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ARTICLE

Chemical and Magnetic Tuneability in Structurally Defined Hetero-Trimetallic Dendrimers

Ingrid Suzana,^a Susanne M. Rupf,^b Cédric Pécou,^a Elodie Rousset,^a A. K. Fazlur Rahman,^{a,c} Bastian Klemke,^d Valérie Marvaud^{*a} and Moritz Malischewski^{*b}Received 00th January 20xx,
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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, or (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 requires 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, 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 dendrimer 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

^a IPCM-CNRS UMR-8232, Sorbonne Université, 4 place Jussieu, 75005 Paris, France. valerie.marvaud@upmc.fr

^b Institut für Chemie und Biochemie – Anorganische Chemie, Freie Universität Berlin, Fabeckstraße 34-36, 14195 Berlin Germany. moritz.malischewski@fu-berlin.de

^c Oklahoma School of Science and Mathematics, Oklahoma City, 1141 N Lincoln Blvd, Oklahoma, OK 73104, United States.

^d Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

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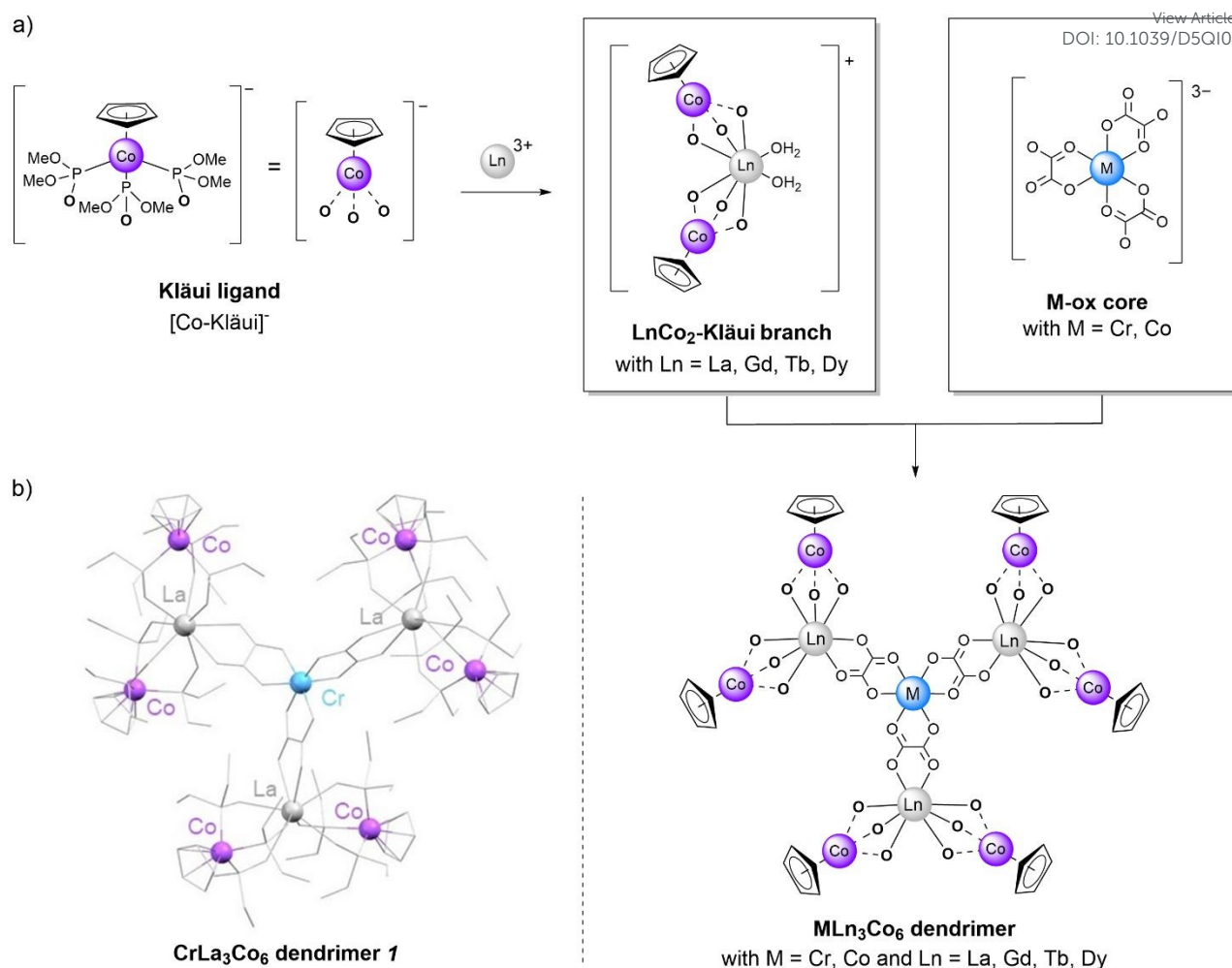


Figure 1. a) Convergent synthesis using a modular approach yielding the hetero-trimetallic dendrimers topology MLn₃Co₆ (M = Cr, Co and Ln = La, Gd, Tb, Dy); b) Crystallographic representation of the decanuclear complex CrLa₃Co₆ **1**. CCDC 2451819. Only metal ions are coloured while hydrogen atoms and solvent molecules are omitted for clarity.

this adaptation is the careful selection of metal centres that provide high spin states, essential for HSs, 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 in a manner that has so far remained out of reach for dendritic systems.

Herein, we report a tuneable hetero-trimetallic dendrimer CrLn₃Co₆ with Ln = La³⁺ **1**, Gd³⁺ **2**, Tb³⁺ **3**, Dy³⁺ **4** alongside its CoDy₃Co₆ **5** analogue. We have employed the kinetically inert tris(oxalato) metallate(III) [M(C₂O₄)₃]³⁻ (M = Cr, Co) anions, abbreviated [Cr-ox]³⁻ and [Co-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 [LnCo₂-Kläui]⁺ where the Ln³⁺ ion is coordinated by three oxygen atoms from each of two Kläui capping ligands [(η⁵-cyclopentadienyl)tris(dimethylphosphito-P)cobalt(III)] [CoCo(PO(OMe)₂)₃]⁻, abbreviated [Co-Kläui]⁻.^[38,39] The two [Co-



Kläui][−] units both magnetically isolate the lanthanoid ions and impose a rigid geometry that supports slow magnetic relaxation.^[40–43] In CrLn₃Co₆, the paramagnetic Cr³⁺ centre promotes a high-spin state via magnetic interactions transmitted through the oxalate ligands while in CoDy₃Co₆, the diamagnetic Co³⁺ core further isolates the lanthanoid centres, supporting slow relaxation of magnetisation.

Results and discussion

Synthesis

The decanuclear MLn₃Co₆ dendrimers were obtained in a one-pot synthesis by coordination driven self-assembly of the [M-ox]^{3−} (M = Cr, Co) and the [Co-Kläui][−] precursors in presence of lanthanoid ions Ln³⁺ (Ln = La, Gd, Tb, Dy) (Figure 1). Six equivalents of Na[Co-Kläui] were first reacted with three equivalents of a lanthanoid salt Ln(NO₃)₃·xH₂O in a MeCN/H₂O (1:1) mixture forming three [LnCo₂-Kläui]⁺ branches *in situ*. It was then followed by the addition of one equivalent of K₃[Cr-ox]. Single crystals of the neutral hetero-trimetallic architectures CrLn₃Co₆ 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 CoDy₃Co₆ **5** was obtained following the same synthetic procedure as for CrLn₃Co₆ **1–4** using the [Co-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 solid state

Single-crystal X-ray structure analysis confirmed 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 (Figure S2), the unit cell parameters for CrLn₃Co₆ dendrimers **1–4** are essentially identical, whereas CoDy₃Co₆ displays slightly different metrics. A representative structure is shown for CrLa₃Co₆ **1** in Figure 1 where metal ions are labelled for clarity. The neutral architecture is composed by a tris(oxalato)chromate(III) core on which three [LaCo₂-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 La³⁺ ions are coordinated by two Kläui ligands, resulting in a coordination number of eight. The bond distances La1-O_{oxalato} (2.48 Å) are distinctly longer than the La-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 bonds 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 Cr³⁺ core lies in the plane defined by the three La³⁺ ions, while the Co³⁺ centres of the Kläui ligand alternate above and below the CrLa₃ 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 all species oriented in a very regular parallel fashion with the inversion centre situated between planes, as better seen following the a axis (Figure S5). Despite the neutrality of CrLa₃Co₆ dendrimer and the absence of counterions, the CrLa₃ 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.

In solution characterisation

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

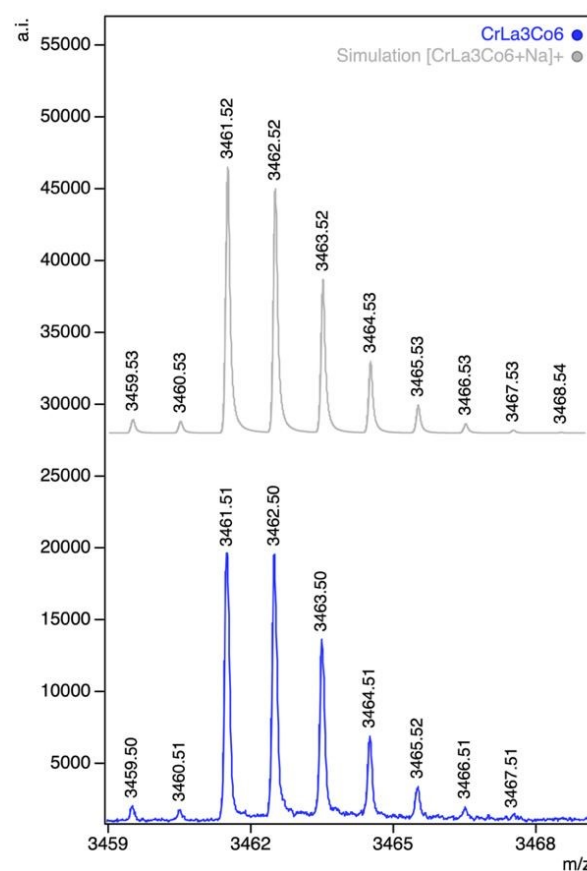


Figure 2. MALDI-TOF spectrum of CrLa₃Co₆ **1** dendrimer with [CrLa₃Co₆+Na]⁺ as an adduct ion. Experimental data are coloured in blue while simulated data are represented in grey.

these are shifted relative to the spectra of the individual building blocks, consistent with their incorporation into the assembled



structure (Figure 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 $[\text{C}_{72}\text{H}_{138}\text{O}_{66}\text{P}_{18}\text{CrLa}_3\text{Co}_6\text{Na}]^+$, confirming the presence of the dendrimer along with a sodium adduct. Notably, the same spectrum exhibited a peak corresponding to the $[\text{LaCo}_2\text{-Kl}\ddot{\text{a}}\text{ui}]^+$ branch, consistent with partial fragmentation (Figure 2). Similar behaviour was observed for CrTb_3Co_6 **3**, where an adduct ion corresponding to the entire dendrimer plus one additional $[\text{TbCo}_2\text{-Kl}\ddot{\text{a}}\text{ui}]^+$ branch was detected. The measured m/z value of 4558.80 Da closely matches the theoretical mass of 4559.49 for $[\text{C}_{94}\text{H}_{184}\text{O}_{84}\text{P}_{24}\text{CrTb}_4\text{Co}_8]^+$. 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 magnetic susceptibility (2.1 to 300 K) under a 1 kOe applied field, (ii) the field-dependent magnetic (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+} ($^8\text{S}_{7/2}$) ions are isotropic, whereas Tb^{3+} ($^7\text{F}_6$) and Dy^{3+} ($^6\text{H}_{15/2}$) 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 χ_{MT} show that compound **1** is purely paramagnetic, while compound **2** exhibit a decreasing in χ_{MT} at low temperatures, indicative of weak anti-ferromagnetic interactions (Figure 3a). Fitting the data for **2** with a Heisenberg-Dirac-Van Vleck Hamiltonian yielded parameters: $J_{\text{CrGd}_3} = -0.12 \text{ cm}^{-1}$, $g = 2.02$ and $zJ' = -0.001 \text{ cm}^{-1}$ consistent with weak anti-ferromagnetic interactions and negligible intermolecular interactions. It coincides with a High-Spin Molecule (HSM) behaviour with a total spin $S = 9$. The saturation of magnetisation values of 2.92 μB for **1** and of 23.63 μB for **2** (Figure 3b) confirm, respectively, an isolated spin carrier and a weak anti-ferromagnetic coupling

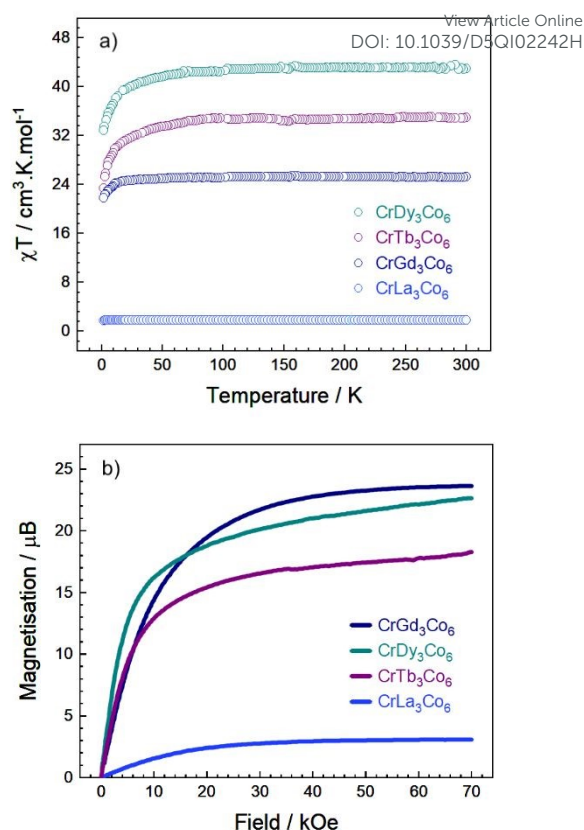


Figure 3. a) Molar susceptibility and temperature product χ_{MT} thermal variation of CrLn_3Co_6 **1-4** in the 2-300 K temperature range at 1 kOe; b) Magnetisation curves of **1-4** in the 0-70 kOe field range at 2 K.

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 (Figure S21) agree well with the theoretical expectations. For the Tb^{3+} **3** and Dy^{3+} **4** analogues, the χ_{MT} values at room temperature (34.44 and 42.14 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, respectively) decrease significantly below 60 K, reaching minimum values of 26.85 and 32.87 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$. 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 χ_{MT} value of 42.28 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at room temperature (Figure S17). In comparison with CrDy_3Co_6 **4**, the χ_{MT} 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 (Figure 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

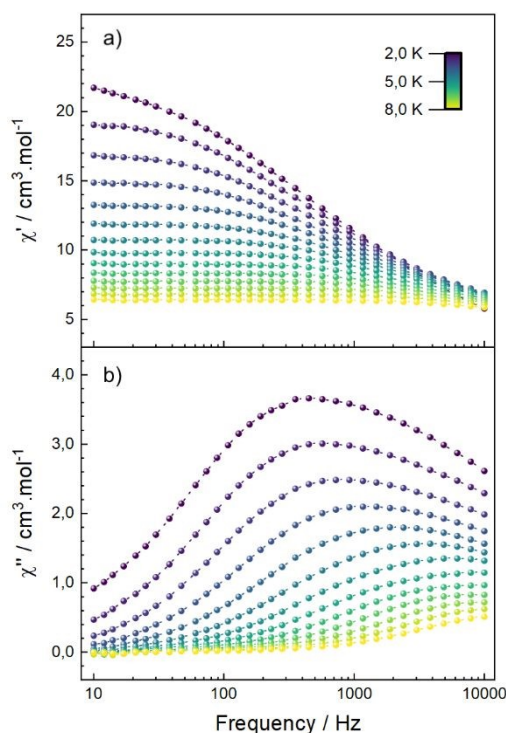


Figure 4. a) χ' and b) χ'' frequency dependence of **5** at 0.6 kOe in the 10-10 kHz frequency and 2.1-8 K temperature range.

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 (Figure 4). However, the broadness of the χ_M'' signals prevent 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 extractions 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.

Conclusions

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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 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 yield a great variety of molecules and magnetic properties, and allow 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 solid state, this family of dendrimer is yet to unravel much 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 the 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 ESI.† Data supporting this manuscript is available within the ESI and available on request. The structures of **1**, **2**, **3**, **4**, **5** in the solid state were determined by single-crystal X-ray diffraction and the crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) with identifiers 2451819 (**1**), 2451820 (**2**), 2451821 (**3**), 2451822 (**4**), and 2451823 (**5**). Copies of the data can be obtained free of charge on application to the CCDC.

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References

- 1 E. Buhleier, W. Wehner, F. Vögtle, 'Cascade'- and 'nonskid-chain-like' syntheses of molecular cavity topologies, *Synthesis*, 1978, **2**, 155–158.
- 2 D. A. Tomalia, J. M. J. Fréchet, Discovery of dendrimers and dendritic polymers: A brief historical perspective, *J. Polym. Sci. Part Polym. Chem.* 2002, **40**, 2719–2728.
- 3 D. Astruc, E. Boisselier, C. Ornelas, Dendrimers designed for functions: from physical, photophysical, and supramolecular properties to applications in sensing, catalysis, molecular electronics, photonics, and nanomedicine, *Chem. Rev.* 2010, **110**, 1857–1959.
- 4 X. Liu, D. Gregurec, J. Irigoyen, A. Martinez, S. Moya, R. Ciganda, P. Hermange, J. Ruiz, D. Astruc, Precise localization of metal nanoparticles in dendrimer nanosnakes or inner periphery and consequences in catalysis, *Nat. Commun.* 2016, **7**, 13152.
- 5 Z. Huang, Q. Shi, J. Guo, F. Meng, Y. Zhang, Y. Lu, Z. Qian, X. Li, N. Zhou, Z. Zhang, X. Zhu, Binary tree-inspired digital dendrimer, *Nat. Commun.* 2019, **10**, 1918.
- 6 G. He, E. M. Churchill, K. R. Parenti, J. Zhang, P. Narayanan, F. Namata, M. Malkoch, D. N. Congreve, A. Cacciuto, M. Y. Sfeir, L. M. Campos, Promoting multiexciton interactions in singlet fission and triplet fusion upconversion dendrimers, *Nat. Commun.* 2023, **14**, 6080.
- 7 E. Apartsin, A.-M. Caminade, Single-component physical hydrogels of dendritic molecules *J. Compos. Sci.* 2023, **7**, 26.
- 8 J. A. Meshanni, E. R. Stevenson, D. Zhang, R. Sun, N. A. Ona, E. K. Reagan, E. Abramova, C.-J. Guo, M. Wilkinson, I. Baboo, Y. Yang, L. Pan, D. S. Maurya, V. Percec, Y. Li, A. Gow, D. Weissman, E. N. Atochina-Vasserman, Targeted delivery of TGF- β mRNA to murine lung parenchyma using one-component ionizable amphiphilic Janus Dendrimers, *Nat. Commun.* 2025, **16**, 1806.
- 9 M. S. Grudev, V. V. Korolev, A. G. Ramazanova, U. V. Chervonova, O. V. Balmasova, Magnetocaloric properties of dendrimer complexes of Fe(III) with substituted Schiff base, *Liq. Cryst.* 2018, **45**, 907–911.
- 10 V. Balzani, L. Moggi, F. Scandola in *Supramol. Photochem.* (Ed.: V. Balzani), Springer Netherlands, Dordrecht, 1987, pp. 1–28.
- 11 S. Campagna, F. Nastasi, G. L. Ganga, S. Serroni, A. Santoro, A. Arrigo, F. Puntoriero, Self-assembled systems for artificial photosynthesis, *Phys. Chem. Chem. Phys.* 2023, **25**, 1504–1512.
- 12 F. Liu, X. Liu, T. Abdiryim, H. Gu, D. Astruc, Heterometallic macromolecules: synthesis, properties and multiple nanomaterial applications, *Coord. Chem. Rev.* 2024, **500**, 215544.
- 13 R. E. Bauer, V. Enkelmann, U. M. Wiesler, A. J. Berresheim, K. Müllen, Single-crystal structures of polyphenylene dendrimers, *Chem. – Eur. J.* 2002, **8**, 3858–3864.
- 14 S. Baeriswyl, S. Javor, A. Stocker, T. Darbre, J.-L. Reymond, X-ray crystal structure of a second-generation peptide dendrimer in complex with pseudomonas aeruginosa lectin LecB, *Helv. Chim. Acta*, 2019, **102**, e1900178.
- 15 J. Bendix, J. Christensen, The Structure of PAMAM DAB-dendr(NH₂)₄ – the First Crystal Structure of a PAMAM-Dendrimer, 2020, ChemRxiv, DOI: 10.26434/chemrxiv.12666296.v1.
- 16 S. Rajca, A. Rajca, J. Wongsriratanakul, P. Butler, S. Choi, Organic spin clusters. A dendritic-macrocyclic poly(arylmethyl) polyradical with very high spin of S = 10 and its derivatives: synthesis, magnetic studies, and small-angle neutron scattering, *J. Am. Chem. Soc.* 2004, **126**, 6972–6986.
- 17 T. Fujigaya, D.-L. Jiang, T. Aida, Spin-crossover dendrimers: generation number-dependent cooperativity for thermal spin transition, *J. Am. Chem. Soc.* 2005, **127**, 5484–5489.
- 18 C. Williams, P. Chellan, P. Govender, G. S. Smith in *Dendrimer Chem. Synth. Approaches Complex Archit.* (Eds.: M. Malkoch, S. García Gallego), The Royal Society Of Chemistry, 2020, pp. 230–260.
- 19 C. B. Gorman, B. L. Parkhurst, W. Y. Su, K.-Y. Chen, Encapsulated electroactive molecules based upon an inorganic cluster surrounded by dendron ligands, *J. Am. Chem. Soc.* 1997, **119**, 1141–1142.
- 20 J.-L. Fillaut, D. Astruc, J. Linares, Single-step six-electron transfer in a heptanuclear complex: isolation of both redox forms, *Angew. Chem. Int. Ed. Engl.* 1995, **33**, 2460–2462.
- 21 K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, H. Chiba, Stepwise radial complexation of imine groups in phenylazomethine dendrimers, *Nature* 2002, **415**, 509–511.
- 22 I. Angurell, O. Rossell, M. Seco, Heterometallogendrimers: a structural outlook, *Inorg. Chim. Acta*, 2014, **409**, 2–11.
- 23 V. Marvaud, D. Astruc, Fe(η^5 -C₅H₅)⁺ initiated construction of hexaruthenium–polypyridine complexes, *Chem. Commun.* 1997, **8**, 773–774.
- 24 T. Imaoka, R. Tanaka, S. Arimoto, M. Sakai, M. Fujii, K. Yamamoto, "Probing stepwise complexation in phenylazomethine dendrimers by a metallo-porphyrin core, *J. Am. Chem. Soc.* 2005, **127**, 13896–13905.
- 25 D. Méry, L. Plault, C. Ornelas, J. Ruiz, S. Nlate, D. Astruc, J.-C. Blais, J. Rodrigues, S. Cordier, K. Kirakci, C. Perrin, From simple monopyridine clusters [Mo₆Br₁₃(Py-R)][n-Bu₄N] and hexapyridine clusters [Mo₆X₈(Py-R)₆][OSO₂CF₃]₄ (X = Br or I) to cluster-cored organometallic stars, dendrons, and dendrimers *Inorg. Chem.* 2006, **45**, 1156–1167.
- 26 L. Le Pleux, Y. Pellegrin, E. Blart, F. Odobel, A. Harriman, Long-lived, charge-shift states in heterometallic, porphyrin-based dendrimers formed via click chemistry, *J. Phys. Chem. A*, 2011, **115**, 5069–5080.
- 27 K. Takanashi, A. Fujii, R. Nakajima, H. Chiba, M. Higuchi, Y. Einaga, K. Yamamoto, Heterometal assembly in dendritic polyphenylazomethines, *Bull. Chem. Soc. Jpn.* 2007, **80**, 1563–1572.
- 28 K. Yamamoto, K. Takanashi, Synthesis and functionality of dendrimer with finely controlled metal assembly, *Polymer* 2008, **49**, 4033–4041.
- 29 F. Vögtle, M. Frank, P. Belser, A. Von Zelewsky, V. Balzani, L. De Cola, F. Barigelletti, L. Flamigni, M. Nieger, Rigid rodlike metal complexes of nanometric dimension: synthesis, luminescence



- properties, and long-range energy transfer, *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1643–1646.
- 30 V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, Luminescent and redox-active polynuclear transition metal complexes, *Chem. Rev.* 1996, **96**, 759–834.
 - 31 S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano, V. Balzani, Arborols based on luminescent and redox-active transition metal complexes, *Angew. Chem. Int. Ed. Engl.* 1992, **31**, 1493–1495.
 - 32 S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto, V. Balzani, Dendrimers of Nanometer Size Based on Metal Complexes: Luminescent and Redox-Active Polynuclear Metal Complexes Containing up to Twenty-Two Metal Centers, *Chem. – Eur. J.* 1995, **1**, 211–221.
 - 33 M. Sommovigo, G. Denti, S. Serroni, S. Campagna, C. Mingazzini, C. Mariotti, A. Juris, Polynuclear polypyridine complexes incorporating Ru(II), Os(II), and Pt(II): decanuclear dendrimeric antennas, *Inorg. Chem.* 2001, **40**, 3318–3323.
 - 34 G. Denti, S. Campagna, S. Serroni, M. Ciano, V. Balzani, Decanuclear homo- and heterometallic polypyridine complexes: syntheses, absorption spectra, luminescence, electrochemical oxidation, and intercomponent energy transfer, *J. Am. Chem. Soc.* 1992, **114**, 2944–2950.
 - 35 K. S. Pedersen, J. Bendix, R. Clérac, Single-molecule magnet engineering: building-block approaches, *Chem. Commun.* 2014, **50**, 4396–4415.
 - 36 S. Decurtins, H. W. Schmalke, P. Schneuwly, J. Ensling, P. Güetlich, A concept for the synthesis of 3-dimensional homo- and bimetallic oxalate-bridged networks $[M_2(ox)_3]_n$. Structural, Mössbauer, and magnetic studies in the field of molecular-based magnets, *J. Am. Chem. Soc.* 1994, **116**, 9521–9528.
 - 37 M. Clemente-León, E. Coronado, C. Martí-Gastaldo, F. M. Romero, Multifunctionality in hybrid magnetic materials based on bimetallic oxalate complexes, *Chem. Soc. Rev.* 2011, **40**, 473–497.
 - 38 W. Kläui, K. Dehnicke, Dreikernige Sandwichkomplexe mit Dialkylphosphonat-Brückenliganden: Synthese, NMR-, IR- und Raman-spektroskopische Untersuchungen, *Chem. Ber.* 1978, **111**, 451–468.
 - 39 W. Kläui, The Coordination Chemistry and Organometallic Chemistry of Tridentate Oxygen Ligands with π -Donor Properties, *Angew. Chem. Int. Ed.* 1990, **29**, 627–637.
 - 40 K. S. Lim, J. J. Baldoví, W. R. Lee, J. H. Song, S. W. Yoon, B. J. Suh, E. Coronado, A. Gaita-Ariño, C. S. Hong, Switching of slow magnetic relaxation dynamics in mononuclear dysprosium(III) compounds with charge density, *Inorg. Chem.* 2016, **55**, 5398–5404.
 - 41 K. S. Lim, D. W. Kang, J. H. Song, H. G. Lee, M. Yang, C. S. Hong, Slow relaxation dynamics of a mononuclear Er(III) complex surrounded by a ligand environment with anisotropic charge density, *Dalton Trans.* 2017, **46**, 739–744.
 - 42 K. S. Lim, J. J. Baldoví, S. Jiang, B. H. Koo, D. W. Kang, W. R. Lee, E. K. Koh, A. Gaita-Ariño, E. Coronado, M. Slota, L. Bogani, C. S. Hong, Custom coordination environments for lanthanoids: tripodal ligands achieve near-perfect octahedral coordination for two dysprosium-based molecular nanomagnets, *Inorg. Chem.* 2017, **56**, 4911–4917.
 - 43 J. H. Song, G. Lee, W. R. Lee, K. S. Lim, Novel heterometallic lanthanide complex using cobalt tripod ligands: synthesis, crystal structure analysis, and magnetic and proton conduction behavior, *Bull. Korean Chem. Soc.* 2020, **41**, 1044–1047.
 - 44 O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, 1993. VIEW ARTICLE ONLINE
DOI: 10.1039/D5QI02242H
 - 45 J. D. Rinehart, J. R. Long, Exploiting single-ion anisotropy in the design of f-element single-molecule magnets, *Chem. Sci.* 2011, **2**, 2078–2085.
 - 46 H. L. C. Feltham, S. Brooker, Review of purely 4f and mixed-metal nd-4f single-molecule magnets containing only one lanthanide ion, *Coord. Chem. Rev.* 2014, **276**, 1–33.
 - 47 T. Glaser, Rational design of single-molecule magnets: a supramolecular approach, *Chem. Commun.* 2010, **47**, 116–130.
 - 48 P.-H. Lin, T. J. Burchell, L. Ungur, L. F. Chibotaru, W. Wernsdorfer, M. Murugesu, A polynuclear lanthanide single-molecule magnet with a record anisotropic barrier, *Angew. Chem. Int. Ed.* 2009, **48**, 9489–9492.
 - 49 P.-H. Lin, W.-B. Sun, M.-F. Yu, G.-M. Li, P.-F. Yan, M. Murugesu, An unsymmetrical coordination environment leading to two slow relaxation modes in a Dy_2 single-molecule magnet, *Chem. Commun.* 2011, **47**, 10993–10995.



The data supporting this article have been included as part of the ESI.† Data supporting this manuscript is available within the ESI and available on request. The structures of **1**, **2**, **3**, **4**, **5** in the solid state were determined by single-crystal X-ray diffraction and the crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) with identifiers 2451819 (**1**), 2451820 (**2**), 2451821 (**3**), 2451822 (**4**), and 2451823 (**5**). Copies of the data can be obtained free of charge on application to the CCDC.

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