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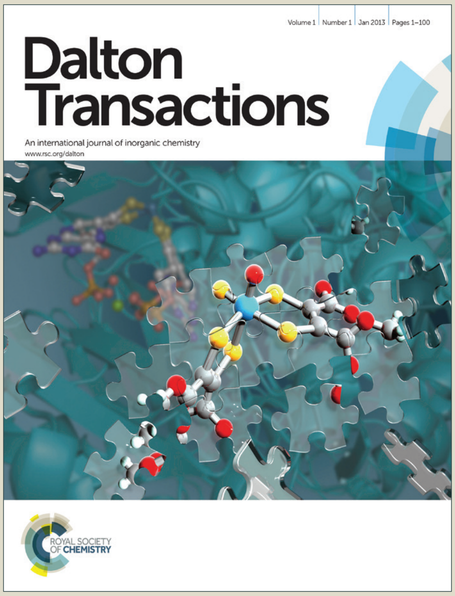

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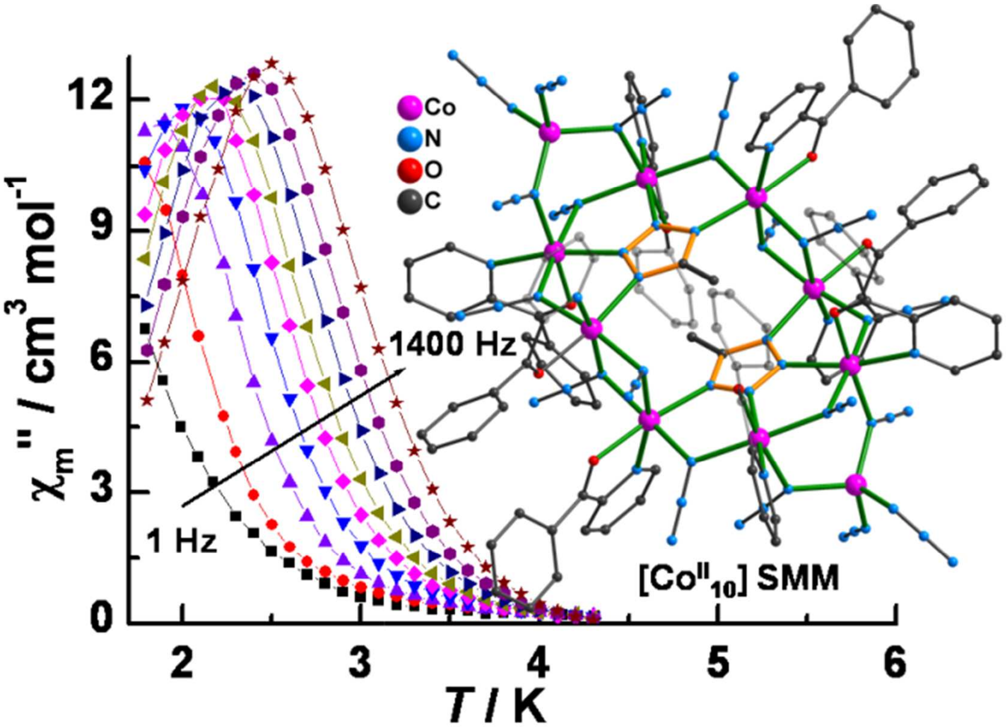

An unprecedented azido-bridged chair-like [Co^{II}_{10}] SMM containing both tetrahedral and octahedral Co(II) ions have been prepared through an *in situ* [2 + 3] cyclo-addition reaction in a sealed system. The magnetic study showed that it exhibited overall intracluster ferromagnetic coupling, and slow magnetic relaxation at both zero and non-zero applied field with an effective barrier for reverse magnetization of 26 K.

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In situ tetrazole templated chair-like decanuclear azido-cobalt(II) SMM containing both tetra- and octa-hedral Co(II) ions

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An azido-bridged chair-like decanuclear cluster: $[Co^{II}_{10}(bzp)_8(Metz)_2(N_3)_{18}]\cdot 4MeOH\cdot 3H_2O$ (1, bzp = 2-benzoylpyridine and HMetz = 5-methyl-1H-tetrazole) was prepared with *in situ* tetrazolate anions as templates in a sealed system. 1 containing both octahedral and tetrahedral Co(II) ions exhibited slow relaxation of magnetization with an effective barrier of 26 K under an applied dc field of 1 kOe.

The last two decades have witnessed extensive expansion in the family of single molecule magnets (SMMs) due to their potential applications for memory storage materials.[1] As an excellent candidate for SMMs, high-spin (HS) Co(II) may exhibit large magnetic anisotropy with flexible zero-field splitting parameter, D_{Co}, very much depending on its coordination geometry and the degree of their distortions. For example, both hard-axis ($D_{Co} > 0$) and easy-axis ($D_{Co} < 0$) anisotropy have been documented when Co(II) is located in a distorted octahedral geometry (such as elongated or compressed).[2,3] A remarkable record $D_{Co} = -115\ cm^{-1}$ was recently reported by Gao's group in a chiral star-like compound, $[HNEt_3][Co^{II}Co^{III}_3L_6]$ (H_2L = R-4-bromo-2-((2-hydroxy-1-phenylethylimino)methyl)phenol), where the only paramagnetic Co(II) ion is located in a slightly distorted triangular prism.[4] Ising-type magnetic anisotropy was also evidenced when Co(II) adopts a distorted tetrahedral geometry with C_{2V}[5] or D_{2d}[6] symmetry, while hard-axis anisotropy was found in C_{3V} geometry.[7] All these findings demonstrate that Co(II) is indeed a promising candidate for building SMMs.[8] However, combining two different geometries in one molecule is still a big challenge.

Till now, most of Co(II)-SMMs are containing octahedral Co(II) ions, except for a square like $[Co^{II}_4]$ example, where each Co(II) ion adopted a distorted trigonal bipyramidal geometry.[9] Although large $[Co_n]$ clusters ($n \geq 10$) are continuously achieved,[10] very few[11] exhibited SMM behavior and only one[12] showed overall intracluster ferromagnetic coupling. Aim to realize a high spin ground state would be benefited from azido ligand, owing to the tendency to transfer ferromagnetic (F) coupling in its end-on mode.[13] In fact, a convenient synthetic route based on metal-assisted [2 + 3] cycloaddition reactions of nitriles with azide, was explored by Sharpless et al.,[14] and developed by Xiong and others for building new coordination polymers via in situ 5-substituted 1H-tetrazoles reaction.[15,16] However, azide anions often reacted completely into tetrazolates under wild conditions (hydro(solvo)thermal, high temperature and pressure), thus the resulted compounds often do not contain azido bridges. Previously, we reported a planar disc SMM of $[Co_7(bzp)_6(N_3)_9(CH_3O)_3][ClO_4]_2\cdot 2H_2O$ isolated via slow evaporation of $Co(ClO_4)_2\cdot 6H_2O$, NaN_3 and 2-benzoylpyridine (bzp) in methanol.[17] Here, we presented an unprecedented chair-like $[Co^{II}_{10}]$ cluster: $[Co^{II}_{10}(bzp)_8(Metz)_2(N_3)_{18}]\cdot 4MeOH\cdot 3H_2O$ (**1**) (HMetz = 5-methyl-1H-tetrazole), as a product of slow diffusion of methanol into the above mixture in methanol/acetonitrile solution in a sealed system and mild conditions. The *in situ* tetrazolates, generated via [2+3] cyclo-addition reaction of azide and acetonitrile,[14] serve as templates in the formation of **1**. The magnetic study found that **1** exhibited overall intracluster ferromagnetic coupling, and slow magnetic relaxation at both zero and non-zero applied field with an effective energy barrier of 26 K under an applied dc field of 1 kOe. To the best of our knowledge, **1** represents the second Co(II)-SMM containing both octahedral and tetrahedral Co(II) ions.[18]

Compound **1** crystallizes in the triclinic $P\bar{1}$ space group. Detailed crystallographic data for **1** is listed in Table S1 and selected bond lengths and angles are listed in Table S2. The structure consists of a neutral centro-symmetric double-seat chair with ten cobalt(II) atoms bridged by end-on (EO) azido groups as well as 5-methyl-tetrazolate in μ_4-η^1:η^1:η^1:η^1 mode.(Fig. 1) The asymmetric unit contains five crystallography independent Co(II) ions: four (Co1 to Co4) adopt a

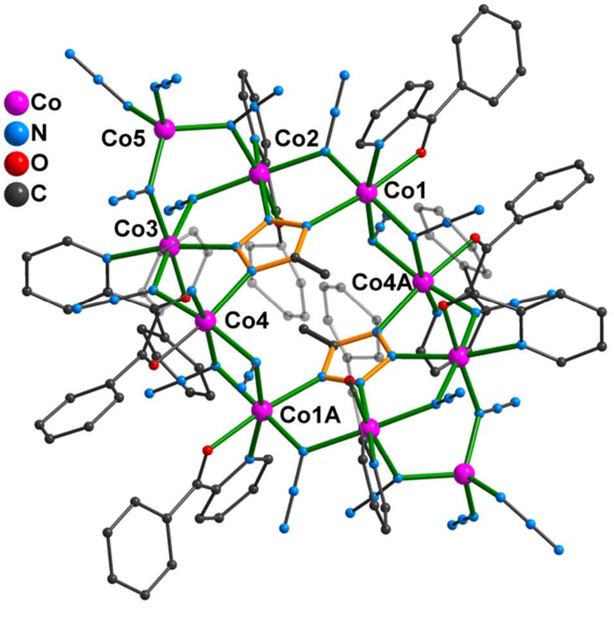

Fig. 1. The double-seat chair-like structure of **1**, lattice solvent and hydrogen atoms are eliminated for clarity.

distorted octahedral (O_h) geometry with cis N–Co–N(O) angles and Co–N(O) bonds in the range of 76.1(2) – 98.0(2)° and 2.074(6)–2.184(4) Å; and Co5 displays a tetrahedral geometry (T_d) with N-Co-N angles and Co-N bonds within the range of 105.9(3) – 117.5(3)° and 1.941(8) – 1.993(6) Å. Co1 to Co4 ions share one methyl tetrazolate ($Metz^-$) in μ_4-η^1:η^1:η^1:η^1 coordination mode,[19] together with three single EO-azido bridges with Co-N-Co angles of 117.8(6)-118.0(2)°, form a semi-circle plane, serving as a chair seat. The tetrahedral Co5 is simultaneously linked to Co3 and Co4 through single EO-azido bridges with larger Co-N-Co angles [117.6(3) and 117.9(3)°], regarded as the backrest part. The asymmetric unit is center-symmetrically extended to the double-seat chair (Fig. S1) through two sets of double EO-azido bridges between Co1 and Co4A as well as Co1A and Co4 with smaller Co–N–Co bridging angles [98.9(2)°], which resulted in the nearest intracluster Co…Co distance of 3.21(2) Å. All the azide ligands are almost linear with the N–N–N angles of 176.9(10)–179.3(8)° and bzp serve as chelating ligands for the O_h Co(II) ions. The clusters are well isolated with the nearest intercluster Co…Co distance of 9.15(2) Å (Fig. S2).

Variable-temperature magnetic susceptibility under an applied direct-current (dc) field of 1 kOe for **1** (per [Co_{10}] unit) is shown in Fig. 2. The χ_mT value [ca. 33.7 cm^3 mol^{-1} K] at 300 K is significantly higher than the spin-only value (18.75 cm^3 mol^{-1} K) for eight O_h and two T_d cobalt(II) ions, indicating strong spin-orbital couplings existing.[20] Upon cooling, the χ_mT value increases steadily to a maximum of 119 cm^3 mol^{-1} K at ca. 7 K before dropping to103 cm^3 mol^{-1} K at 2 K, likely due to the zero-field splitting and/or field saturation effect. The smooth increase of χ_mT from 300 to 7 K clearly suggests an overall ferromagnetic (F) coupling between the neighboring Co(II) ions within the cluster. Significant F coupling between a Co(II) pair bridged by EO-azido groups has been well documented with the exchange parameter (J) of 3.5 – 7.2 cm^{-1} based on $2J$ model,[3a, 3b] while weak antiferromagnetic coupling (J = ca. -2 cm^{-1}) was found though the path of Co-N-N-Co.[21] Thus, it is reasonable that the two competing pathways led to the overall F coupling. However, no suitable model for further analysis of the data was attempted because of the complicated topology.

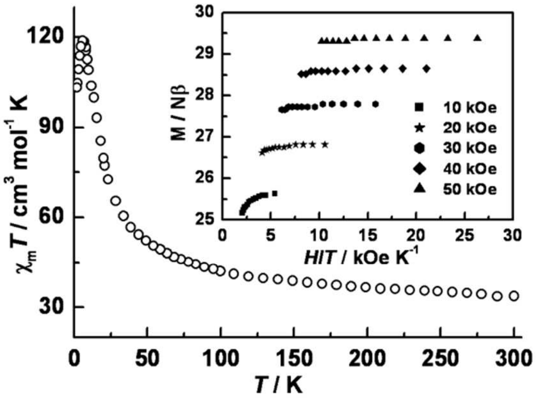

Fig. 2. χ_MT vs T plot for **1** at H_{dc} = 1 kOe (χ_m is defined as the molar magnetic susceptibility). Inset: Magnetization vs H/T between 1.9 and 4.9 K.

The isothermal magnetization (M) vs. the applied field (H) was collected at 1.8 K.(Fig. S3) The steep variation further confirm the intracluster F coupling between Co(II) ions, while, even under 70 kOe, the magnetization value [30.5 Nβ] are not fully saturated (g > 2), suggesting that significant magnetic anisotropy is present. This assumption is further evidenced by the isofield (1 – 5 T) magnetizations at temperatures in the range of 1.9 – 4.9 K, where the lines are far from superposition.(Inset of Fig. 2) Unfortunately, our effort to extract reliable axial (D) and transverse (E) ZFS parameters did not succeed. It should be mentioned that no magnetic hysteresis loop was observed at above 1.8 K.(Fig. S4)

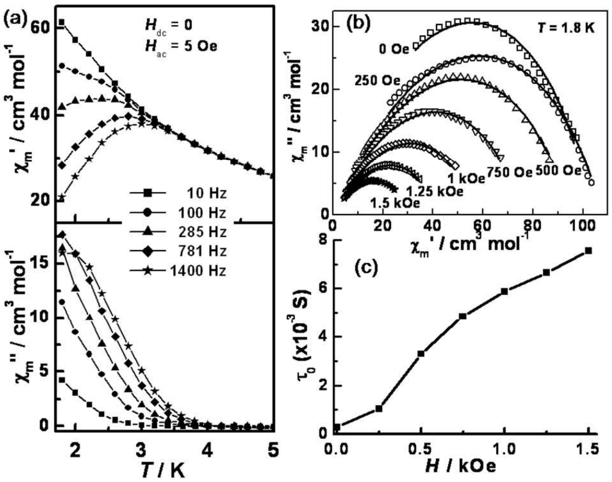

Fig. 3 (a) Variable-temperature in-phase (χ_m', up) and out-of-phase (χ_m'', down) ac magnetic susceptibility data under H_{dc} = 0 and H_{ac} = 5 Oe; (b) Cole-Cole diagrams at 1.8 K with applied dc fields (0-1500 Oe) and an ac field of 5 Oe, the solid lines are least-square fittings of the data; (c) Plot of relaxation time (τ_0) *vs.* H_{dc} field.

To check the possible SMM behaviour of **1**, variable-temperature alternate-current (ac) susceptibility was collected below 5 K at different frequencies under fields of H_{dc} = 0 and H_{ac} = 5 Oe. Strongly frequency-dependent in-phase (χ_m') and out-of-phase (χ_m'') components were clearly observed.(Fig.3a) The shift of peak temperatures (T_p) of χ_m', estimated by a parameter $\phi = (\Delta T_p/T_p)/\Delta(\log f)$ = 0.22, is well consistent with that for a superparamagnet (ϕ = 0.1 – 0.3), suggesting that **1** might be an SMM.[21] To verify its energy barrier, variable-frequency ac data was collected in the temperatures (1.80 – 2.10 K) in the absence of a dc field.(Fig. S5) The relaxation time (τ), extracted from the peaks of the out-of phase signals, follows an Arrhenius law: $\tau = \tau_0 \exp(U_{eff}/k_BT)$ with an effective energy barrier (U_{eff}/k_B = 10.3 K) and $\tau_0 = 9.0 \times 10^{-7}$ s. (Fig. S6) These values are well consistent with those for well-known Co(II)-SMMs.[8]

Magnetization may relax through the quantum tunnelling pathway and the thermally activated mode. Especially, Co(II)-SMMs are known to show a high prevalence of fast quantum tunnelling relaxation at zero field.[8] In order to verify this, additional ac measurements were collected under small dc fields (H_{dc} ≤ 1500 Oe) at 1.8 K. Indeed, a dramatic reduction of the characteristic frequency (maximum in the χ_m'' vs ν plot) from 579 Hz (H_{dc} = 0 Oe) to a minimum value of 40 Hz (H_{dc} > 500 Oe).(Fig. S7) The Cole−Cole plots fitted by the generalized Debye model[21] gave α parameters of 0.32-0.58 and the relaxation times (2.9×10^{-4} to 7.54×10^{-3} S).(Fig. 3b, Table S3) Even under a very small dc field of 500 Oe, the relaxation became ten times slower, indicating that dc fields could efficiently reduce the probability of the relaxation through the quantum tunnelling pathway.

To further estimate the effective energy barrier, ac magnetic susceptibility was measured as a function of both temperature (1.8 – 4.5 K) and frequency (1-1500 Hz) in an applied dc field of 1 kOe. As shown in Fig. 4a, strong frequency dependent peaks of both χ_m' and χ_m'' components are visible. The out-of phase for variable-frequency ac data collected in the temperatures 1.8 – 2.4 K also show highly frequency dependent peaks.(Fig. 4b) Two close sets of the relaxation

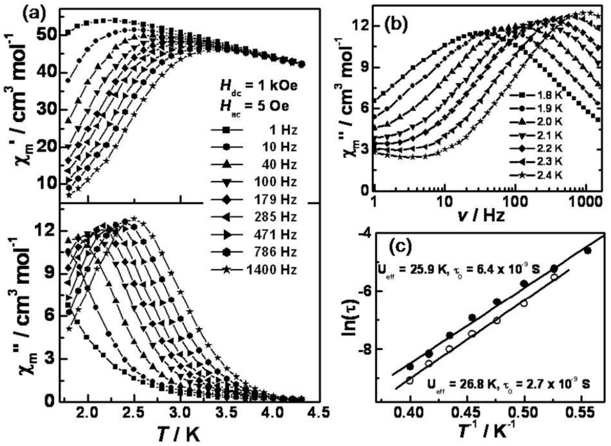

Fig. 4 (a) Variable-temperature and (b) Variable-frequency ac magnetic susceptibility data for **1** under 1 kOe dc field; (c) Arrhenius plots of the relaxation time, as determined through variable-temperature (○) and variable-frequency (●) ac susceptibility data.

time, extracted from the above ac data, both obey an Arrhenius law with: U_{eff}(1 kOe) = 26.8 K, τ_0(1 kOe) = 2.7 × 10^{-9} s for variable-temperature ac data; U_{eff}(1 kOe) = 25.9 K, τ_0(1 kOe) = 6.4 × 10^{-9} s for variable-frequency ac data.(Fig. 4c) The slight difference might be due to the systematic error and the latter set is usually more accurate. The Cole−Cole plots fitted to the generalized Debye model gave α parameters of 0.45-0.52, indicative of a relative wide distribution of relaxation times, likely due to the intercluster interactions and/or multi relaxation modes.(Fig. S8)

Conclusions

In summary, an azido-bridged chair-like [Co^{II}_{10}] SMM containing both tetrahedral and octahedral Co(II) ions has been prepared through an *in situ* [2 + 3] cyclo-addition reaction that produced the templating tetrazolates in a sealed system. Our result demonstrated a possible convenient one-pot procedure for the synthesis of compounds mixed-bridged by azide and tetrazolate ligands. Replacement of the terminal azide groups by other halide ligands could lead to a C_{2V} distortion for Co5, and significant impact on the global anisotropy may be achieved.

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Notes and references

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‡ Synthesis of **1**: NaN_3 (1.00 mmol, 65.3 mg) and bzp (0.410 mmol, 75.2 mg) was dissolved in 5 mL of methanol before being added to the acetonitrile solution (5 mL) of $[Co(OH_2)_6][ClO_4]_2$ (0.505 mmol, 185 mg). The resulting dark-red solution was transferred into several single tubes (ϕ = 6 mm) and then layered with methanol. The tubes were sealed and stood quietly at room temperature. Dark-red block crystals were formed within two weeks. Yield: 31.5 mg, 19.8 %. Anal. Calc.: C, 39.53; H, 3.19; N, 31.03. Found: C, 40.19; H, 2.69; N, 31.96 %. IR (cm^{-1}): 2064 (sh, vs) and 2093 (vs) for stretching of azide. The sample for SQUID was checked by PXRD. (Fig. S9)

§ Crystal data of **1**: $C_{104}H_{100}Co_{10}N_{70}O_{15}$, *F.W.* = 3159.84, triclinic, space group *P*-1, a = 13.565(9), b = 16.584(11), c = 18.065(12) Å, α = 63.652(7)°, β = 76.183(7)°, γ = 83.562(8)°, V = 3536(4) Å^3, T = 110(2) K, Z = 1, μ = 1.222 mm^{-1}, ρ_{calcd} = 1.484 Mg m^{-3}, R_1 = 0.0636, wR_2 = 0.1651.

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