Ferromagnetic interaction and slow magnetic relaxation in a Co$_3$ cluster-based three-dimensional framework$^\dagger$

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A Co$_3$ cluster-based three-dimensional (3D) framework, [Co$_3$(4-ptz)$_4$(N$_3$)$_2$(H$_2$O)$_2$·4DMF (1; 4-Hptz = 4-(1H-tetrazol-5-yl)pyridine), exhibits ferromagnetic interactions and slow-magnetic relaxation behavior.

The development of assembling molecules in a predetermined multidimensional coordination environment with the use of intermolecular interactions is a major topic of increasing scientific interest.$^1$ In the past decade, this methodology has given birth to several novel areas of research, including the preparation of rotaxanes,$^2$ molecular building blocks,$^3$ host–guest chemistry,$^4$ and metal–organic frameworks (MOFs).$^5$ A potential application of this research resides in high-capacity data storage for electronic devices,$^6$ which can be achieved by organizing molecular nanomagnets, which are referred to as single-molecule magnets (SMMs), in a multidimensional environment.$^7$ Theoretically, such an arrangement of molecular magnets in a crystalline material would enable magnetization probing without interference by magnetic ordering, allowing researchers to study the exact nature of the retention of magnetization for SMMs.$^8$ They display slow magnetic relaxation phenomena such as magnetization hysteresis loops, and frequency-dependent signal measurements of out-of-phase alternating current (AC) magnetic susceptibility arise from a large anisotropy energy barrier of alternating current (AC) magnetic susceptibility arise from a frequency-dependent signal measurements of out-of-phase magnetization hysteresis loops, and relaxation probing without interference by magnetic ordering, allowing researchers to study the exact nature of the retention of magnetization for SMMs.$^8$ They display slow magnetic relaxation phenomena such as magnetization hysteresis loops, and frequency-dependent signal measurements of out-of-phase alternating current (AC) magnetic susceptibility arise from a large anisotropy energy barrier.

The asymmetric unit consists of two Co$_2+$ centers, one bridging the azido ligand, one the 4-ptz ligand, one a coordinated water molecule, and two disordered DMF guest molecules (Fig. 1a). The two nonequivalent Co atoms adopt a distorted octahedral structure but also dominate a significant magnetic exchange interaction.$^9$ Compounds that contain Co$^{2+}$ ions have been reported as SMMs recently, including some multi-nuclear Co$^{2+}$ clusters and a complex containing a single-ion of Co$^{2+}$,$^{10}$ which are considered as good candidates for use in preparing multi-dimensional magnetic materials; however, only one example of a Co-SMM-based 3D compound has been reported.$^{11}$

We herein report on the preparation of a 3D Co$_3$-based framework, [Co$_3$(4-ptz)$_4$(N$_3$)$_2$(H$_2$O)$_2$·4DMF (1), obtained by the bridging of 4-Hptz and azide. 4-Hptz and azide, the selected ligands, not only connect the Co$^{2+}$ into a multidimensional structure but also dominate a significant magnetic exchange interaction which results in the formation of a ferromagnetic Co$_3$ building unit that exhibits slow magnetic relaxation behavior.

The reaction of Co(OAc)$_2$·4H$_2$O (1 equiv.), 4-Hptz (1 equiv.), with NaN$_3$ (1 equiv.) in DMF at 80 °C in a Teflon-lined stainless autoclave for 3 days resulted in the formation of very fine purple crystals of [Co$_3$(4-ptz)$_4$(N$_3$)$_2$(H$_2$O)$_2$·4DMF (1) in 68% yield.

An X-ray crystal$^\dagger$ structure analysis (see ESI†) showed that 1 crystallizes in the orthorhombic space group Pnmm. The structure of [Co$_3$(4-ptz)$_4$(N$_3$)$_2$(H$_2$O)$_2$·4DMF (1) is shown in Fig. 1. The asymmetric unit consists of two Co$^{2+}$ centers, one bridging the azido ligand, one the 4-ptz ligand, one a coordinated water molecule, and two disordered DMF guest molecules (Fig. 1a). The two nonequivalent Co atoms adopt a distorted octahedral structure but also dominate a significant magnetic exchange interaction which results in the formation of a ferromagnetic Co$_3$ building unit that exhibits slow magnetic relaxation behavior.

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In view of the diverse network structure of compound 1, it is best elucidated on the basis of the types of connectivities of the Co3 cluster moieties through the 4-ptz linker. As shown in Fig. 1c, the Co3 moieties of compound 1 are arranged such that each Co3 unit is connected to eight neighboring Co3 clusters, and can be considered to be a planar 8-connected node. As a result, the net assembly based on the 8-connected node leads to the formation of a CsCl-like 3D network with a buc topology.

Solid-state, variable-temperature magnetic susceptibility measurements were performed on a microcrystalline sample of complex 1 in the 2.0–300 K range in a 1 kG magnetic field, which was suspended in eicosane to prevent torquing. The temperature dependence of the χMT value of 1 is shown in Fig. 2. The χMT value at 300 K is 9.04 emu mol⁻¹ K, much larger than the 5.63 emu mol⁻¹ K value for three non-interacting CoII ions. This could be a result of the depopulation of the higher Kramers doublets, caused by the splitting of the 4T1g ground triplet under the combined action of the spin–orbit coupling and non-cubic crystal-field terms. Upon cooling, the χMT value remains constant until the temperature reaches approximately 50 K, where it then begins to increase to a maximum value of 11.88 emu K mol⁻¹ at 8 K before dropping sharply below this temperature. The sharp increase in the χMT value at temperatures above 8 K is a characteristic of ferromagnetic behavior, leading to a non-zero ground state, and the decrease below 8 K can be attributed to the combined effect of zero-field splitting, the Zeeman effect and weak interunit interactions through the 4-ptz ligand, which has been reported as a weak antiferromagnetic interaction in the literature.

The inverse of the dc susceptibility decreases linearly from 300 to 50 K following Curie–Weiss behavior with C = 9.01 emu mol⁻¹ K and θ = 1.1 K (Fig. 4S†). The positive Weiss constant (θ) indicates the existence of a ferromagnetic interaction within complex 1. Because of the complications introduced by the orbital contributions of CoII ions, a quantitative treatment of the magnetic susceptibility data of 1 in the whole 2.0–300 K temperature range was not attempted. However, the low temperature region (10–35 K) of magnetic susceptibility can be roughly fitted using a linear CoIII Heisenberg–van Vleck model of $H = −2\{S_sS_s + S_sS_l\}$ based on an $S_{eff} = 1/2$ for each CoII ion (solid line in Fig. 2), which gives the best fit parameters of $g' = 5.2, J = 11.2$ cm⁻¹. The positive $J$ value confirms the intranet ferromagnetic interaction and the maximum $\chi_M T$ value of 11.88 emu mol⁻¹ K at 8 K is consistent with the theoretical value of 12.7 calculated for $g' = 5.2$ and $S_s = 3/2$. The isotherm magnetization of 1 at 2 K was collected and no hysteresis loop was observed (Fig. 5S†). The magnetization shows the onset of saturation above 10 kG (Fig. 2, inset) and the saturation is not complete up to 50 kG; its value of 5.9N$\mu_B$ is lower than the theoretical value of 7.8N$\mu_B$ (calculated by $g' = 5.2$ and $S_s = 3/2$), which is indicative of very close levels in 1. Moreover, the field-dependent magnetization (0.25–5 T at 1.8–4 K) and $\chi_M T$ vs. $T$ under different applied fields confirm the participation of low-lying excited states and the very close levels and crossing of the levels, respectively (Fig. 6S and 7S†).

Alternating current (AC) susceptibility measurements were carried out for complex 1 under a zero DC field. As shown in the ESI, Fig. 8S† complex 1 shows frequency-dependent in-phase ($\chi_M'$) and out-of-phase ($\chi_M''$) signals, indicating a significant barrier to magnetization relaxation and precludes 3D ordering. However, no maxima were observed for $\chi_M''$ in the temperature and frequency range studied. This behavior can be attributed to the zero-field fast tunneling of the magnetization, and the application of an external field is usually
mental data gives parameters for the effective energy barriers as a function of the inverse of temperature for the reversal of magnetization of 24 K and 2.1 K. The Arrhenius equation was applied to fit the data to an activation energy barrier of this complex was obtained. The plot of the relaxation time as a function of the inverse of temperature for complex 1 was shown in Fig. 4a. The best fitting of the experimental data gives parameters for the effective energy barriers for the reversal of magnetization of 24 K and \( \tau_0 = 3.4 \times 10^{-9} \) s. This energy barrier may originate from the combination of the high-spin ground state and magnetic anisotropy of Co\(^{II}\) ions of complex 1, which is consistent with those reported for Co\(^{II}\) SMMs.\(^{10}\) Furthermore, at a fixed temperature of 2.2 K, we obtained a semicircle Cole–Cole diagram (\( \chi_M'' \) vs. \( \chi_M' \)), which could be fitted to a generalized Debye model,\(^{15}\) with \( \alpha \) parameters of 0.18, which indicates a moderate distribution in relaxation time (Fig. 4b).

For a reported Co\(_3\)SMM-based 3D compound, a relatively stronger interunit interaction is evident from a shorter \( \tau \) carboxylate bridging and a crossover of the \( \chi_M'' \) curves has been seen in the AC data. In contrast, the longer 4-ptz ligand participated in a weak interunit interaction in 1 and no crossover of \( \chi_M'' \) curves was observed.

In the heat capacity measurements of 1 that were performed on powdered crystals, no \( \lambda \) peak was observed in \( C_p \) on cooling to 2 K (Fig. 11S†), suggesting the absence of bulk magnetic ordering.

### Conclusions

A Co\(_3\) cluster-based 3D framework was built up with Co\(^{II}\) ions using N\(_3^–\) and the nitrogen donor ligand 4-pyridinyl-tetrazo5-(4-pyridyl)-tetrazole resulting in a becu-type topology. A magnetic analysis reveals that the compound shows ferromagnetic interactions within the Co\(_3\) cluster and slow-magnetic relaxation behavior.

### Notes and references

†The complex analyzed as (C, H, N) 1, calcld (found): C, 36.82 (36.58); H, 4.13 (4.12); N, 35.85 (35.60). Crystal-structure data for 1, \( \text{C}_{60}\text{H}_{42}\text{Co}_{3}\text{N}_{30}\text{O}_{6} \), \( M = 1173.83 \), orthorhombic, \( Pnmn \), \( a = 12.2143(13) \) Å, \( b = 13.8051(15) \) Å, \( c = 16.5293(17) \) Å, \( V = 2987.2(5) \) Å\(^3\), \( T = 150(2) \) K, \( Z = 2 \). \( R_{\text{rel}} = 0.0847 \), 2557 parameters, \( R(R_0) = 0.1039(0.2530) \) with \( I > 2\sigma(I) \).


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**Fig. 3** Plots of out-of-phase (\( \chi_M'' \)) of AC susceptibility vs. frequency in a 3.5 G AC field oscillating and 500 G DC field at the indicated temperatures for complex 1.

**Fig. 4** (a) Arrhenius plot for 1: the solid line denotes the least-squares of maxima \( \chi_M'' \) to the Arrhenius equation. (b) Cole–Cole diagram at 2.2 K for 1: the red solid line represents the least-squares fit obtained using a Debye model.


