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Chiral biomolecule based dodecanuclear dysprosium(III)–copper(II) clusters: structural analyses and magnetic properties†

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An isostructural family of three dodecanuclear chiral M_4Cu_8 ($M = Dy, Y$) complexes has been synthesized by adopting a mixed-ligand strategy, wherein one of the constituent linkers, pyroglutamic acid, a recognized biomolecule, has been credibly functioning as the chiral precursor imparting the chirality to the aforementioned complex. The highly symmetric new-fangled M_4Cu_8 coordination-core, comprising of four square-symmetrically coordinated Dy/Y-vertex sharing M_2Cu_2 cubane units, has been synthesized as an unprecedented discrete coordination complex, which has been analysed by magnetic measurements.

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Introduction

Discrete coordination architectures of diverse nuclearities have steadily drawn the attention of chemists and materials scientists for the intriguing functional aspects emanating from the simple design principles based on coordination chemistry driven self-assembly processes involving metal nodes and a vast spectrum of numerous linkers.^{1–6} Among these, coordination architectures with excellent symmetric features have been the most investigated ones owing to their captivating coordination environments, giving rise to utilitarian attributes as a consequence of their symmetry-aided structure–property correlation.^{7–13} The inherent symmetry in such complexes makes the structure–property correlation much easier to predict, leading to a strategic rationale based design principle for attaining the target properties and an insight therein. Over the decades, employment of a binary or ternary combination of linkers for yielding such complexes has proved quite an efficient protocol. Since the multiple coordination sites involved with their distinct denticities and coordination geometries, in unison with the associated non-covalent inter-

actions, govern the crucial nuclearity aspect for such species; more than one appropriately functionalized linker is frequently employed for obtaining coordination complexes promising from the standpoint of application.^{14–25} Higher nuclearity-lanthanide discrete complexes or clusters have been the most sought-after ones considering the flurry of such materials evolved in the last decade exhibiting slow magnetic relaxation-triggered single molecule magnet (SMM) characteristics,^{26–31} ubiquitously imperative behind the development of novel molecular nanomagnets functioning as miniaturized devices for high-density information storage, molecule spintronics and quantum computing.^{32–40}

Biomolecules can be expediently employed as the building blocks of functional coordination complexes considering their biocompatibility, structural diversity, intrinsic self-assembly characteristics *via* their different metal-binding sites, low cost and ample availability coupled with individual chiral signatures of the precursor biomolecule-based synthons.^{41–45} The chiral features with multidentate facets particularly make such biomolecule-based coordination complexes an exciting domain to investigate, because of their prospective biological applications, including drug delivery or intracellular imaging. Although much effort has been devoted to lanthanide (4f)-based and lanthanide-transition (3d–4f)-based coordination complexes, resulting into the discovery of noteworthy magnetic properties such as slow magnetic relaxation-triggered single molecule magnet behaviour, magnetic refrigeration *etc.*; biomolecule based coordination complexes⁴⁶ have never been the focus from the standpoint of magnetism phenomena, in spite of the recently explored spectrum of applications presented by this emerging class of materials.^{46–52} Despite some recent reports, pyroglutamic acid (PGA) or pidolic acid, a scar-

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†Electronic supplementary information (ESI) available: Ligand structures for L and D enantiomers, IR and EDX data (for metal analyses) for all three reported compounds, along with crystal data and structure refinement for compound **1L**. CCDC 1403754 for **1L**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5qi00090d



cely found proline derivative recently commercialized as a dietary supplement, wherein the free amino group of glutamic acid or glutamine undergoes cyclization to form a lactam, is yet to be comprehensively harnessed for coordination complex reactions.^{53–57} Importantly, this oxo-derivative of a secondary amino acid and a noteworthy metabolite in the glutathione cycle is a vital biomolecule possessing memory-enhancement effect, hair-follicle growth and dermal penetration enhancing consequences.^{58–60} Hence, the employment of PGA in the construction of 3d–4f based coordination complexes seems quite a daunting task, considering the unification of the dual features of biocompatibility and magnetism in a single discrete coordination entity. This indeed seems crucial from the standpoint of exploring magnetic materials with the requisite biocompatibility.^{61,62}

Furthermore, to synthesize such desired coordination complexes based on hard Lewis acid (PGA) with high hydroxophilic Ln^{III} and Cu^{II} ions,^{63–69} we have purposefully chosen pyridine-based auxiliary ligands with flexible alkoxide ends, which might act as chelating and bridging ligands, owing to hard Lewis base O and N binding sites. Herein, we have exploited the oxophilic biomolecule-linker PGA (L and D enantiomers) with ancillary ligand 2-(2-hydroxyethyl)pyridine (HEP) (Fig. S1†) for the synthesis of a series of three isostructural, chiral biomolecule based M₄Cu₈ coordination complexes [M₄Cu₈(HEP)₈(PGA)₈(OH)₈(NO₃)₄] (M = Dy and Y) and have analyzed their magnetism properties with the aid of direct and alternate current susceptibility measurements by SQUID (superconducting quantum interference device). The difference brought about by the presence of the high-anisotropy Dy (III) centres, while coupled with Cu(II) centres in this aforementioned core, was to be compared with the isostructural Y₄Cu₈ core, highlighting the role of 3d–4f interactions in the Dy-analogue in exhibiting magnetic properties.

Experimental section

Materials and measurements

All the reagents and solvents were commercially available and were used without further purification. The powder X-ray patterns (PXRD) were recorded on Bruker D8 Advanced X-ray diffractometer at room temperature using Cu K α radiation (λ = 1.5406 Å). FT-IR spectra were measured on NICOLET 6700 FT-IR Spectrophotometer using KBr pellets.

Synthesis of [Dy₄Cu₈(HEP)₈(L-PGA)₈(OH)₈(NO₃)₄] (1L). To a sonicated methanolic solution (5 mL) of HEP (11.3 μ L, 0.1 mmol) and NaOH (4 mg, 0.1 mmol), another well-sonicated solution of PGA (16.1 mg, 0.125 mmol) and NaOH (5 mg, 0.125 mmol) dissolved in 5 mL MeOH was added. A 15 mL binary solvent mixture (1 : 2) of MeOH and MeCN was further added to the aforementioned reaction mixture, following which solid Cu(NO₃)₂·3H₂O (12.1 mg, 0.05 mmol) and 3 mL of 0.03 mmol (13.6 mg) methanolic solution of Dy(NO₃)₃·xH₂O is slowly added while sonicating continuously. Slow evaporation of solvent mixture over the next ten days

with no mechanical disturbance, yielded excellent quality blue cube-shaped single crystals of compound [Dy₄Cu₈(HEP)₈(L-PGA)₈(OH)₈(NO₃)₄] (1L), suitable for single crystal X-ray analysis. Yield ~60%. IR (KBr, cm⁻¹): 3644(s), 2845(m), 2719(m), 2407(m), 2086(w), 1709(b), 1428(w), 1291(w), 1234(w), 1160(m), 1088(w), 1033(s), 971(w), 879(s), 779(s), 652(s) (Fig. S2†). Anal. Calcd (found) for C₉₆ H₁₁₂ Cu₈ Dy₄ N₁₆ O₄₀: C, 35.06 (35.38); H, 3.43 (2.98); N, 6.82 (6.65)%.

Synthesis of [Dy₄Cu₈(HEP)₈(D-PGA)₈(OH)₈(NO₃)₄] (1D) and [Y₄Cu₈(HEP)₈(L-PGA)₈(OH)₈(NO₃)₄] (2L). A similar reaction protocol as mentioned for 1L was followed for the syntheses of 1D from D-PGA (instead of L-PGA) and Dy(NO₃)₃·xH₂O; 2L from L-PGA and Y(NO₃)₃·6H₂O (replacing Dy(NO₃)₃·xH₂O). The similar PXRD nature for the bulk phases of these two compounds along with the similar IR stretching frequencies and elemental analyses reinstates the isostructural nature for these two compounds, with respect to compound 1L. Repeated trials to obtain the D-PGA based analogous compound to 2L could not be obtained due to encountered precipitation issues, hence has not been included in the report.

IR (KBr, cm⁻¹) for 1D: 3634(s), 2663(w), 2720(w), 2401(m), 2083(w), 1701(b), 1426(b), 1292(m), 1159(sh), 1088(w), 1034(s), 968(w) (Fig. S2†). IR (KBr, cm⁻¹) for 2L: 3630(s), 2848(m), 2729(m), 2391(m), 2080(w), 1699(b), 1443(w), 1295(w), 1234(w), 1155(m), 1083(w), 1037(s), 967(w), 880(s), 778(s), 653(s) (Fig. S2†). Anal. Found for 1D (%): C, 35.13; H, 3.11; N, 6.90. Anal. Found for 2L (%): C, 35.29; H, 3.57; N, 6.77.

X-ray structural studies

Single-crystal X-ray data of compound 1L was collected at 200 K on a Bruker KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). A cube-shaped blue crystal was mounted using nylon CryoLoops (Hampton Research) with Paratone-N (Hampton Research). The data integration and reduction were processed with SAINT⁷⁰ software. A multi-scan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL⁷¹ and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97⁷² program package within the WINGX⁷³ programme. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. The structures were scrutinized by the Adsym subroutine of PLATON⁷⁴ to ensure that no additional symmetry could be applied to the models. Crystal data and structure refinement details for complex 1L is summarized in Table S1.†

Magnetic measurement details

Magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. The direct current (dc) measurements were collected with an external magnetic field of 1000 Oe in the temperature range 1.9–300 K, and the alternating-current (ac)



measurements were carried out in a 3.0 Oe ac field oscillating at 1000 Hz in the temperature range 2–40 K. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's tables and sample holder calibration.⁷⁵

Results and discussion

Compounds **1L** and **2L** derived from L-PGA, and **1D** derived from D-PGA were prepared at room temperature by slow evaporation of the respective reaction mixtures, as described in the Experimental section. Single crystal X-ray analysis reveals that compound **1L** crystallized in the tetragonal space group $P4_222$ with $Z = 1$. The molecular structure of compound **1L**, showing the central square-shaped Dy_4 core flanked by four Dy_2Cu_2 cubanes at each of the central Dy-centres is shown in Fig. 1; the precise arrangement of which is shown in sharper detail in Fig. 2a. The 3d–4f heterometallic dodecahedron (Dy_4Cu_8) is highly symmetric, since all the cubanes and each of the analogous elements therein are found to have crystallographically identical features (Fig. 2a). The four cubanes are interconnected *via* the $\text{Dy}(\text{III})$ vertices in a typical vertex-sharing arrangement. Interestingly, considering the entire bimetallic central core, only one type of $\text{Dy}(\text{III})$: Dy1, one kind of $\text{Cu}(\text{II})$: Cu1, and just two different types of O atoms (O1 and O5) constitute the entire assemblage of $\text{Dy}_4\text{Cu}_8\text{O}_{16}$, providing testimony to the symmetric attributes of this cluster core. While O1 centers are found to connect the two different metals $\text{Dy}(\text{III})$ and $\text{Cu}(\text{II})$, O5 centers act as bridging oxo-linkers between the 4f- $\text{Dy}(\text{III})$ apices of this bimetallic core.

The bond angles and intermetallic distances spanned across each of the solitary cubane units have been represented in Fig. 2b. Considering the homometallic pairs; while the two larger $\text{Dy}(\text{III})$ centers are separated by a distance of 3.87 Å, at the very central core of the motif, the distant $\text{Cu}(\text{II})$ centers are in quite close proximity (3.22 Å), resulting in the observed sets of acute and obtuse angles across the metal-vertices, characteristic of a typical cubane. Since the Cu_2O_2 and Dy_2O_2 units are apically connected *via* O-bridges (O1 and O5 respectively), the Cu–Dy closest intermetallic distance (3.42 Å) falls midway in view of the ones between the smaller $\text{Cu}(\text{II})$ duo (3.22 Å) and the larger $\text{Dy}(\text{III})$ pair (3.87 Å), which is quite in accord with the structural predictions regarding heterometallic cubane species.

Similar PXRD profiles being recorded for two of the analogues unequivocally indicate the isostructural attributes for both the phases **1D** and **2L**, in comparison to that of **1L** (Fig. 3a), while similar IR stretching frequencies and elemental analyses for these merely reinstate the same fact.

Solid state CD spectra for two isostructural complexes (**1D** and **1L**) arising out of different enantiomeric ligands (D and L respectively) are the reverse of each other as predicted (Fig. 3b). Although few in number, some chiral coordination complexes with interesting magnetic properties have been reported in the literature;^{76–82} however, biomolecule-derived

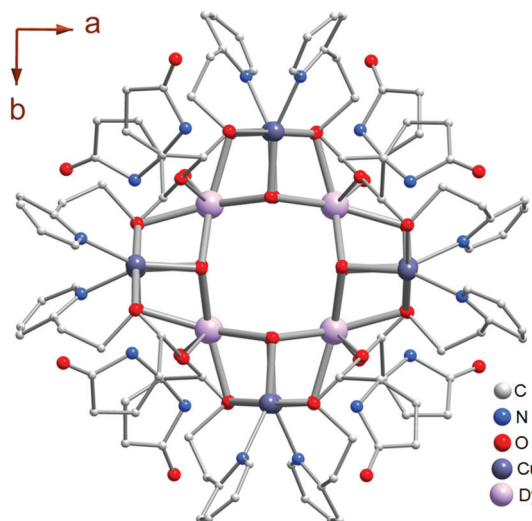
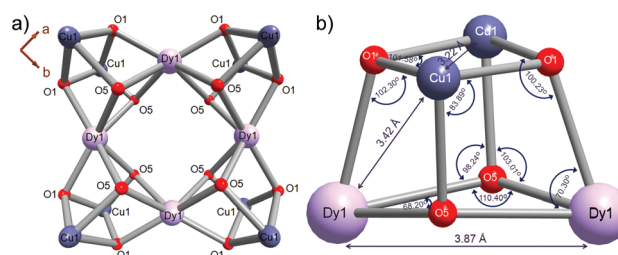


Fig. 1 Molecular structure of complex **1L** (along crystallographic c-axis), as obtained from SC-XRD analyses presenting a highly symmetric $\text{Dy}(\text{III})$ -vertex sharing tetracubane-assemblage based dodecahedral Dy_4Cu_8 heterometallic cluster core.



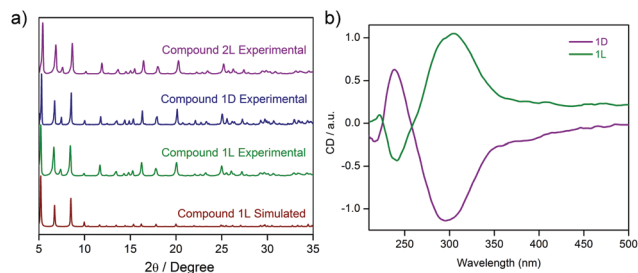


Fig. 3 (a) PXRD profiles suggesting a similar nature and phase purity for the three analogous M_4Cu_8 compounds reported herein, viz. **1L**, **1D**, and **2L** respectively, as compared to the simulated pattern for the L-PGA based cluster **1L**; (b) solid-state CD spectra of **1L** and **1D**; the two chiral clusters synthesized from PGA ligands with different chirality signatures, viz. L-PGA and D-PGA respectively.

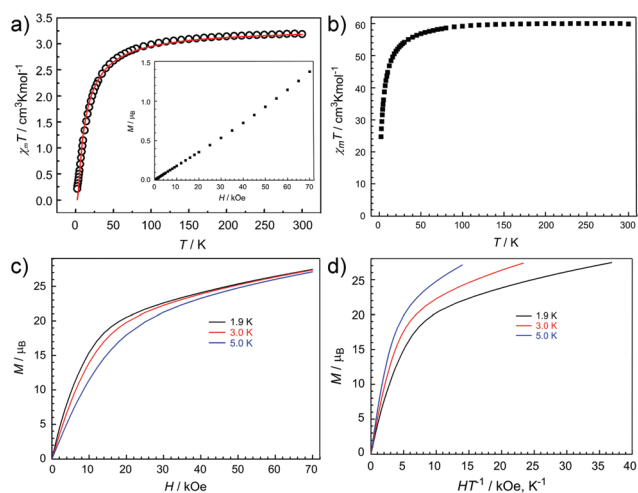


Fig. 4 Temperature dependence of $\chi_M T$ in **2L** (left; a) and **1L** (right; b) under 1000 Oe field, χ_M being the molar magnetic susceptibility. The red solid line corresponds to the calculated behavior of compound **2L**. Inset of a: plot of field dependence of the magnetization (M) of **2L** at 2 K; (c) Plots of M vs. H (left) and (d) the reduced magnetization M versus H/T (right) at the indicated temperatures for compound **1L**.

actions among Cu^{II} ions. In order to quantify the magnetic coupling, we simulated the magnetic data by using one J coupling parameter. The experimental susceptibility data for **2L** was fitted by *PHI* program⁸³ using the isotropic one- J model and the Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$, where J represents the exchange parameter between Cu^{II} ions. The fit provides a set of parameters, $J = -5.71 \text{ cm}^{-1}$, $g = 2.10$ and the intermolecular antiferromagnetic interactions $zj = -0.5 \text{ cm}^{-1}$. The variable-field magnetization measurement of **2L** at 1.8 K is shown in the inset of Fig. 4a. Moreover, the field-dependent magnetization at low temperatures reveals a steady increase approaching the value of $1.4\mu_B$ for **2L** at 70 kOe without saturation (Fig. 4a, inset). The profile of the M vs. H plot confirms the existence of antiferromagnetic interactions within the clusters.

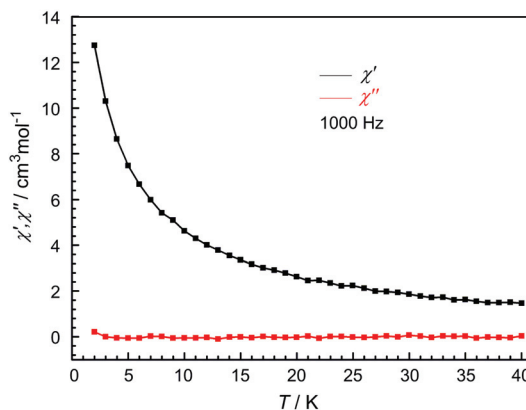


Fig. 5 Temperature dependence of in-phase (χ') (black) and out-of-phase (χ'') (red) ac susceptibilities of **1L** at 1000 Hz in zero dc field and 3 Oe ac field.

Upon cooling, the $\chi_M T$ value for **1L** gradually decreases from 300 to 50 K, subsequently followed by further rapid decline to reach the minimum of $24.70 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. This thermal evolution may be ascribed to the depopulation of the Stark sublevels and/or significant magnetic anisotropy present in Dy-containing systems,^{84,85} and does not preclude very weak antiferromagnetic magnetic interactions between spin carriers.

Magnetization (M) data for **1L** were collected in the 0–70 kOe field range below 5 K. The field dependence of the magnetization (M) shows that M increases smoothly with increasing applied dc field without saturation even at 7 T (Fig. 4c), which is ascribed to the anisotropy and the crystal-field effect.⁸⁶ Furthermore, The non-superimpose M vs. H/T plot (Fig. 4d) also indicates the presence of significant magnetic anisotropy and/or low-lying excited states.

In order to investigate the dynamics of the magnetization, temperature dependence of the in-phase (χ') and out-of-phase (χ'') alternating current (ac) susceptibility measurements were carried out at 1000 Hz in zero dc field and 3 Oe ac field for **1L**. However, the absence of signals in the out-of-phase magnetic susceptibility operating in a 3.0 Oe ac field and a zero dc field (Fig. 5) indicates the lack of slow magnetic relaxation. This may be ascribed to the fast quantum tunneling phenomena.

Conclusions

In conclusion, magnetic studies on a biomolecule based symmetric chiral M_4Cu_8 cluster core are reported, which might be further exploited in the future to develop biocompatible magnetic materials from simple inexpensive precursors by coordination chemistry-driven self-assembly guided design principles. Considering the much less-explored domain of biomolecule-based magnetic materials, this report should help to make new inroads for the development of this new class of materials featuring the unique fusion of magnetism and biocompatibility.



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