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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.
An azido-bridged chair-like decanuclear cluster: [

\[ \text{Co}^{II}_{10}\text{(bzp)}_{6}\text{(Metz)}_{2}\text{(N}_{3}\text{)}_{18}]\text{4MeOH}\text{-3H}_{2}\text{O} \]

(I, \text{bzp} = 2-benzoylpyridine and \text{HMetz} = 5-methyl-1H-tetrazole) was prepared with \textit{in situ} tetrazolate anions as templates in a sealed system. 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, \(D_{\text{eff}}\), very much depending on its coordination geometry and the degree of their distortions. For example, both hard-axis (\(D_{\text{Co}} > 0\)) and easy-axis (\(D_{\text{Co}} < 0\)) anisotropy have been documented when Co(II) is located in a distorted octahedral geometry (such as elongated or compressed).\(^2,3\) A remarkable record \(D_{\text{Co}} = -115 \text{ cm}^{-1}\) was recently reported by Gao’s group in a chiral star-like compound, \([\text{HNET}_{3}]\text{[Co}^{III}_{3}\text{Co}^{II}_{5}\text{L}_{3}]\) (H\(_2\)L = 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 \(C_{3v}\) or \(D_{2d}\) symmetry, while hard-axis anisotropy was found in \(C_{3v}\) geometry.\(^5\) All these findings demonstrate that Co(II) is indeed a promising candidate for building SMMs.\(^6\) 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\(^{III}\)]\(_2\) example, where each Co(II) ion adopted a distorted trigonal bipyramidal geometry.\(^7\) Although large [Co\(_n\)] clusters (\(n \geq 10\)) are continuously achieved,\(^8\) very few\(^9\) exhibited SMM behavior and only one\(^10\) showed overall intralcluster 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.\(^11\) In fact, a convenient synthetic route based on metal-assisted \([2 + 3]\) cycloaddition reactions of nitriles with azide, was explored by Sharpless et al.,\(^12\) and developed by Xiong and others for building new coordination polymers via in situ 5-substituted 1H-tetrazoles reaction.\(^13\) 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\(_3\)(bzp)\(_6\)(N\(_3\))\(_3\)](ClO\(_4\))\(_2\)-2H\(_2\)O isolated via slow evaporation of Co(ClO\(_4\))\(_2\)-6H\(_2\)O, Na\(_3\), and 2-benzoylpyridine (bzp) in methanol.\(^14\) Here, we presented an unprecedented chair-like [Co\(^{II}\)]\(_8\) cluster: [Co\(^{III}_{8}\text{(bzp)}_{9}\text{(Metz)}_{2}\text{(N}_{3}\text{)}_{18}]\text{4MeOH}\text{-3H}_{2}\text{O} \]

(I) (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 \textit{in situ} tetrazolates, generated via \([2+3]\) cycloaddition reaction of azide and acetonitrile,\(^15\) serve as templates in the formation of I. The magnetic study found that I exhibited overall intralcluster 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, I represents the second Co(II)-SMM containing both octahedral and tetrahedral Co(II) ions.\(^16\)

Compound I crystallizes in the triclinic \(P1\) space group. Detailed crystallographic data for I 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 \(\mu_3\)-\(\eta^1\)-\(\eta^1\)-\(\eta^1\) 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 I, lattice solvent and hydrogen atoms are eliminated for clarity.](https://example.com/fig1.jpg)
distorted octahedral ($O_6$) geometry with cis N–Co–N(O) angles and Co–N(O) bonds in the range of 76.1(2) – 98.0(2)$^\circ$ 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)$^\circ$ and 1.941(8) – 1.993(6) Å. Co1 to Co4 ions share one methyl tetrathiolite (Metz$^\circ$) in $\mu_4$-$\eta^1$-$\eta^1$-$\eta^1$ coordination mode,$^{25}$ together with three single EO-azido bridges with Co-FN-CO angles of 117.8(6)–118.0(2)$^\circ$, 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)$^\circ$], 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)$^\circ$], which resulted in the nearest intrachuster 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)$^\circ$–179.3(8)$^\circ$ and bzp serve as chelating ligands for the $O_6$ 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$_2$]) unit is shown in Fig. 2. The $\chi_m T$ value [ca. 33.7 cm$^3$ mol$^{-1}$ K$^{-1}$] at 300 K is significantly higher than the spin-only value (18.75 cm$^3$ mol$^{-1}$ K$^{-1}$) for eight $O_6$ and two $T_d$ cobalt(II) ions, indicating strong spin-orbital couplings existing.$^{28}$ Upon cooling, the $\chi_m T$ value increases steadily to a maximum of 119 cm$^3$ mol$^{-1}$ K at 7 K before dropping to 103 cm$^3$ mol$^{-1}$ K at 2 K, likely due to the zero-field splitting and/or field saturation effect. The smooth increase of $\chi_m T$ 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 2$J$ model,$^{29,30}$ while weak antiferromagnetic coupling ($J$ = ca. 2 cm$^{-1}$) was found though the path of Co-N-N-Co.$^{31}$ 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.

The isothermal magnetization ($M$) vs. the applied field ($H$) was collected at 1.8 K (Fig. S3) The steep increase further confirms the intracluster $F$ coupling between Co(II) ions, while, even under 70 kOe, the magnetization value [30.5 NEMU] 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).

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 $H_{dc}$ = 5 Oe. Strongly frequency-dependent in-phase ($\chi_m''$) and out-of-phase ($\chi_m'$) components were clearly observed (Fig. 3a) The shift of peak temperatures ($T_p$) of $\chi_m''$, estimated by a parameter $\phi = (\Delta T_p / \Delta \log(\nu)) = 0.22$, is well consistent with that for a superparamagnet ($\phi = 0.1 – 0.3$), suggesting that 1 might be an SMM.$^{25}$ 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 ($\tau$), 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 ($U_{eff}$) = 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. 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 $\chi_m''$ vs $\nu$ 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 generalised Debye model$^{21}$ gave $\alpha$ 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 $\chi_m''$ and $\chi_m'$ 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 I under 1 kOe dc field; (c) Arrhenius plots of the relaxation time, as determined through variable-temperature (●) and variable-frequency (●) ac susceptibility data.

Conclusions

In summary, an azido-bridged chair-like [Co<sup>II</sup>]<sub>10</sub> 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 tetratolene ligands. Replacement of the terminal azide groups by other halide ligands could lead to a C<sub>2V</sub> distortion for CoS<sub>5</sub>, and significant impact on the global anisotropy may be achieved.

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Notes and references

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‡ Electronic Supplementary Information (ESI) available: Additional crystallographic and magnetic data. CCDC-997583 (1). See DOI: 10.1039/c000000c

§ Crystal data of I: C<sub>43</sub>H<sub>57</sub>N<sub>43</sub>O<sub>23</sub>, F<sub>W</sub> = 3150.84, triclinic, space group P1-1, a = 13.565(9), b = 16.584(11), c = 18.065(12) Å, β = 63.652(7), γ = 76.183(7), V = 5356(4) Å<sup>3</sup>, T = 110(2) K, Z = 1, μ = 1.222 mm<sup>-1</sup>, μ<sub>eff</sub> = 1.484 Mg m<sup>-1</sup>, R<sub>1</sub> = 0.0636, wR<sub>2</sub> = 0.1651.


