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Ferromagnetic interaction and slow magnetic relaxation in a Co_3 cluster-based three-dimensional framework†

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A Co_3 cluster-based three-dimensional (3D) framework, $[Co_3(4\text{-ptz})_4(N_3)_2(H_2O)_2]\cdot 4DMF$ (1; 4-Hptz = 4-(1*H*-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 $KV = |D|S_z^2$ which results from the combination of a large-spin ground state (S) and an Ising-type magnetic anisotropy (negative zero-field splitting parameter D).[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, $[Co_3(4\text{-ptz})_4(N_3)_2(H_2O)_2]\cdot 4DMF$ (**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 which results in the formation of a ferromagnetic Co_3 building unit that exhibits slow magnetic relaxation behavior.

The reaction of $Co(OAc)_2\cdot 4H_2O$ (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 $[Co_3(4\text{-ptz})_3(N_3)_2(H_2O)_2]\cdot 4DMF$ (**1**) in 68% yield.

An X-ray crystal‡ structure analysis (see ESI†) showed that **1** crystallizes in the orthorhombic space group *Pnnm*. The structure of $[Co_3(4\text{-ptz})_4(N_3)_2(H_2O)_2]\cdot 4DMF$ (**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 CoN6 and CoN5O coordination geometry for Co1 and Co2, respectively. Co1 is bound to four tetrazole nitrogen atoms and two nitrogen atoms from two end-on (EO) N_3 ligands, and the Co2 is bound to two tetrazole nitrogen atoms, two pyridyl nitrogen atoms, one nitrogen atom from EO-N_3, and one coordinated water molecule. The cobalt–cobalt separation, bridged by the azido and tetrazole moiety of the 4-ptz ligands, is 3.394(1) Å. The tetrazole ligands adopt a bridging mode with a coordinating pyridyl group and an η^2,μ^2-tetrazolato bridge with its 1,2-nitrogen atoms. This connects each Co_3 unit to a 3D framework (Fig. 1b). Except for the coordinated water molecules, all of the donor atoms form reasonably strong bonds with the cobalt atoms. All of the Co–N and Co–O distances are in the range between 2.062(8) and 2.153(6) Å.

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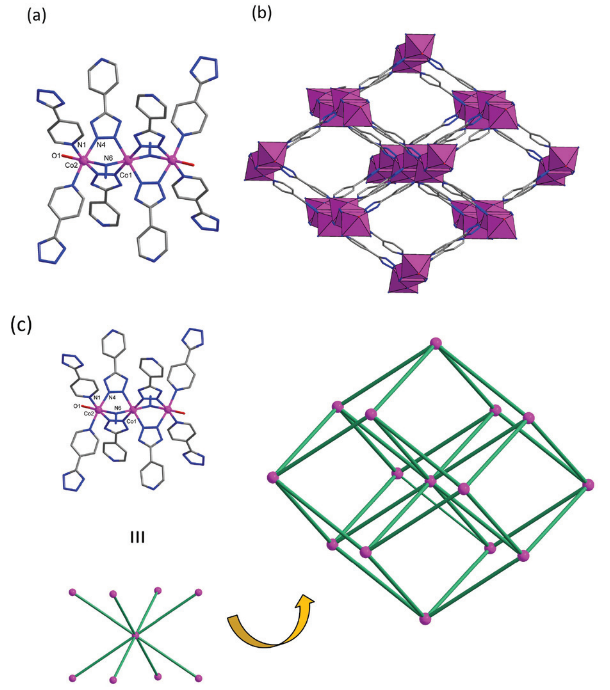

Fig. 1 (a) Local coordination environment of Co^{II} in **1**; hydrogen atoms have been omitted for clarity; (b) 3D framework of **1** constructed by a Co_3 subunit (shown in polyhedron); (c) simplified view of an eight-connected Co_3L_8 node and perspective view of the network of **1** to the **bcu** net topology.

In view of the diverse network structure of compound **1**, it is best elucidated on the basis of the types of connectivities of the Co_3 cluster moieties through the 4-ptz linker. As shown in Fig. 1c, the Co_3 moieties of compound **1** are arranged such that each Co_3 unit is connected to eight neighboring Co_3 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 **bcu**-type 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 $\chi_M T$ value of **1** is shown in Fig. 2. The $\chi_M T$ 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 Co^{II} ions. This could be a result of the depopulation of the higher Kramers doublets, caused by the splitting of the $^4T_{1g}$ ground triplet under the combined action of the spin–orbit coupling and non-cubic crystal-field terms.[12] Upon cooling, the $\chi_M T$ 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 $\chi_M T$ 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.[13] 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 Co^{II} 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 Co^{II}_3 Heisenberg–van Vleck model of $H = -2J(S_1S_2 + S_2S_3)$ based on an S_{eff} = 1/2 for each Co^{II} 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 intraunit 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_T = 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 5.9$N\beta$ is lower than the theoretical value of 7.8$N\beta$ (calculated by g' = 5.2 and S_T = 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†).

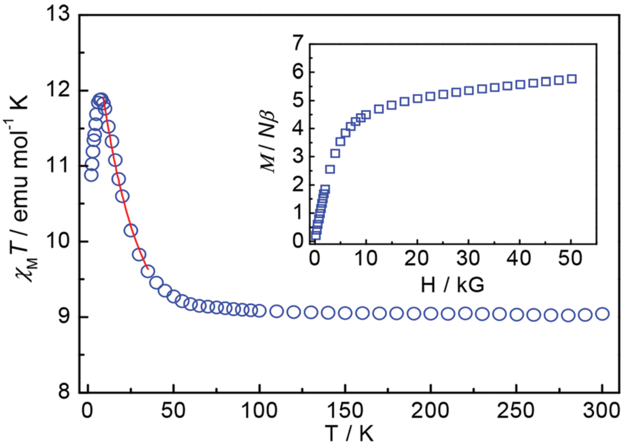

Fig. 2 Plot of $\chi_M T$ *versus* T for **1** in an applied field of 1 kG from 2.0 to 300 K. The solid line represents the best fit given in the text. The inset shows a 2 K magnetization isotherm collected between 0 and 50 kG.

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 (χ_M') and out-of-phase (χ_M'') signals, indicating a significant barrier to magnetization relaxation and precludes 3D ordering. However, no maxima were observed for χ_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

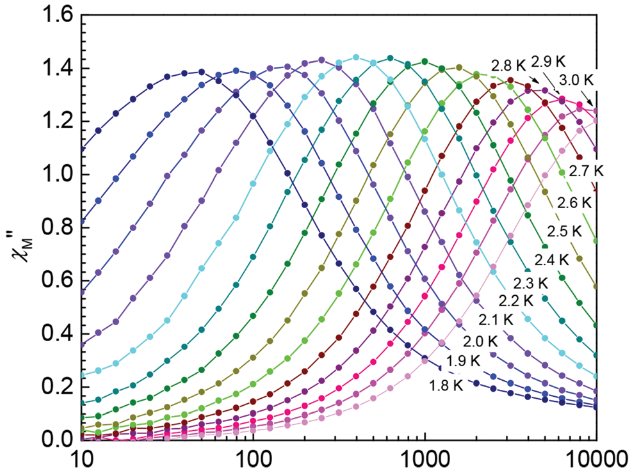

Fig. 3 Plots of out-of-phase (χ_M'') of AC susceptibility *vs.* frequency in a 3.5 G AC field oscillating and 500 G DC field at the indicated temperatures for complex **1**.

sufficient to partially suppress this fast tunneling.[10,14] The χ_M'' signals under an applied field of 500 G were collected and these data are shown in Fig. 3. As the frequency of the AC field changed from 10 000 to 10 Hz, the χ_M'' peak shifted from 3.4 to 2.1 K. The Arrhenius equation was applied to fit the data with the rate for the reversal of magnetization and the effective energy barrier of this complex was obtained. The plot of the relaxation time as a function of the inverse of temperature for complex **1** is 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 $\tau_0 = 5.3 \times 10^{-9}$ 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 (χ_M'' *vs.* χ_M'), which could be fitted to a generalized Debye model,[15] with α parameters of 0.18, which indicates a moderate distribution in relaxation time (Fig. 4b).

For a reported Co$_4$-SMM-based 3D compound, a relatively stronger interunit interaction is evident from a shorter *syn–anti* carboxlate bridging and a crossover of the χ_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 χ_M'' curves was observed.

In the heat capacity measurements of **1** that were performed on powdered crystals, no λ 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-pyridinely-tetrazo5-(4-pyridyl)-tetrazole resulting in a **bcu**-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**, calcd (found): C, 36.82 (36.58); H, 4.13 (4.12); N, 35.85 (35.60)%. Crystal-structure data for **1**, $C_{36}H_{48}Co_3N_{30}O_6$, *M* = 1173.83, orthorhombic, *Pnnm*, *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_{int} = 0.0847), 2557 parameters, $R(R_w)$ = 0.1039(0.2530) with $[I > 2\sigma(I)]$.

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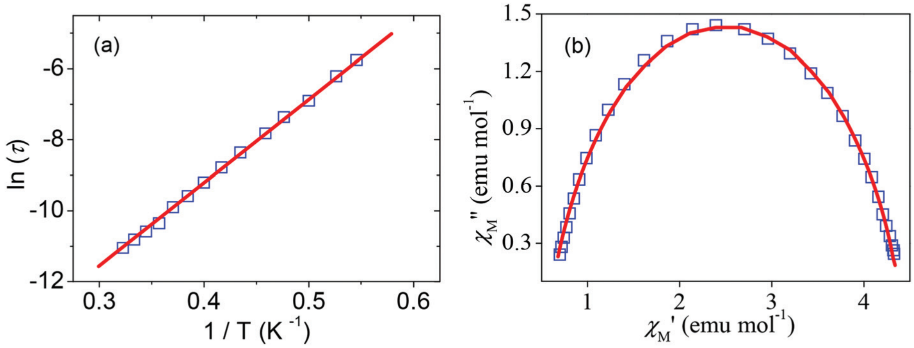

Fig. 4 (a) Arrhenius plot for **1**; the solid line denotes the least-squares of maxima χ_M'' to the Arrhenius equation. (b) Cole–Cole diagram at 2.2 K for **1**; the red solid line represents the least-squares fit obtained using a Debye model.

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