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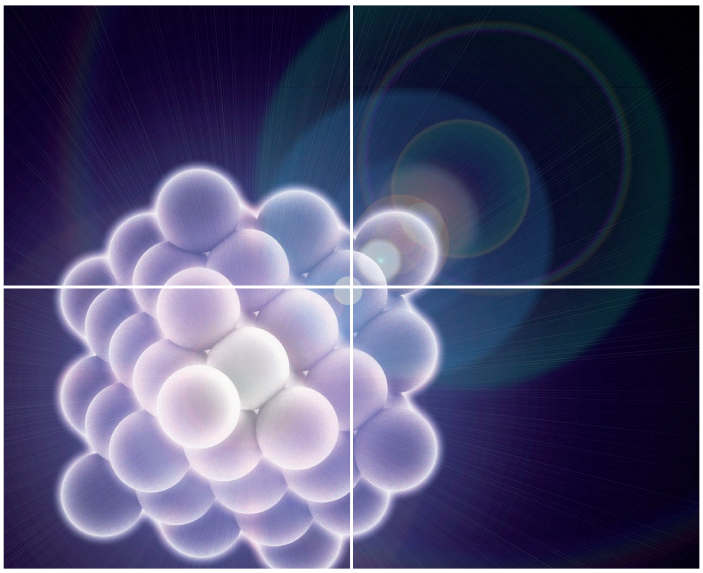

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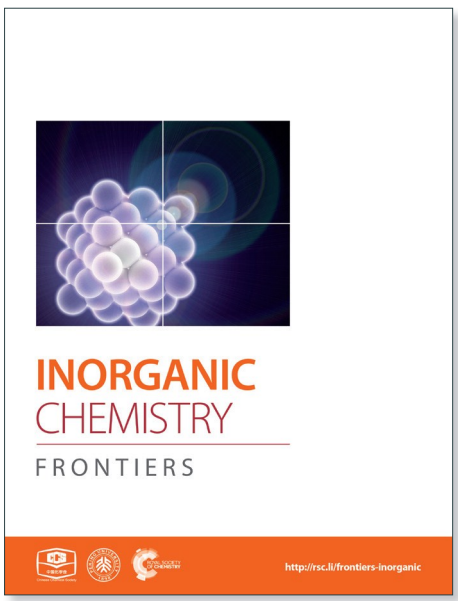

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Inorganic Chemistry Frontiers

ARTICLE

Chiral Biomolecule Based Dodecanuclear Dysprosium(III)-Copper(II) Clusters: Structural Analyses and Magnetic Properties

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The 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 linker 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 cordination-core, comprising of four square-symmetricallly 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 measuremnets.

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 process involving metal nodes and a vast spectra of numerous linkers.[1-6] Among these, coordination architectures pertaining to excellent symmetric features have been the most flanked 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 priorly conceive, leading to a strategic rationale based design principle for attainment of targeted properties and therefore to gain an insight into the same. 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 interactions 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-standpoint.[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 introspect, because of their prospective applications in biological applications, including drug delivery or intracellular imaging. Although lot of efforts have been put together to introspect lanthanide (4f)-based and lanthanide-transition (3d-4f)-based coordination complexes, resulting into the revelation of noteworthy magnetic properties such as, slow magnetic relaxation-triggered single molecule magnet behaviour, magnetic refrigeration etc.; biomolecule based coordination complexes[46] have never been the focus from the standpoint of magnetism phenomena, in spite of the recently explored spectra of applications presented by this emerging class of materials.[46-52] Despite some reports of late, Pyroglutamic acid (PGA) or pidolic acid, a scarcely found proline derivative recently commercialized as a dietary supplement, wherein the free amino group of glutamic acid or glutamine undergoes

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cyclization to form a lactam, is yet to be comprehensively harnessed for coordination complex reactions.[53-57] Importantly, this oxo-derivative of secondary amino acid being a noteworthy metabolite in the glutathione cycle is one of the 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 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 requisite biocompatibility.[61, 62]

Furthermore, to synthesize such desired coordination complexes based on hard Lewis acid (PGA) with high hydrooxophilic Ln^{III} and Cu^{II} ions,[63-69] we have purposefully chosen pyridine-based auxiliary ligands having 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 syntheses of a series of three isostructural, chiral biomolecule based M_4Cu_8 coordination complexes $[M_4Cu_8(HEP)_8(PGA)_8(OH)_8(NO_3)_4]$ (M = Dy and Y) and have analyzed their magnetism properties by 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 Y_4Cu_8 core, henceforth highlighting the role of 3d-4f interactions in the Dy-analogue behind 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 Kα radiation (λ = 1.5406 Å). FT-IR spectra were measured on NICOLET 6700 FT-IR Spectrophotometer using KBr pellets.

Synthesis of $[Dy_4Cu_8(HEP)_8(L\text{-}PGA)_8(OH)_8(NO_3)_4]$ (1L)

To a sonicated methanolic solution (5 mL) of HEP (11.3 µL, 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 on to the aforementioned reaction mixture, following which solid $Cu(NO_3)_2.3H_2O$ (12.1 mg, 0.05 mmol) and 3 ml of 0.03 mmol (13.6 mg) methanolic solution of $Dy(NO_3)_3.xH_2O$ is slowly added while sonicating continuously. Slow evaporation of solvent mixture over next ten days with no mechanical disturbance, yielded excellent quality blue cube-shaped single crystals of compound $[Dy_4Cu_8(HEP)_8(L\text{-}PGA)_8(OH)_8(NO_3)_4]$ (**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 $C_{96}H_{112}Cu_8Dy_4N_{16}O_{40}$: C, 35.06 (35.38); H, 3.43 (2.98); N, 6.82 (6.65)%.

Synthesis of $[Dy_4Cu_8(HEP)_8(D\text{-}PGA)_8(OH)_8(NO_3)_4]$ (1D) and $[Y_4Cu_8(HEP)_8(L\text{-}PGA)_8(OH)_8(NO_3)_4]$ (2L)

Similar reaction protocol as mentioned for **1L** was followed for the syntheses of **1D** from D-PGA (instead of L-PGA) and $Dy(NO_3)_3.xH_2O$; **2L** from L-PGA and $Y(NO_3)_3.6H_2O$ (replacing $Dy(NO_3)_3.xH_2O$). 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 Kα 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 SAINT[70] software. A multi-scan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL[71] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97[72] program package within the WINGX[73] 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 PLATON[74] 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 the compound **1L** was crystallized in tetragonal space group *P4222* with Z = 1. The molecular structure of

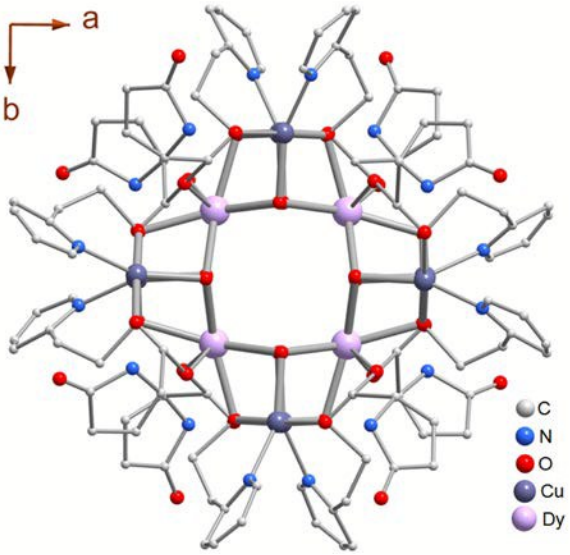

Figure 1: Molecular structure of complex **1L** (along crystallographic *c*-axis), as obtained from SC-XRD analyses presenting a highly symmetric Dy(III)-vertex sharing tetracubane-assemblage based dodecahedral Dy_4Cu_8 heterometallic cluster core.

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 Figure 1; the precise arrangement of which is even more focused in Figure 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 (Figure 2a). The four cubanes are tacitly interconnected via the Dy(III) vertices in a typical vertex-sharing arrangement. Interestingly, considering the entire bimetallic central core, only one type of Dy(III): Dy1, one kind of Cu(II): Cu1, and just two different types of O atoms (O1 and O5) constitute the entire assemblage of $Dy_4Cu_8O_{16}$, providing testimony to the symmetric attributes of this cluster core. While O1 centers are found to interconnect the two different metals Dy(III) and Cu(II), O5 centers act as bridging oxo-linkers between the 4f-Dy(III) apices of this bimetallic core.

The bond angles and intermetallic distances spanned across each of the solitary cubane units have been represented in Figure 2b. Considering the homometallic pairs;

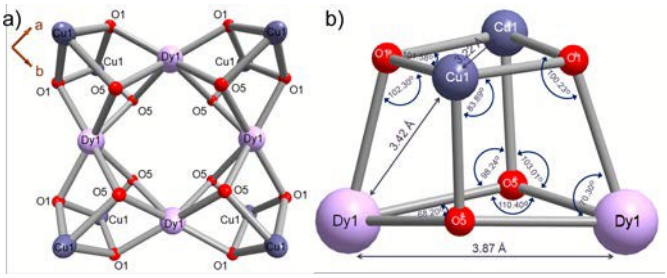

Figure 2: a) The Dy(III) vertex-sharing arrangement of four Dy_2Cu_2 cubanes to constitute a Dy_4Cu_8 dodecahedron architecture, viewed along *c*-axis; b) intermetallic distances and bond angles spanned at different vertices of each of the four Dy_2Cu_2 constituent cubanes of the symmetric heterometallic core.

while the two larger Dy(III) centers are separated by a distance of 3.87 Å, at the very central core of the motif, the distant Cu(II) centers are in quite close proximity (3.22 Å), resulting into 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 Cu(II) duo (3.22 Å) and the larger Dy(III) pair (3.87 Å), which is quite in accord to the structural anticipation regarding heterometallic cubane species.

Exactly similar PXRD profiles getting recorded for two of the analogous mates, unequivocally indicates the isostructural attributes for both the phases **1D** and **2L**, in comparison to that of **1L** (Figure 3a), while similar IR stretching frequencies and elemental analyses for these merely reinstates the same fact.

Solid state CD spectra for two isostructural complexes (1D and 1L), arising out of different enantiomeric ligands (D and L respectively) is just reverse to each other as anticipated (Figure 3b). Although few in numbers, some chiral coordination complexes with interesting magnetic properties have been reported in the literature;[76-82] but, biomolecule-derived chirality based coordination complex acting as molecular magnets are not yet reported.

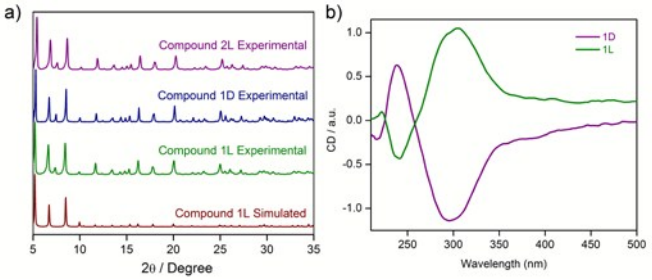

Figure 3: a) PXRD profiles suggesting the similar nature and phase purity for the three analogous M_4Cu_8 compounds reported herein, viz. **1L**, **1D**, and **2L** respectively, as compared to the simulated pattern for the L-PGA based cluster **1L**; b) Solid-state CD spectra of **1L** and **1D**; the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

Direct-current (dc) magnetic susceptibilities of **1L** and **2L** have been measured in an applied dc magnetic field of 1000 Oe between 300 and 2 K. The plots of $\chi_M T$ versus T, where χ_M is the molar magnetic susceptibility, are shown in Figures 4a and 4b. At room temperature, the corresponding $\chi_M T$ values equal

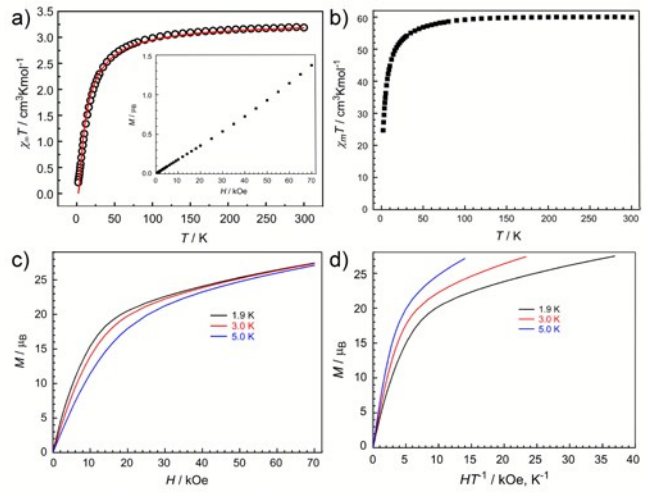

Figure 4: Temperature dependences of $\chi_M T$ in **2L (**left; a) and **1L** (right; b) under 1000 Oe field, χ_M being the molar magnetic susceptibility. The red solid line corresponds to the calculated behavior of compound **2L**. Inset of Fig. 4a: Plot of field dependence of the magnetization (M) 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**.

3.19 and 59.87 cm^3 K mol^{-1} for **2L** and **1L** respectively (Figures 4a and 4b), are in agreement with the expected values for eight uncoupled Cu^{II} ions (S = 1/2, g = 2, C = 0.375 cm^3 K mol^{-1}) for **2L** and eight uncoupled Cu^{II} ions altogether with four uncoupled Dy^{III} ions (S = 5/2, L = 5, $^6H_{15/2}$, g = 4/3, C = 14.18 cm^3 K mol^{-1}) for **1L** in the free-ion approximation.

For **2L**, the χ_MT value stays unchanged with decreases temperature until about 100 K, where it sharply decreases to 0.21 cm^3 K mol^{-1} at 2 K. Considering the diamagnetic Y^{III} ion, this decrease means the occurrence of antiferromagnetic interactions in character among Cu^{II} ions. In order to quantify the magnetic coupling, we simulate the magnetic data by using one J coupling parameter. The experimental susceptibility data for **2L** was fitted by *PHI* program[83] 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 cm^{-1}, g = 2.10 and the intermolecular antiferromagnetic interactions zj = − 0.5 cm^{-1}. The variable-field magnetization measurement of **2L** at 1.8 K is shown in inset of Figure 4a. Moreover, the field-dependent magnetization at low temperatures reveals a steady increase approaching about the value of 1.4 μ_B for **2L** at 70 kOe without saturation (Figure 4a, inset). The profile of M vs. H plot confirms the existence of antiferromagnetic interactions within the clusters.

Upon cooling, the χ_MT value for **1L** gradually decrease from 300 to 50 K, subsequently followed by further rapid decline to reach the minimum of 24.70 cm^3 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 (Figure 4c), which is ascribed to the anisotropy and the crystal-field effect.[86] Furthermore, The non-superimpose M vs. H/T plot (Figure 4d) also indicates the presence of significant magnetic anisotropy and/or low-lying excited states.

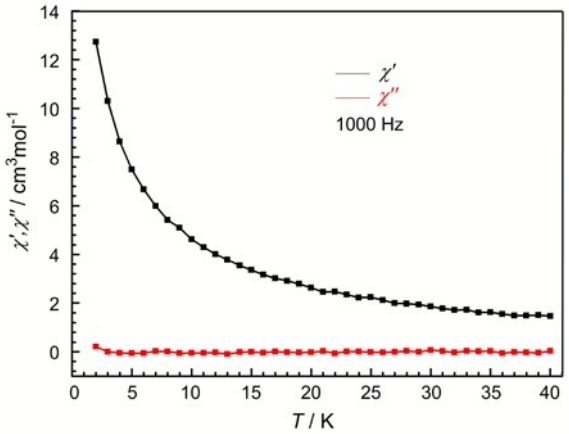

Figure 5: Temperature dependences of in-phase (χ') (black) and out-of-phase (χ'') (red) ac susceptibilities of **1L** at 1000 Hz in zero dc field and 3 Oe ac field.

In order to investigate the dynamics of the magnetization, temperature dependences 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 (Figure 5) indicates the lack of slow magnetic relaxation. This may be ascribed to the fast quantum tunneling phenomena.

Conclusions

In conclusion, the magnetic studies on a biomolecule based symmetric chiral M_4Cu_8 cluster core is reported, which might be further exploited in future to develop biocompatible magnetic materials from simple inexpensive precursors by coordination chemistry-driven self-assembly guided design principle. 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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Notes and references

Crystallographic data for compound **1L** : CCDC 1403754
Supporting information includes 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**.

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