define precise coordination geometries to maximise anisotropy but also facilitate magnetic exchange interactions among metal centres.[35] Additionally, fine control over oxidation states, molecular symmetry and peripheral functionalisation enables modulation of magnetic properties while preserving the dendrimer's structural integrity and solubility. This preservation is critical to promote crystallisation and enable detailed structural characterisation through single-crystal X-ray diffraction studies.

Guided by these principles, we sought to develop a new family of dendritic architectures amenable to structural characterisation in both the solid state and in solution, whilst capable of integrating multiple metal centres with magnetic functionality. The synthetic realisation of such systems has proved elusive to date, not only because of the inherent synthetic challenges but also due to the difficulty of achieving robust, well-defined architectures that permit comprehensive characterisation, including by single-crystal X-ray diffraction. Establishing discrete heterometallic dendrimers that can be fully characterised constitutes a significant advance, as it enables systematic tuning of magnetic properties through metal selection and precise architectural control. This tunability paves the way for exploring magneto-structural correlations

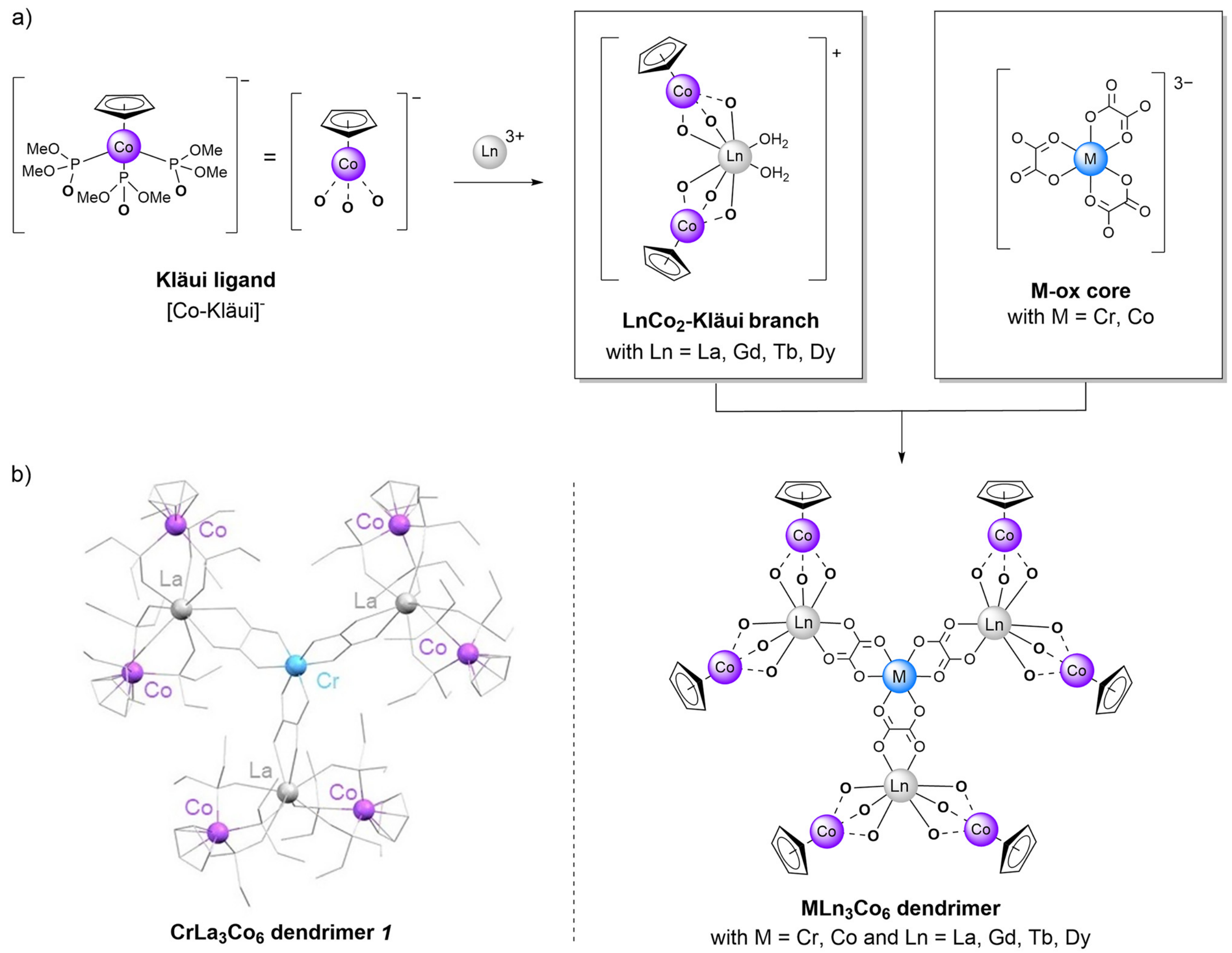

Fig. 1 (a) Convergent synthesis using a modular approach yielding the hetero-trimetallic dendrimer topology MLn_3Co_6 (M = Cr, Co and Ln = La, Gd, Tb, Dy); (b) crystallographic representation of the decanuclear complex $CrLa_3Co_6$ **1**. CCDC 2451819. Only metal ions are coloured while hydrogen atoms and solvent molecules are omitted for clarity.

in a manner that has so far remained out of reach for dendritic systems.

Herein, we report a tuneable hetero-trimetallic dendrimer $CrLn_3Co_6$ with Ln = La^{3+} **1**, Gd^{3+} **2**, Tb^{3+} **3**, Dy^{3+} **4** alongside its $CoDy_3Co_6$ **5** analogue. We have employed the kinetically inert tris(oxalato) metallate(III) $[M(C_2O_4)_3]^{3-}$ (M = Cr, Co) anions, abbreviated $[Cr\text{-}ox]^{3-}$ and $[Co\text{-}ox]^{3-}$, as a trifunctional core. These oxalato complexes not only direct assembly but also offer mediation of magnetic coupling through oxalate bridges.[36,37] As dendritic branches, we have used the hetero-bimetallic complex $[LnCo_2\text{-Kläui}]^+$ where the Ln^{3+} ion is coordinated by three oxygen atoms from each of two Kläui capping ligands [(η^5-cyclopentadienyl)tris(dimethylphosphito-P)cobalt(III)] $[CpCo(PO(OMe)_2)_3]^-$, abbreviated $[Co\text{-Kläui}]^-$.[38,39] Both the $[Co\text{-Kläui}]^-$ units magnetically isolate the lanthanoid ions and impose a rigid geometry that supports slow magnetic relaxation.[40–43] In $CrLn_3Co_6$, the paramagnetic Cr^{3+} centre promotes a high-spin state *via* magnetic interactions transmitted through the oxalate ligands while in $CoDy_3Co_6$, the diamagnetic Co^{3+} core further isolates the lanthanoid centres, supporting slow relaxation of magnetisation.

Results and discussion

Synthesis

The decanuclear MLn_3Co_6 dendrimers were obtained in a one-pot synthesis by coordination-driven self-assembly of the $[M\text{-}ox]^{3-}$ (M = Cr, Co) and $[Co\text{-Kläui}]^-$ precursors in the presence of lanthanoid ions Ln^{3+} (Ln = La, Gd, Tb, Dy) (Fig. 1). Six equivalents of Na[Co-Kläui] were first reacted with three equivalents of a lanthanoid salt $Ln(NO_3)_3\cdot xH_2O$ in a $MeCN/H_2O$ (1 : 1) mixture, forming three $[LnCo_2\text{-Kläui}]^+$ branches *in situ*. It was then followed by the addition of one equivalent of $K_3[Cr\text{-}ox]$. Single crystals of the neutral hetero-trimetallic architectures $CrLn_3Co_6$ with Ln = La **1**, Gd **2**, Tb **3**, and Dy **4** formed within a few days upon evaporation of the solvent mixture in yields ranging from 80 to 85%. The dendrimer $CoDy_3Co_6$ **5** was obtained following the same synthetic procedure as for $CrLn_3Co_6$ **1–4** using the $[Co\text{-}ox]^{3-}$ precursor. The decanuclear complex was obtained as light green prism-shaped crystals in 70% yield. The successful assembly of these decanuclear species in a single synthetic step underscores the remarkable organisational power of coordination-driven strategies. Given the extreme scarcity of well-defined metallo-dendrimers, the consistently high yields and crystallinity of these assemblies are significant and suggest that the kinetically stable architectures are strongly favoured under our conditions.

Characterisation in the solid state

Single-crystal X-ray structure analysis confirmed that all five dendrimers **1–5** are isostructural and crystallise in the triclinic space group $P\bar{1}$ (Table S1). Their unit cells contain both enantiomeric forms of the dendrimer. As anticipated from the overlapping IR spectra (Fig. S2), the unit cell parameters for $CrLn_3Co_6$ dendrimers **1–4** are essentially identical, whereas $CoDy_3Co_6$ displays slightly different metrics. A representative structure is shown for $CrLa_3Co_6$ **1** in Fig. 1 where metal ions are labelled for clarity. The neutral architecture is composed of a tris(oxalato)chromate(III) core on which three $[LaCo_2\text{-Kläui}]^+$ branches are attached through a Cr-ox-La bridge. The tris(oxalato)chromate(III) core adopts a distorted octahedral geometry, with Cr–O bond lengths of 1.96–1.98 Å and average O–Cr–O angles of 83.4°. Each oxalate ligand bridges a lanthanum(III) ion with La⋯Cr distances of approximately 5.7 Å. All La^{3+} ions are coordinated by two Kläui ligands, resulting in a coordination number of eight. The bond distances $La1\text{–}O_{oxalato}$ (2.48 Å) are distinctly longer than the $La\text{–}O_{Kläui}$ distances (2.35 Å). Despite small differences among the La sites, all three lanthanum(III) ions are best described by Shape measures as distorted square antiprisms (Table S2). Within each Kläui ligand, cobalt(III) ions bind to five carbon atoms of the Cp^- group and three phosphorus atoms of the phosphito groups, with Co–C bond distances ranging from 2.072(2) Å to 2.092(2) Å and long Co–P distances of 2.162(7) Å to 2.193(3) Å.

The Cr^{3+} core lies in the plane defined by the three La^{3+} ions, while the Co^{3+} centres of the Kläui ligand alternate above and below the $CrLa_3$ plane, introducing chirality driven by the bidentate oxalate bridges. The other isomer is generated by the inversion centre of the $P\bar{1}$ triclinic space group, yielding a racemic mixture at the level of the unit cell. The crystal packing shows that all species are oriented in a very regular parallel fashion with the inversion centre situated between the planes, as better seen following the *a* axis (Fig. S5). Despite the neutrality of the $CrLa_3Co_6$ dendrimer and the absence of counterions, the $CrLa_3$ units are very well isolated in the crystal lattice, thanks to the bulky Kläui ligand. The shortest distance is between two lanthanum(III) ions with a value of 8.725(1) Å. They therefore represent a new family of metallo-dendrimers that, for the first time, have been fully characterized by single-crystal X-ray diffraction, offering unprecedented structural insights into their hierarchical organisation and metal coordination.

Characterisation in solution

Beyond the solid state, the stability of these dendrimers in solution was confirmed by a combination of MALDI-TOF spectrometry and UV-vis spectroscopy. The absorption spectra reveal features corresponding to both the dendritic core and the branches, although these are shifted relative to the spectra of the individual building blocks, consistent with their incorporation into the assembled structure (Fig. S15). Particularly noteworthy is the successful detection of intact $CrLn_3Co_6$ ions by mass spectrometry, which remains unusual for such large, multinuclear dendritic species. For $CrLa_3Co_6$ **1**, MALDI-TOF analysis in dichloromethane or THF revealed the molecular peak at m/z = 3461.51 Da, in excellent agreement with the theoretical value of 3461.52 Da for the formula $[C_{72}H_{138}O_{66}P_{18}CrLa_3Co_6Na]^+$, confirming the presence of the dendrimer along with a sodium adduct. Notably, the same spectrum exhibited a peak corresponding to the $[LaCo_2\text{-Kläui}]^+$ branch, consistent with partial fragmentation (Fig. 2). Similar behaviour was observed for $CrTb_3Co_6$ **3**, where an adduct ion

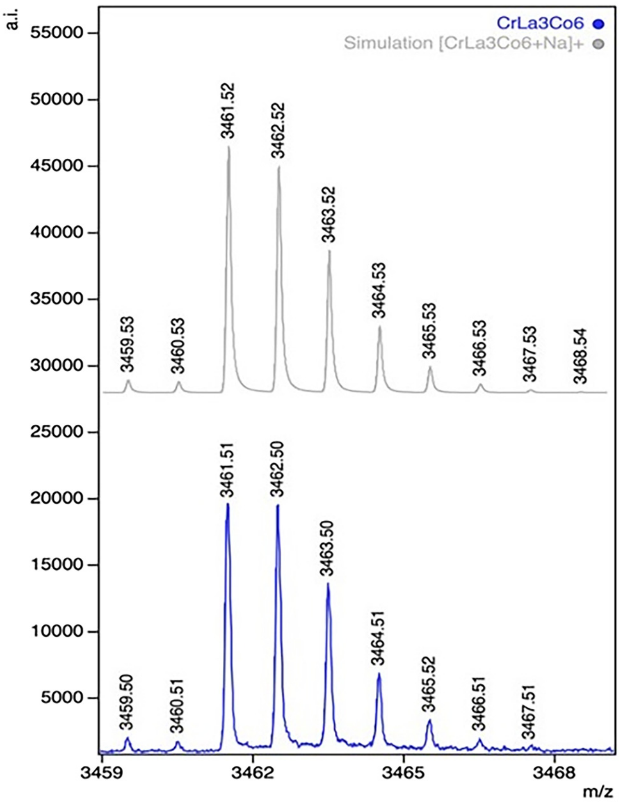

Fig. 2 MALDI-TOF spectrum of the $CrLa_3Co_6$ **1** dendrimer with $[CrLa_3Co_6 + Na]^+$ as an adduct ion. Experimental data are coloured in blue while simulated data are represented in grey.

corresponding to the entire dendrimer plus one additional $[TbCo_2\text{-Kläui}]^+$ branch was detected. The measured *m*/*z* value of 4558.80 Da closely matches the theoretical mass of 4559.49 for $[C_{94}H_{184}O_{84}P_{24}CrTb_4Co_8]^+$. The $CrGd_3Co_6$ and $CrDy_3Co_6$ dendrimers were also detected as intact species in the presence of alkali metal adducts such as Na^+ and K^+, indicating strong interactions with these cations in solution. Such clear mass spectrometric signatures of dendrimeric assemblies are exceedingly rare. These observations thus provide compelling evidence for the stability of our hetero-trimetallic dendrimers in solution and mark one of the very few documented examples of coordination dendrimers being directly observed as molecular ions. Having firmly established the structure of these dendrimers, we next turned to exploring their magnetic properties in order to probe the interplay between architecture and magnetic behaviour.

Direct-current (dc) magnetic measurements

All dendrimers **1–5** were studied by SQUID magnetometry to assess the nature of magnetic interactions involved between the spin carriers.[44] Three types of dc measurements were performed: (i) the temperature-dependent magnetisation (2.1 to 300 K) under a 1 kOe applied field, (ii) the field-dependent magnetisation (0–70 kOe) at 2.1 K, and (iii) the reduced magnetisation in the 0–70 kOe magnetic field range at 2, 3, 5 and 8 K. The series spans compounds featuring either a single spin carrier ($CrLa_3Co_6$, **1**), three spin carriers ($CoDy_3Co_6$, **5**) or four spin carriers in $CrGd_3Co_6$ **2**, $CrTb_3Co_6$ **3** and $CrDy_3Co_6$ **4**. The Cr^{3+} ($S = 3/2$) and Gd^{3+} ($^8S_{7/2}$) ions are isotropic, whereas Tb^{3+} ($^7F_6$) and Dy^{3+} ($^6H_{15/2}$) exhibit significant magnetic anisotropy as they are oblate non-Kramers and Kramers ions, respectively.[45] Parallel studies of spin only analogues and comparisons between Kramer and non-Kramer systems have been crucial to disentangle the contributions to magnetic behaviour.

For the La **1** and Gd **2** analogues, the thermal variation of the molar magnetic susceptibility χ_M and the temperature T product $\chi_M T$ show that compound **1** is purely paramagnetic, while compound **2** shows a decrease in $\chi_M T$ at low temperatures, indicative of weak anti-ferromagnetic interactions (Fig. 3a). Fitting the data for **2** with a Heisenberg–Dirac–Van Vleck Hamiltonian yielded parameters: $J_{CrGd_3} = -0.12\ cm^{-1}$, $g = 2.02$ and $zJ' = -0.001\ cm^{-1}$ consistent with weak anti-ferromagnetic interactions and negligible intermolecular inter-

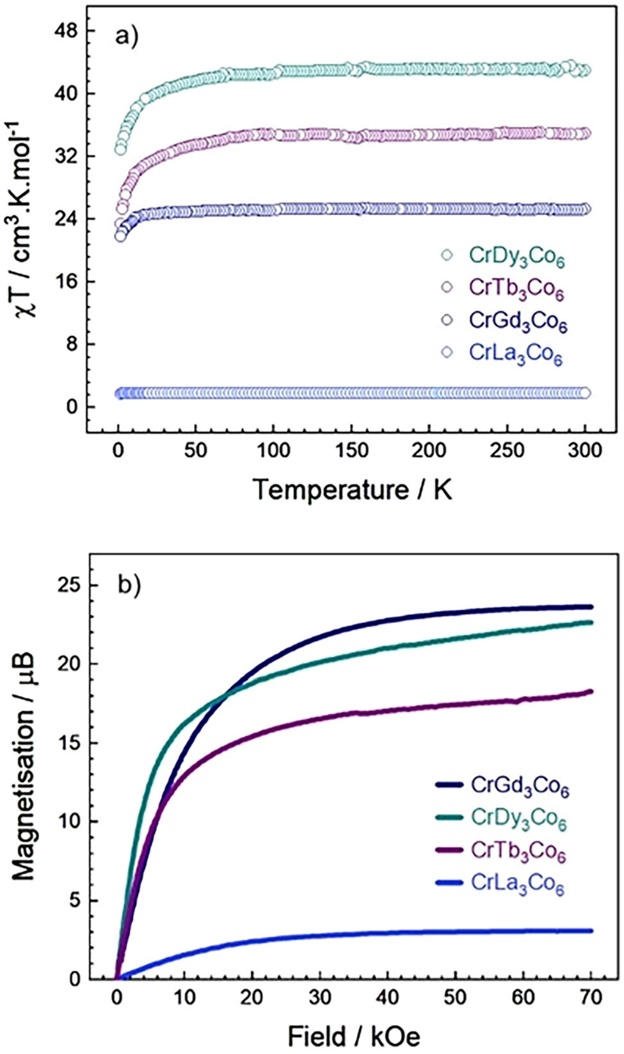

Fig. 3 (a) Molar susceptibility and temperature product $\chi_M T$ thermal variation of $CrLn_3Co_6$ **1–4** in the 2–300 K temperature range at 1 kOe; (b) magnetisation curves of **1–4** in the 0–70 kOe field range at 2 K.

actions. It coincides with a High-Spin Molecule (HSM) behaviour with a total spin $S = 9$. The saturation of magnetisation values of $2.92\mu_B$ for **1** and of $23.63\mu_B$ for **2** (Fig. 3b) confirm, respectively, an isolated spin carrier and a weak anti-ferromagnetic coupling between the Cr^{3+} and Gd^{3+} ions, which can be easily decoupled by an applied magnetic field. The superimpositions of the reduced magnetisation curves (Fig. S21) agree well with the theoretical expectations. For the Tb^{3+} **3** and Dy^{3+} **4** analogues, the $\chi_M T$ values at room temperature (34.44 and 42.14 cm^3 K mol^{-1}, respectively) decrease significantly below 60 K, reaching minimum values of 26.85 and 32.87 cm^3 K mol^{-1}. Unlike the gentle decline observed in **2**, this pronounced drop suggests not only anti-ferromagnetic interactions but also magnetic anisotropy and/or thermal depopulation of Stark sublevels.[46] The $CoDy_3Co_6$ dendrimer **5** displays a $\chi_M T$ value of 42.28 cm^3 K mol^{-1} at room temperature (Fig. S17). In comparison with $CrDy_3Co_6$ **4**, the $\chi_M T$ product for **5** decreases less sharply upon cooling, suggesting the absence of intramolecular interactions. Field dependence magnetisation data of **3**, **4** and **5** show no sign of saturation up to 70 kOe while reduced magnetisation curves do not superimpose, reinforcing the presence of substantial anisotropy associated with the Tb^{3+} and Dy^{3+} ions (Fig. S19).[46]

Alternating-current (ac) magnetic measurements

To probe dynamic magnetic properties, alternating-current (ac) susceptibility measurements were conducted on $CrTb_3Co_6$ **3**, $CrDy_3Co_6$ **4** and $CoDy_3Co_6$ **5** across 2.1–10 K and 10–10 kHz under zero-field and under dc-fields in the 200–2 kOe range. No frequency-dependent signal was observed in **3** under any conditions, likely due to the lack of axial symmetry around the Tb^{3+} ion and the non-degenerate ground state, ruling out a pseudo-Kramer doublet. As for $CrDy_3Co_6$ **4**, frequency-dependent out-of-phase components χ''_M under a 2 kOe dc-field reveal two different peaks at low frequency and high frequency. However, the absence of maxima in the 10–10 kHz frequency window precludes classifying **4** as a Single-Molecule Magnet (SMM). It is well established that anti-ferromagnetic interactions can hinder slow relaxation processes, prompting us to explore designs that isolate the Dy^{3+} centres more effectively.[47]

This strategy proved successful in $CoDy_3Co_6$ **5**, where the diamagnetic Co^{3+} core isolates magnetically the Dy^{3+} ions. Under a 0.6 kOe applied field, the frequency-dependent out-of-phase components χ''_M significantly deviate from zero for each set of temperature until 8 K and indicate a field-induced SMM behaviour (Fig. 4). However, the broadness of the χ''_M signals prevents extraction of the relaxation times τ, suggesting multiple overlapping relaxation processes arising from crystallographically distinct Dy^{3+} sites that individually block magnetisation. Similar behaviour has been reported in Dy-based clusters containing multiple crystallographically distinct ions, where overlapping processes complicate the extraction of discrete energy barriers.[48,49] Taken together, these magnetic studies demonstrate how precise architectural control in hetero-trimetallic dendrimers enables access to both high-spin molecules and field-induced single-molecule magnets, underscoring the unique potential of this modular platform.

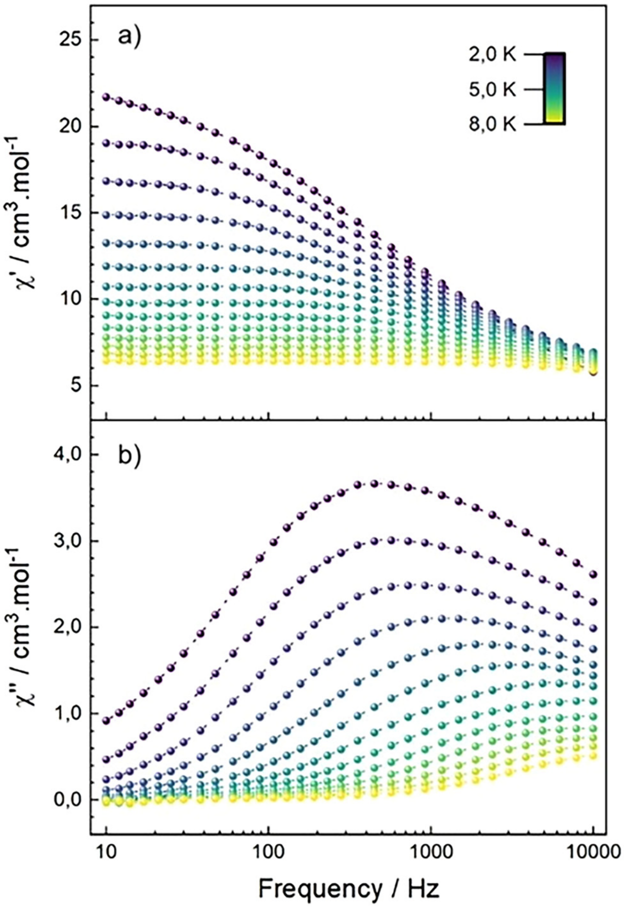

Fig. 4 (a) χ' and (b) χ'' frequency dependence of **5** at 0.6 kOe in the 10–10 kHz frequency and 2.1–8 K temperature range.

Conclusions

The MLn_3Co_6 series introduces a new class of chemically and magnetically tuneable metallo-dendrimers. The rapid and straightforward synthesis as well as the diversity of analogues underlines the undeniable efficiency of the modular methodology. The simultaneous characterisation in solution by mass spectrometry and in the solid state by single crystal X-ray diffraction is unprecedented when it comes to either hetero-trimetallic or magnetic dendrimers. Most remarkably, the chemical tuneability of this edifice yields a great variety of molecules and magnetic properties and allows discrimination of the most remarkable systems. Depending on the featured lanthanoid ions and the type of metallic core, whether it is paramagnetic or diamagnetic, the resulting edifices may either be a high-spin molecule ($CrGd_3Co_6$, **2**) or a field-induced single-molecule magnet ($CoDy_3Co_6$, **5**). Given the possible synthetic modifications and the ability to work in both solution and the solid state, this family of dendrimers has yet to unravel many more functionalities and potential applications.

Author contributions

I. S. was responsible for study conceptualisation, synthesis, investigation, formal analysis, measuring and interpreting the magnetic data, and writing the original draft. S. M. R. conducted the single-crystal X-ray analysis. C. P. undertook the mass spectrometry and UV-vis spectroscopy studies. E. R. interpreted the X-ray and magnetic data and edited the manuscript. A. K. F. R. synthesized the first dendrimers. B. K. undertook the SQUID study. V. M. was responsible for study conceptualisation, manuscript review and editing, and supervision. M. M. was responsible for study conceptualisation, synthesis, investigation, formal analysis, writing the original draft, supervision and project administration.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI) and are available upon request. The structures of **1**, **2**, **3**, **4**, **5** in the solid state were determined by single-crystal X-ray diffraction. Supplementary information is available. See DOI: **https://doi.org/10.1039/d5qi02242h**.

CCDC 2451819–2451823 (**1–5**) contain the supplementary crystallographic data for this paper.[50a–e]

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